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*Editors*

# Urbanization: Challenge and Opportunity for Soil Functions and Ecosystem Services

Proceedings of the 9th SUITMA Congress

 Springer

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# Urbanization: Challenge and Opportunity for Soil Functions and Ecosystem Services

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# Preface

This edited volume contains a selection of refereed and revised papers originally presented at the ninth International Congress on Soils of Urban, Industrial, Traffic, Mining and Military Areas (SUITMAs) entitled “Urbanization as a challenge and an opportunity for soils functions and ecosystem services.” The congress was organized in RUDN University, Moscow, Russia, on May 22–7, 2017. The congress introduced SUITMAs, considering their unique features, spatial–temporal variability and potential to provide functions and services important for environment and society. The SUITMA 9 congress developed a platform for international and interdisciplinary discussion between soil and environmental scientists, landscape designers, urban planners, and policy-makers involved in sustainable urban development. We would like to thank more than 300 participants and 210 speakers who contributed with plenary, oral and poster presentations, roundtables, and field excursions. We wish to express our especial gratitude to the authors who contributed to these proceedings. The proceedings include an introduction and 34 research papers, which were selected by the scientific committee with additional help of external expert reviewers from 95 submissions. The authors were asked to consider the reviewers’ comments and make all necessary edits to improve the quality of the papers.

The conference was organized under the umbrella of the International Union of Soil Sciences. The organizational and financial support to the SUITMA 9 Congress was provided by “RUDN University Program 5-100” and the “Erasmus+ Jean Monnet project “European traditions in governance, design and environmental management of megacities: search for solutions (EDEM5).” We would like to express our gratitude to the many people who put essential efforts to ensure this successful conference: keynote speakers, members of organizing and scientific committees, conveners of sessions and roundtables, reviewers and technical editors. We wish to express our sincere thanks to Dr. Michael Leuchner, Publishing Editor, Earth Sciences, Geography and Environment, and Rajan Muthu, Project coordinator, for their help and cooperation.

We hope these proceedings will serve as a valuable reference for researchers, practitioners, and policy-makers in the related fields.

Viacheslav Vasenev  
Elvira Dovletyarova  
Zhongqi Cheng  
Tatiana V. Prokof'eva  
Jean Louis Morel  
Nadezhda D. Ananyeva

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# SUITMA 9: Urbanization as a Challenge and an Opportunity for Soils Functions and Ecosystem Services

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**Abstract.** Soils of Urban, Industrial, Traffic, Mining and Military Areas (SUITMAs) present a novel, interesting and very important topic for investigation and discussion. Soil-forming factors, properties and processes of SUITMAs are completely different from those of natural soils. SUITMAs' functions and ecosystem services are still rarely studied and likely underestimated. The 9<sup>th</sup> SUITMA congress provided a platform to discuss theoretical and practical aspects of monitoring, assessment, modelling and management of SUITMAs to understand their roles in environment and society.

**Keywords:** SUITMA · Urban soils and ecosystems · Megapolis  
Soil assessment and management · Sustainable development

Globally, urbanization is progressing rapidly and coincides with substantial changes in vegetation and soils (Pickett et al. 2011, Levin et al. 2017). In response to these issues, policy agendas are focusing on achieving and maintaining optimal functioning and sustainable use of urban ecosystems and their components, for present and future generations. Soil is a key component of urban ecosystems, responsible for multiple functions and services, contributing to environment and quality of life in cities (Lorenz and Lal 2009, Morel et al. 2015). Soils of Urban, Industrial, Traffic, Mining and Military Areas (SUITMAs) represent a relatively new and rapidly developing direction in environmental and ecosystem sciences. The acronym SUITMA also refers to a working group of the International Union of Soil Science (IUSS) and is a world leading scientific community dedicated to investigating urban and technogenic soils (Morel and Heinrich 2008). SUITMAs differ substantially from natural counterparts in their physical, chemical and biological features, their functions and services. Therefore, studying SUITMAs raises new research questions in soil classification, morphology, monitoring, assessment and management.

Traditional views of urban ecology have emphasized the negative anthropogenic impacts on SUITMAs (e.g. contamination, salinization and over-compaction)

(Stroganova et al. 1997, Yang and Zhang 2016). However, the more recent views on sustainable urban development highlight capacity of SUITMAs to provide important functions and services, including substrate and support for greenery, water purification, transport and storage, habitat for microorganisms, contribution to carbon and nitrogen cycles and climate mitigation (Gomez-Baggethun et al. 2013, Morel et al. 2015). Reviewing and summarizing the experiences and existing methodologies in analyses, assessments, and modeling of properties and processes of SUITMAs, their vulnerability to anthropogenic impacts and global climate changes is needed. This will help improve understanding of the SUITMAs' role for human and environment and to develop policies and strategies enhancing their functions and ecosystem services. The 9<sup>th</sup> SUITMA congress provided an international and interdisciplinary platform to discuss challenges and opportunities of urbanization for soil functions and ecosystem services.

The SUITMA9 Proceedings introduce SUITMAs, considering their unique features, spatial variability, temporal dynamics anthropogenic threats and potentials to provide important functions and ecosystem services. The volume includes 34 papers, covering different aspects of SUITMAs' study, assessment and management. These papers are organized into nine different thematic sections (i) classification and genesis (papers 1 to 5), (ii) pollution and mitigation (papers 6 to 9); (iii) carbon stocks and fluxes (papers 10 to 14); (iv) life phase and biodiversity (papers 15 and 16); (v) engineered soils and urban green infrastructure (papers 17 to 20); (vi) assessment and mapping (papers 21 to 23); (vii) SUITMAs in different climates (papers 24 to 27); (viii) advanced techniques in monitoring SUITMAs (papers 28 to 30); and (ix) policies and practices of soil management for sustainable urban development (papers 31 to 34). The volume starts from more conventional issues of SUITMAs' study, continues with functions and services provided by SUITMAs and finishes with perspectives of SUITMAs for sustainable urban development.

The variability in soil forming factors, processes, features and management practices results in uniquely high heterogeneity of SUITMAs, which is a challenge for classification (Rossiter 2007, Levin et al. 2017). Current opinions on classification are presented in Paper 1, devoted to the memory of Marya Stroganova - a well-known Russian soil scientist and an expert in SUITMAs' classification. Genesis and morphology of SUITMAs are presented in Section 1 with case studies of Moscow in Russia and Zielona Góra in Poland. Soil pollution with trace metals and organic contaminants remain among the main threats for human health and this is demonstrated in Section 2 by examples from Russia and USA. Urban environment brings a set of specific conditions and processes affecting carbon stocks and fluxes in soil, thus SUITMAs can become hotspots of carbon accumulation or important sources of carbon emission. Balance between carbon stocks and fluxes in SUITMAs is mainly driven by land management and climatic conditions and it is shown in Section 3. Sections 4 and 5 present important services of SUITMAs to protect biodiversity and support urban green infrastructures. Urban soils are exposed to anthropogenic pressure and influenced by traditional soil-forming factors; therefore relict zonal signs are complemented and complicated by new technogenic and anthropogenic features. Spatial variability and regional specifics of SUITMAs are clearly demonstrated in Sections 6 and 7, where results from arctic to arid zones are presented. Advanced techniques in studying and

monitoring SUITMAs' properties, including XRF screening, tomographic methods and equilibrium centrifuging are described in Section 8. Finally, papers of Section 9 discuss the legal issues of SUITMAs management, as well as practices and perspectives of implementing data and knowledge of SUITMAs for urban planning, food security and adaptation to climate change. In such a way, a wide range of relevant topics was discussed in 9 thematic sessions of SUITMA 9 Proceedings.

The SUITMA 9 congress attracted a broad audience, including scientists, policy-makers and practitioners in urban planning, management and development, which allowed an inter-disciplinary discussion of environmental and social roles of SUITMAs for sustainable urban development.

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# Functional-Environmental and Properties-Oriented Approaches in Classifying Urban Soils (In Memoriam Marina Stroganova)

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**Abstract.** Professor of Moscow Lomonosov University Marina Stroganova was the first in Russia to acknowledge urban soils as soils, name them by their location and/or functions and partly by their properties. Her system is popular among specialists, and urbanozems, ekranozems, culturozems and similar soils are recognized as mapping units and study objects for ecologists. Global progress in classifying soils resulted in the shift of priorities in the choice of diagnostic criteria: from soil-forming factors to soil properties. However, for urban soils, strongly affected or even constructed by humans, soil-forming factors, processes, and properties remain important as seen from the expert evaluation of criteria in WRB, Soil Taxonomy and French system. In Russia, an attempt to insert urban soils in the basic classification system, without violating its substantive principles is described.

**Keywords:** Soil functions · Soil classification · Soil names

## 1 Introduction

A first comprehensive classification of urban soils in Russia was proposed by Marina Stroganova in the 1990-s, and it became very popular among soil scientists and specialists in urban management and planning. The system was described in her book on soils of Moscow; its English version edited by W. Burghardt was published in 1998 – the year of birth SUITMA (Soils of Urban, Industrial, Transport, Military, and Mining Areas) [1]. Judging by publications of Lehman and Stahr [2, 3] and Capra *et al.* [4], there was a fantastic growth of interest to urban soils in the late 1990-s, and Stroganova's system was more than timely then. Moreover, Lehman and Stahr noted that since the mid-1990-s, urban soils were studied as soils





rather than objects of pollution [3]. Stroganova's system was based on data collected in the course of working in projects on the ecological status of Moscow, and it had therefore a distinct ecological bias [1, 5].

This classification was the first one identifying urban soils as soils and not as sediments or garbage, which is illustrated by emphasizing the difference between the terms «urban soils» and «soils of the city». The names Stroganova proposed for all urban soils have a formative element “zem” used for soils in Russian classifications (chernozem, cryozem), and the “prefixes” are indicating the functions performed by soils, and *urbanozem* was the first soil among them (Table 1). The others are: *indus-trizem*, *necrozem*, *recreazem*, *culturozem*, etc. Similar names were used in early Polish [6] and Slovak systems [7]; this functional nomenclature was clear and easy for users. The classification of Stroganova has elements of a hierarchical system, although not strictly implemented at the upper taxonomic levels unlike the lower ones, where rules and criteria inherent to the traditional Russian soil systematic were applied. This feature has its rationale: it is available to users, habitual to soil scientists, and facilitates connections with the basic classification system.

## 2 Soil-Forming Agents or Soil Properties?

This dualism of the approach to anthropogenic soils is clearly illustrated by the paper of R. Dudal with co-authors in early 2000-s, where he considered economic activities as a “human factor of soil formation” on one hand, and proposed a broad scheme of man-made soils classified by the features of their profiles: horizons, parent materials degree of disturbance, on the other hand [10]. The current concepts concerning the diversity of urban soils and environments with emphasis on regimes are outlined in the recent review by W. Burghardt [11].

It is a trivial statement that principles of soil classification are implemented at the upper taxonomic levels. In our case, all the above-listed “zems” derive more of functions and location of soils (*recreazem*, *necrozem*) rather than of assessing soil properties; hence, the priority is given in this system to the environment and land-use features.

However, there is one exception – *urbanozems*. The main diagnostic criterion for *urbanozems* is the presence of the *diagnostic urbic horizon*, which was defined by Stroganova in mid-1990-s according to its properties and origin [1]. *Urbic horizon* has a broad range of properties, however, the following ones are most common: dark color, light texture, neutral to weakly alkaline pH, varying density 1.1–1.6 g/cm<sup>3</sup>, weak crumb structure, high BS, higher humus content than that in the reference soils, more than 10% artifacts, and upward growth due to additions. *Urbic horizon* is composed of the fragments of initial natural soil horizons, cultural layers, natural and/or artificial materials; the ratio of these ingredients varies in different urban environments.

Other urban soils in the system of Marina Stroganova are identified less strictly, and mostly in accordance with their functions or their location, although sometimes soil characteristics are mentioned as supplementary information. Thus, *culturozems* are deep (> 50 cm) humus-rich soils of botanical gardens, old kitchen gardens; they contain artificial organic materials, sometimes as layers, are underlain by the remnants of initial subsoils or cultural layer or any materials. Chemically modified soils comprise

Table 1. System of soils and non-soils in the city [1, 8].

Open areas		Sealed areas		
Soils		Soils& soil-like bodies	Materials	Buildings
Natural	Human-modified	Artificial	Natural	Under asphalt or other pavements
	Topsoil			
	Profile			
	<b>Urbosoils</b>	<b>Technozem, replantozem, constructozem</b>	<b>Natural (in situ), technogenic (ex situ)</b>	<b>Ekramozem</b>
	<b>Urbanozem, necrozem, intruzem, culturozem, industrizem</b>			<b>Sealed materials</b>

Short comments to the table: (1) natural soils are conventionally natural, since they are affected by technogenic emissions, even those in urban forests, or they might have been plowed and/or drained in the past; (2) urbo-soils are identified by their subsoils, more or less intact, and urbo-podzolic and urbo-alluvial soils may serve as examples; (3) solid-phase objects on technogenic materials, either filled, or cut are referred to “Technogenic Surface Formations” coined by V. Tonkonogov [9].

*industrizems* and *intruzems*; the former occur near industrial enterprises and are strongly polluted by any toxicants reducing, if not destroying soil biota, the latter are confined to filling sites and parking zones, where impregnation of any soils or materials by oil products is common. Human-made urban soils have similar origin: they are created by filling several layers on the former soil, or on any material with the humus-enriched top layer. The targets to construct such soils may be different: *replantozems* or *recreazems* are produced by rehabilitation of disturbed lands or made in the public gardens, for example, for flower beds. *Constructozems* are completely artificial soils intended for some special purposes, for example, for playgrounds, and their construction is oriented on moisture balance and stability. The origin and functions of *technozems* are related to coalfields, where stabilization of heaps of overburden rocks was required; and this was the initial meaning of this term proposed as early as in 1989 by L. Eterevsckaya [8]. Later on, the term acquired a broader connotation. The essence of *necrozems* and *ekranozems* does not need comments.

This list clearly shows the priority of criteria used for the definitions of urban soils hardly related to soil properties, which couldn't be different in the early studies. Probably, there were two main reasons. In the late 1990-s, soil scientists needed to prove the importance of their objects and their status of soils, therefore, such 'site or functional' names were understandable and indicated the soil-forming conditions. On the other hand, properties of urban soils were not sufficiently known, although it was already clear that they strongly vary within the city and even within its functional zones.

Fast development of urban soils knowledge and concepts, along with current trends to the priority of substantive elements in soil classifications, resulted in a shift to properties-oriented diagnostic criteria. We tried to make an expert evaluation of the ratio of criteria in most advanced systems by applying to qualifiers for humanly modified objects, although it was not always easy to discriminate among the results of intended anthropogenic impacts and properties produced by them (Table 2). For example, in WRB, the Relocatic qualifier is referred to factors, while Lignic denominates property. In the third version of the French system (Référenciel pédologique [12]), there are many "double" qualifiers, such "mixed" or "truncated" comprising factors – processes – results in their definitions. The objects comprise broader groups of soils than only urban ones in all systems; these are also soils of other SUITMAS.

**Table 2.** Types of criteria used to classify urban soils in three classification systems.

Classification system, soils	Diagnostics based on:		
	properties	factors	both
WRB – 2014 (2015), Technosols, all qualifiers [13]	40	16	8
Référenciel pédologique, 2008, grand ensemble de références – Anthrosols [12]	6	3	8
Keys to Soil Taxonomy, 2014. Characteristics for human-altered and human-transported soils [14]	6	6	2

Despite a certain ambiguity of the procedure, it is clear that soil-forming factors and soil properties are of similar diagnostic significance. Presumably, it is explained by the nature itself of urban soils, hence, the unfeasibility to make “a purely substantive” system for them. Moreover, at the upper taxonomic levels, functional or factor perception of soils concealed in their names seems to be attractive for users because of their clarity and universality. Soil properties, as criteria for further subdivision are removed to lower levels. There, they are implemented by specialists to differentiate urban soils within functional units, to designate details in their properties, origin and functioning, record current changes and/or spatial variability.

### 3 Should Urban Soils Be Classified Apart from Other Soils?

One more novel feature of Stroganova’s system is the introduction of *intergrades* – urbo-soils (urbo-podzolic, urbo-chernozems, urbo-alluvial). These are soils with an urbic horizon  $\leq 50$  cm thick underlain by the remnants of former subsoils; In case the depth of urbic horizon is  $\geq 50$  cm, soils are qualified for urbanozems. Intergrades mostly occur in the suburbs of megapolises and in small settlements. In the downtown, they may appear in the gardens among urbanozems, replantozems and ekranozems.

In terms of taxonomy, urbo-soils in Stroganova’s system correspond to subtypes, and are further subdivided into genera, species, subspecies, varieties and phases in accordance with the criteria of the basic system for properties of the natural soils. For example, a soil in a Moscow suburb may receive a full name: urbo-podzolic surface-gleyic, few-artifactual, PAH-polluted loamy sandy on glaciofluvial sands.

The importance of intergrades for working with urban soils is triple: (i) they are needed for mapping as being real spatial bodies; (ii) they provide confidence to the non-traditional ‘urban’ terminology, since new names are mixed with the habitual ones; (iii) they serve as bridges to the basic soil classification. In her system, Marina Stroganova applied the approach to intergrades used in the recent basic classification of soils of Russia [15]. Agro-soils are introduced there at the type level because they have acquired a new agro- (plow) horizon as compared to their archetype (natural soil), and according to the rules of this system, soil types are identified by their ‘profile formulas’, which are the assemblages of diagnostic horizons; subtypes derive of them by adding qualifiers indicating additional superimposed processes. Hence, the initial soddy-podzolic soil type has the following profile formula: AY-EL-BEL-BT-C, and its plowed variant looks like: P-(EL)-BEL-BT-C, the eluvial EL horizon may be either included into the agro-horizon P, or partially preserved. By adding lowercase index “g” to BEL and/or BT diagnostic horizons it is possible to record gley features, if they are observed.

These examples with soddy-podzolic soils enable us to show the possibility of inserting urban soils into the basic system of Russian soil classification without serious difficulties. Urbic horizon was accepted as diagnostic, and it may be introduced in the profile formula of any intergrade within the trunk of postlithogenic soils, if its depth does not exceed 50 cm. Thus, urbo-(soddy)-podzolic and urbo-chernozems may be specified. Since the profiles of urban soils are growing upward owing to all kinds of additions, so that the depth of their urbic horizons exceeds 50 cm, they should be

referred to the trunk of synlithogenic soils, order of stratozems, and types of *urbostratozems*; depending on the underlying material types of typical urbostratozems or urbostratozems on buried soils may be identified (UR-C, UR-D or UR-[ABC], respectively). In case of thin urbic horizons or weak manifestations of urbic properties, a subtype qualifier may be added to the original name of soil; this is an “urbostratified genetic property”, which already exists in the Russian system.

Recently, a group of soil scientists made efforts to come to agreement on embedding urban soils into the classification system of soils of Russia [16] following its concepts and diagnostic criteria. The definition of urbic horizon was formulated more strictly; the taxonomic position of soils with different manifestations of urbic elements was found; other horizons related to urbanization were defined: technogenic and recultivation-mixed with corresponding subtype qualifiers; technogenic material and its several variants were proposed for soils occurring in natural and urban environments.

The experience gained confirmed suitability of classifying urban soils together with the natural ones in a sequence: natural soils – intergrades – urban soils – non-soils (Technogenic Surface Formations - TSF). Looking for boundaries between the last two members is an objective for further research.

## 4 Conclusions

The definition and grouping of urban soils by their location and functions was first proposed in Russia by Marina Stroganova, and remains broadly used by soil scientists and ecologists owing to its ecological bias and functional soil names. At the upper levels of most soil classifications, the criteria related to soil-forming factors are of almost equal importance as those derived of soil properties, which does not completely coincide with the principles of WRB, Soil Taxonomy, new Russian and some other systems. However, this seems to be inevitable because of the anthropogenic nature of urban soils: the composition of soil profiles depends on the purpose and way of their formation and materials used. In the same time, urban soils should be classified together with the natural and semi-natural soils in the same open hierarchical systems.

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# Anthropogenic Materials as Bedrock of Urban Technosols

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**Abstract.** Technogenic materials are common in SUITMA's and may cause significant changes in the properties of soils covering urban areas. Investigations showing the diversification of properties of these materials to consider their role as a bedrock of Technosols are of interest of soil scientists and urban planners. The research was carried out in Zielona Gora urban area (western Poland). The technogenic materials were collected from anthropogenic deposits building layers 0–20(40) cm of the urban Technosols. A high content of technogenic materials deposited in urban Technosols is frequently occurred and expected situation. Many of the analysed materials have a high chemical reactivity, which can induce significant changes in the properties of urban soils, mainly in terms of pH, the content of CaCO<sub>3</sub>, carbon and EC. Some materials like slags, ashes and sewage sludges contain significant quantities of Cd, Cu, Fe, Ni, Pb and Zn. The diversification of artefacts should be reflected in the soil classification system, especially when boundary conditions are specified for inclusion of soils into the Technosol group.

**Keywords:** SUITMA · Technogenic parent soil material · Anthropogenic soils Technosols

## 1 Introduction

The soil cover in cities results from the impact of different human activities in time and space as well as other soil-forming factors on various parent materials, both natural and anthropogenic ones [1–8].

Anthropogenic soil-forming materials are significant factor of changes in the properties of urban soils [6, 9–13]. The most common anthropogenic materials in urban soils are: building debris, slags, dusts and ashes, translocated rock material, communal wastes, sludges, subgrades and mulches. The most commonly described artefacts in Technosols are widespread admixtures of building materials, wastes and waste building materials produced as a result of mass demolition of buildings [1, 12–14]. Due to the construction technologies that were used, materials such as brick rubble, cement-lime rubble, as well as bonding, covering and insulating building materials can be found in the soils of built-up areas. A number of authors mention consequences of their presence in the soil mass such as changes in the physical, chemical and biological properties of

soils in urban areas [11, 15, 16], as well as in their functionality [9, 17, 18] and evolution line [19].

Literature often describes the effect of anthropogenic modification of the chemical composition of soils as a consequence of polluting them with various types of waste. One of the confirmed facts in this aspect is an increase in the content of heavy metals in technogenic soils [3, 15, 17, 20]. Another issue is the environmental risk connected with the presence of pollutants in Technosols. El Kahlil et al. [15] found that the physical alteration of technic materials deposited in Technosols is leading to metal contamination of the soil solution. The release of metallic ions from wastes to soil solution can lead further to inhibition of germination and plant growth disturbances.

Materials of technogenic origin, such as construction debris, slag, dust, rock material, lignite, coal, municipal waste and sludge, are currently considered to be parent materials for Technosols [21]. Admixtures of materials found in technogenic soils can be introduced in different ways, always with the activity of humans. In the WRB soil classification system [21], anthropogenic admixtures are called artefacts – solid or liquid substances created or modified by humans, or brought to the surface by human activity from a depth and deposited in an environment. They should have substantially the same chemical and mineralogical properties as when first manufactured, modified or excavated. All artefacts are treated in the same way by the WRB classification without distinguishing their susceptibility to weathering or the intensity of their influence on soil material. Only one – quantitative determinant of the presence of artefacts in Technosols was indicated  $\geq 20\%$  by volume, weighted average in the upper 100 cm from the soil surface or to continuous rock or technic hard material or a cemented or indurated layer.

The goal of the paper is to present the properties of anthropogenic materials deposited in the surface soil layers as factors having a direct and different impact on the soils in urban areas.

## 2 Material and Methods

Zielona Gora is almost 700 years old town on the Polish-German borderland (51°56'23" N, 15°30'18" E), inhabited in 2016 by about 140 thousand residents. From the geological and geomorphological point of view, Zielona Gora is located on the Middle-Odra-Land. Most of geological materials building superficial layers of the Zielona Gora locality are medium and coarse sands of glacial and water origin, gravels and in some areas silts and clays within glacitectonically disturbed moraine structures [22]. In 61% of soils samples taken from the soil profiles of Zielona Gora area different technogenic materials have been noted [20, 23, 24].

The technogenic materials were collected from anthropogenic deposits covering the soils in 30 sites in Zielona Gora, building their layer from 0 to 20(40) cm. Fragments of plastering material (cement-lime plaster) with a diameter of 20–50 mm were sampled from the wall of a residential building and from the soil at a distance of up to 100 cm from it. The building had been plastered about 20 years before sampling. Particular kinds of technogenic materials (Fig. 1) were separated in laboratory conditions, mixed



up in order to obtain an average. For the chemical and physic-chemical analyses the fraction with a diameter of less than 2 mm was obtained by sieving.



**Fig. 1.** Selected technogenic materials analysed in the paper: neat plaster, aerated concrete, bricks, asbestos-cement roof plank, building sand and municipal sewage sludge

Sorption properties were determined by the Pallmann method, pH-H<sub>2</sub>O and pH-1 M KCl values were measured with a glass electrode WTW SenTix 41 in the supernatant of a 1:2.5 soil: water suspension, electrical conductivity (EC) of the soil-water 1:2 extract was determined using the conductometric method, heavy metals content in aqua regia extract (3HCl:HNO<sub>3</sub> acc. to ISO 11466) using the ICP-OES technique (Perkin Elmer Optima 8000) and the total carbon (TC) content using the Shimadzu VCNS analyser. For the determination of the content of carbonates in the soil samples the ISO 10693 method was used, based on the displacement of carbon dioxide by hydrochloric acid addition. Extracts in aqua regia were prepared and analysed both for the soils and anthropogenic materials as well. All analyses were carried out three times.

The mineralogical composition of technogenic materials (analysis of solid crystalline, semi-crystalline and amorphous materials) was conducted using GE X-ray Diffraction System Seifert XRD 3003, with method of reflection, refraction and possible X-ray enhancement on the planes and nodes of crystalline meshes of crystalline substance. Settings – Method: 1 Strongest Lines; Deleted Phases: used; Long Search; Error Window: 0.1° \* (1 + sin(Theta)); Theta Shift: 0.200°; Max proposals: 100; rel. Intensity Level: 60%; Intensity Threshold: 0%; Database: without Subfile selection.

### 3 Results

Many anthropogenic materials varying in terms of properties and their potential impact on the environment are deposited in the soils of urban areas. It is possible to find ones with a high chemical reactivity (neat plaster, asbestos-cement roof plank, slags and ashes) and chemically neutral ones (bricks, building sands and gravels) or ones that improve the properties of soils acting as fertilizers (compost, bed materials), Table 1.

**Table 1.** Selected properties of technogenic materials deposited on the soil surface [4, 17]\*

Material	pH	EC <sub>1:2</sub>	CaCO <sub>3</sub>
	in H <sub>2</sub> O	mS·cm <sup>-1</sup>	%
Neat plaster	10.1–12.2	0.6–6.8	26.6–57.4
Aerated concrete	8.3–8.6	0.9–2.1	29.7
Roof tiles and bricks	7.6–8.2	2.3–3.0	20.7
Clinker brick (factory chimney)	7.8–8.2	1.1–3.8	30.4
Asbestos-cement roof plank	11.8–12.2	4.5–8.4	36.3
slag	8.7–9.2	7.0–9.0	4.0–15.0
Ash after biomass combustion	10.2–10.3	7.8–11.6	32.2
Building sands and gravels	7.4–9.3	0.2–0.7	20.4
Bed for coniferous plants	4.3–5.0	0.2	1.7
Bed for deciduous plants	5.8–6.5	0.3	4.2
Compost of green wastes	6.7–7.1	0.3	5.0–10.0
Municipal sewage sludge	7.1–12.4	0.6–18.0	10.0–44.5

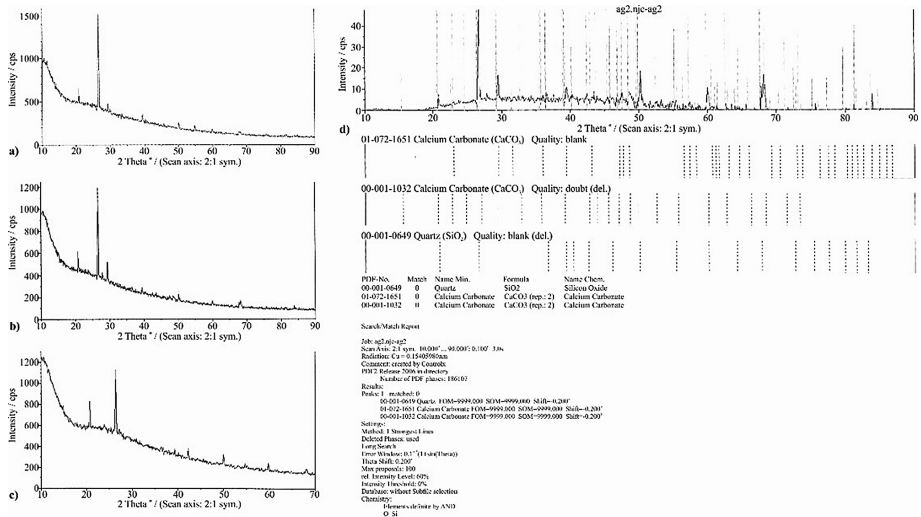
\*expanded

Neat plaster, asbestos-cement roof plank, ash after biomass combustion and some municipal sewage sludges (lime treated) are materials characterized by a very high pH – 10.1–12.4. Building sands and gravels are very different materials because of admixtures and impurities – pH between 7.4 and 9.3. Other technogenic materials such as aerated concrete, roof tiles, clinker bricks and slag are also alkalic, with a lower pH, between 7.4 and 9.2. Compost of green wastes and some municipal sewage sludges is almost neutral – pH 6.9–7.1. Only artificially prepared beds for ornamental plants were acid, with pH 4.3–5.8. Slag, ash after biomass combustion and lime treated sewage sludges having the highest EC level in the range of 9.0–18.0 mS·cm<sup>-1</sup> can influence the soil salinity level. Neat plaster and asbestos-cement roof planks can also have a high EC level (even 6.8–8.4 mS·cm<sup>-1</sup>). Other technogenic materials are characterized by lower EC values being in the range – from 0.6 to 3.8 mS·cm<sup>-1</sup>.

Typical for the most of construction artefacts is high CaCO<sub>3</sub> content. Analysed rubble materials have been characterised by the carbonates content ranged from 20.4 to 57.4%. The carbonates content in ashes was lower – 4–15%, and in ashes very similar – av. 32.2%. The carbonates content in compost and sewage sludge was dependent from the technology of sanitation of them – with addition of different doses of lime.

In the case of the cement-lime plaster samples it was found that retention in the soil changes the properties of the material. After about 20 years' retention of the material in the soil, the CaCO<sub>3</sub> content decreased from 57.4 to 26.6% in comparison with the material sampled from the wall of a neighbouring building. For the material extracted from the soil, an average EC score of 6.82 mS·cm<sup>-1</sup> was obtained in comparison with 1.72 mS·cm<sup>-1</sup> for the material sampled from the wall of the building. In this context it was also found that the pH of the materials analysed increased from 10.1 to 12.2 (Table 1).

The X-ray analysis showed the quartz's dominance among the minerals contained in the samples, which was the expected result – higher peaks by 21, 27, 36, 50 and 60° (Fig. 2a–c). In the cases of neat plaster, building sands and gravels and Technosols samples, important content of calcite and other Ca minerals was established. Very interesting is a comparison between neat plaster materials taken from the wall of building and from the soil of adjacent area (Fig. 2a and b). Besides the characteristic high peaks of quartz, carbonate lines are present on the diffraction pattern, slightly different for these two samples. In the sample from the wall are visible Ca minerals different than calcite – probably calcium oxide/calcium hydroxide (peak by the 68°). It is noticeable that there is a bigger peak corresponding to these calcium compounds in the case of a sample of neat plaster that does not come in contact with the soil (Fig. 2b).



**Fig. 2.** X-ray analysis of the chosen technogenic materials; a – neat plaster from the soil, b – neat plaster from the wall, c – Technosol with carbonates from rubble materials; d: x-ray lines matched in analyse of the neat plaster from the wall

Some materials – mainly slags and ashes may contain quantities of heavy metals significant for the natural environment. An especially high content was estimated for slag (1 mg Cd·kg<sup>-1</sup>, 34 mg Cu·kg<sup>-1</sup>, 140 mg Ni·kg<sup>-1</sup>, 205 mg Pb·kg<sup>-1</sup>), ash after biomass combustion (4.8 mg Cd·kg<sup>-1</sup>, 88 mg Cu·kg<sup>-1</sup>, 43 mg Ni·kg<sup>-1</sup>,

400 mg Zn·kg<sup>-1</sup>), compost of green wastes (1.1 mg Cd·kg<sup>-1</sup>, 24.5 mg Cu·kg<sup>-1</sup>, 258 mg Zn·kg<sup>-1</sup>) and municipal sewage sludge (4.1 mg Cd·kg<sup>-1</sup>, 37.3 mg Cu·kg<sup>-1</sup>, 55.7 mg Pb·kg<sup>-1</sup>, 313 mg Zn·kg<sup>-1</sup>). The materials described also include significant quantities of Fe, from 1.2 to 4.8% (Table 2).

**Table 2.** Heavy metal subtotal content in technogenic materials deposited on the soil surface

Material	Cd	Cu	Fe	Ni	Pb	Zn
	Average values in mg·kg <sup>-1</sup>					
Neat plaster	0.2	3.7	88	6.0	2.8	26
Aerated concrete	0.2	1.0	n.d.*	5.0	1.7	2.4
Roof tiles and bricks	0.2	8.3	3060	2.0	n.d.	34
Clinker brick (factory chimney)	0.2	17	3750	1.3	n.d.	41
Asbestos-cement roof plank	0.2	5.7	n.d.	4.3	4.6	3.2
Slag	1.0	33.7	48400	140	205	76
Ash after biomass combustion	4.8	88	18700	43	5.8	400
Building sands and gravels	0.2	8.6	2842	9.0	11.4	28.4
Bed for coniferous plants	0.1	2.2	1160	1.1	6.8	9.1
Bed for deciduous plants	0.1	1.2	2610	0.4	11.1	10.1
Compost of green wastes	1.1	24.5	27620	6.9	39.9	258
Municipal sewage sludge	4.1	37.3	11896	12.8	55.7	313

\*n.d. – not detected

## 4 Discussion

A characteristic feature of urban regions is the presence of technogenic parent materials of soils made or transformed by man. Technogenic materials are characterised by a high diversity of constituents, a high spatial variability, and a range of temporal discontinuities [10, 11, 17, 25]. Their presence significantly modifies the morphology of soils and their properties. Furthermore, this may be a factor explicitly determining the directions of soil-forming processes and the evolution of soils [5, 12, 17, 26].

This induces an effect of heterogeneous soil properties in urban areas (even small ones). Since a significant part of wastes introduced into soils has dimensions of the soil skeleton, they affect the surface soil layers by acting as a drainage medium. Regional and linear introduction of wastes leads to the creation of extensive waste layers, deposited at varying depths. In addition, they change the flow and deposition of soil solution, which results in an unusual variation of the chemical composition of the soils.

Some technogenic materials are found in soils in the form of large particles, which are classified as the soil skeleton. This can be seen when a content of 0.0 to 4.7%, typical of the skeleton in the Zielona Gora soils of natural origin, is compared to the content in Technosols, which reaches a dozen or even dozens of percent. The presence of soil layers with a content of technogenic materials of up to 96% was also found, mainly in urban and transport areas. An increase in skeletal properties, as a symptom of

transformations typical of Technosols, has been widely described in literature [1, 4, 12–14, 27, 28].

Different materials introduced into soils or onto their surface have different physical and chemical properties (Table 1). The introduction of construction rubble into soils, consisting of various wastes containing lime, caused a considerable increase in the content of  $\text{CaCO}_3$  (Table 2, Fig. 2). In the surroundings of Zielona Gora natural soils are non-carbonic. Technosols created by the introduction of building sand and gravel into the soil as well as municipal wastes are similar in this respect, though some differences have also been found. They resulted from the contamination of mineral building materials with lime and cement and from mixing municipal wastes with alkalizing materials. Technosols including rubble had a content of carbonates ranging from 3.7 to 25%. Mazurek et al. [11] found that the surface levels of Technosols were significantly enriched with  $\text{CaCO}_3$ .

The pH of the technogenic materials analysed ranged from acid to strongly alkaline, they also contained varying amounts of chemical compounds with different solubility in water (as indicated by EC values). This largely affects the reactivity between these materials and the soil. A higher percentage of brick rubble (pH 8.1–8.9) than of sandy soil material of natural origin (pH 6.4–7.7) was described by Nehls et al. [12] as a typical phenomenon. Wessolek et al. [13] found that occurrence of soils containing rubble with a pH- $\text{CaCl}_2$  value of less than 7.0 was unlikely.

Nehls et al. [12] also found that the EC value increased as a result of the presence of rubble in the soil. This interesting observation made by these authors about an increase in the EC value in rubble materials deposited in the soil in comparison with raw building materials, caused by their intensive weathering, was fully confirmed by the research carried out in Zielona Gora – in the case of plastering materials it was  $6.82 \text{ mS}\cdot\text{cm}^{-1}$  in soil material and  $1.72 \text{ mS}\cdot\text{cm}^{-1}$  in the material from building walls. Slag, ash after biomass combustion and lime treated sewage sludges having a high EC level ( $9.0\text{--}18.0 \text{ mS}\cdot\text{cm}^{-1}$ ) can influencing the soil salinity level, which is very low for the local, sandy soils of natural origin ( $0.1\text{--}0.2 \text{ mS}\cdot\text{cm}^{-1}$ ). Neat plaster and asbestos-cement roof planks can also have a high EC level (even  $6.8\text{--}8.4 \text{ mS}\cdot\text{cm}^{-1}$ ). Other technogenic materials are characterized by lower EC values being in the range of  $0.6$  to  $3.8 \text{ mS}\cdot\text{cm}^{-1}$ . Wessolek et al. [13] described the soils in Berlin in post-World War II rubble as not very salty, with an EC value of 75% in samples collected below  $0.14 \text{ mS}\cdot\text{cm}^{-1}$ . The EC value of soils above  $2 \text{ mS}\cdot\text{cm}^{-1}$  can be a problem to plant growth and development [29].

A higher content of organic carbon (2.6–6.4%) was caused by two situations – in the case of the surface soil layers by the application of horticultural substrates, and in the case of the deeper layers, mainly by the presence of ash, slag and mixed municipal waste.

In a vast majority of Technosols values of sorption capacity close to those typical of soils of natural origin were found. This is consistent with research done by other authors indicating a CEC value for rubble of  $6 \text{ cmol}(+)\cdot\text{kg}^{-1}$  [12], which is not substantially different from the CEC value of soil material. Technosols containing building rubble have a BS value of up to 80–100% but only Technosols built of non-calcareous technogenic materials have a BS value similar to natural soils (32–73%).

An increase in the content of heavy metals is commonly regarded as a phenomenon typical of urban centres [28]. However, it is difficult to directly attribute this increase to the weathering of technogenic materials.

Literature widely describes significant differences in the weathering of technogenic materials and the effects of such variation on Technosols [10, 30]. The research presents the concept of differentiation of artefact types in the context of their lower content in soils, enabling the classification of such soils as Technosols. The PSSS Anthropogenic Soil Working Group suggests dividing technogenic materials into two groups. The first would cover chemically reactive artefacts - they have a significant impact on the physical, chemical and biological properties of soils and their presence poses environmental or health risks (e.g. lime and derived products without concrete, blast furnace slag, slag and ash after coal combustion, post-flotation metal ore wastes, rock materials containing sulphides and sulphur, phosphogypsum, petrochemical and chemical wastes, bones and household wastes, etc.). The second group would include low-reactive artefacts – they may have a significant impact on the physical and physical-chemical properties of soils, but they are not highly toxic and do not pose environmental or health risks (e.g. sand, gravel, building dusts, rock materials not containing sulphides and sulphur, selected fractions of loose rocks, glass, concrete, building and household ceramics, timber and household wood, etc.).

After the recognition that some artefacts have a very high impact on soil properties because of their chemical reactivity, it would be desirable to consider reducing their necessary content in order to classify soils as Technosols. Charzyński et al. [31] proposed a content of 10%<sub>vol.</sub> in a layer with a thickness of  $\geq 30$  cm present to a depth of 100 cm below ground level as a sufficient boundary condition.

## 5 Conclusions

A high content of anthropogenic materials deposited in urban Technosols is frequently occurred and expected situation.

Many anthropogenic materials have a high chemical reactivity, which can result significant change in the properties of urban soils, mainly in terms of pH, the content of  $\text{CaCO}_3$ , carbon and EC.

Some materials like slags, ashes and sewage sludges contain significant quantities of Cd, Cu, Fe, Ni, Pb and Zn.

The diversification of artefacts should be reflected in the soil classification system, especially when boundary conditions are specified for inclusion of soils into the Technosol group.

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# Influence of Technic Surfaces on the Selected Properties of Ekranic Technosols

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**Abstract.** Soil sealing is the most common type of soil degradation in the urban areas. Soil under the different pavement and road covers shows many important disturbances in the exchange of matter and energy between the biosphere, hydrosphere, and atmosphere, what is leading to further disorders. Many important differences between the Ekranic Technosols behaviour are connected with the tightness of technic surface. As usual a diversification between soil properties under the complete (e.g. asphalt roads) and non-complete sealing (pavement bricks) is observed. The paper presents the physico-chemical properties of Ekranic Technosols overhung under bitumen surface, concrete slabs and concrete paving stones. The effect of top layers compaction is visible in all cases, especially in the bulk density, total porosity and capillary water capacity. The pH of the soils was different belonging on soil material and land preparation technique. The top layers of the tested soils can be characterized by the low content of organic carbon. The technogenic layers located directly under the sealed surface showed a lower content of some heavy metals (Cd, Cu, Pb, Zn) than the layers below. However, in some cases the opposite situation can be seen. There were no significant differences in the content of trace elements under different technic surfaces.

**Keywords:** Soil sealing · Urban soils · Anthropogenic soils

## 1 Introduction

Urban areas are significantly different comparing with located outside the city, when describing the ecological problems, including the quality of soil cover. Many of soils of the urban area are degraded in a consequence of the strong human impact. Soil sealing is one of the main forms of soil degradation, additionally constantly growing [1–6]. Soil sealing is the situation when soil surface is constructed as a layer of impervious material [6] or wider – sealing over of soil through urban development. The problem of soil sealing has been shown as influencing on the most of the total area of urban development [1, 7]. It is relative complicated to define the borders of contemporary urban development, especially through the soil transformation. Contemporary urban area takes ca. 6% of the European continent, and this value increases every 5 years by 0.34–0.50% [8]. In the city from a few to above 80% of the total area is covered with

impermeable surface [9–11] dependent on size, spatial economy of the city and the form of land development [12, 13].

An impermeable layer, like asphalt or concrete, strongly reduces the infiltration of rainwater into the soil profile and interferes with gas exchange between the soil and the atmosphere. All kinds of soil sealing can disturb the water-gas balance in soil and affect physio-chemical processes within the soil profile. It also significantly reduces the possibility of retention of water in urban areas (increased water runoff) [6, 14]. Today these phenomena are regarded as the more formidable ones as far as sustainable urban development is concerned [14–16].

In general, the urban areas can be divided into:

- non-sealed (urban greenery, backyards),
- semi-permeable (porous roads, paving and squares),
- impermeable (asphalt and concrete sealing, area under the buildings).

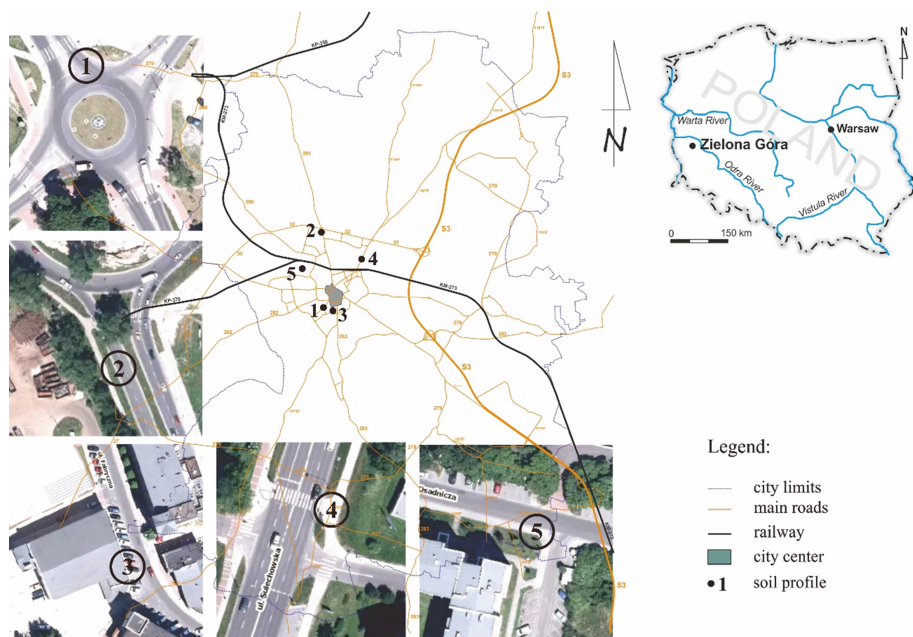
The morphology of the Ekranic Technosols is very different because of various superficial layers development and construction techniques have been used [17]. The most frequently used technic surfaces are made of: bitumen, concrete, large and small concrete slabs, concrete paving stone and porous materials (slags of different origin and building aggregates) [18–20]. Below the superficial layers, different technogenic materials are putted in, creating binder course, load-bearing layer, anti-freeze course and other artificial layers of Ekranic Technosols profile [10].

In general, raised level of the heavy metals content is typical phenomena for the urban sites [1, 10, 21]. The sources of heavy metals in urban soils and urban road dusts are mainly derived from traffic sources and industrial sources. From this point of view, sealed areas can be protected against the immision of contaminants from the outside of the soil. It does not act in situation of the direct input of contaminants to soil with different wastes [10]. Many of the artificial materials used for road foundation can be contaminated with different elements and substances. In the built-up area of Zielona Góra, per example, slag is widespread in soils as an effect of areas levelling and soil reinforcement [18–20]. A large amount of different contaminants are brought to the soil with mixed building rubble also. Due to the non-agricultural use of the most urban soils, the attention is focused on the chemical safety of soil for inhabitants in the case of direct input. In this respect, they are essential pathways of heavy metals and other contaminants from the soil into the human body. Some authors described the influence of different kinds of surface sealing on the chemical composition of soil and distribution of contaminants in soil profile [1, 21].

The aim of the study was to characterise chosen influences of the soil sealing to its properties. The research gives information about the geochemistry of Ekranic Technosols – frequently occurred urban soils, impacted by the heavy construction works.

## 2 Materials and Methods

The study was conducted in Zielona Góra – the medium size city, located in the western part of Poland ( $51^{\circ}56'07''$  N,  $15^{\circ}30'13''$  E). The research was carried out in the central districts of Zielona Góra city (Fig. 1).



**Fig. 1.** Location of the investigation sites in Zielona Góra urban area.

Particular locations were selected in areas with different soil surfaces: bitumen sealing form, concrete slabs and concrete paving stone – 5 soil profiles at a depth of 150 cm (samples from each of the morphological layers or genetic horizons).

The soil samples were air-dried and sieved using the mesh 2 mm in diameter. Sorption properties were determined by the Pallmann method, pH in 0.01 M  $\text{CaCl}_2$  values were measured with a glass electrode WTW SenTix 41 in the supernatant of a 1:2.5 soil: water suspension, total organic carbon (TOC) content using a Shimadzu  $\text{V}_{\text{CNS}}$  analyser, particle size distribution – using hydrometer method. The  $\text{CaCO}_3$  content was determined by loss of weight, and the total content of heavy metals by the inductively coupled plasma optical emission spectrometry (ICP-OES) in samples after mineralisation in aqua-regia. All analyses were carried out in triplicate.

### 3 Results

Ekranic Technosols have specific soil profiles not only due to the presence in topsoil roads and pavements construction materials – impermeable or semi-impermeable. Construction works, related to the roads, sidewalks and squares formation, consist in a number of activities that drastically change the soil profile. They begin with the removal of organic and humic (non-bearing) soil horizons, after which the surface is sealing formed with mineral aggregate. It creates a cut-off layer between the surface and the soil levels. The horizons located lower in the soil profile are reach indifferent wastes, usually not removed from the soil – unless they are undesirable for construction reasons (Fig. 2).



**Fig. 2.** Ekranic Technosols profiles from Zielona Góra urban area

A characteristic feature of the sealed soils is the impairment of the physical properties in at least some horizons. This is because of the compaction of the material to ensure the stability of the solid surface. The described density of tested soil ranges between 2.63–2.86 g cm<sup>-3</sup> in layers below the sealed surface and 2.54–2.79 g·cm<sup>-3</sup> of less than 20(35) cm. The bulk density varies from 1.36 to 1.68 g·cm<sup>-3</sup> in layers below the sealed surface and 1.54–1.71 g·cm<sup>-3</sup> below 20(35) cm. The effect of compaction of top layers is visible. The bulk density of other layers also indicates strong compaction. Total porosity reaches values of 16.7-34.6%. Capillary water capacity is 9.9-15.1%.

The reaction of the soils was neutral to alkaline (with one exception in the bottom of soil profile No. 3 – light acid). The following pH indices have been found: 6.8–7.3 for soil sealed with bitumen, 5.8–7.4 for soil sealed with concrete slabs and 6.9–7.4 concrete paving stone. There is no significant dependences between the pH value and sealing material or place of sampling in the soil profile.

The basic sorption properties of analysed soils are typical for soil cover of Zielona Góra area with exception of very low level of hydrolytic acidity (0.08–0.65 cmol(+).kg<sup>-1</sup>). Because of the sandy texture and low total organic carbon content (0.12–1.08%), total exchange bases and cation exchange capacity are low, respectively: 2.18–17.05 and 2.38–17.27 cmol(+).kg<sup>-1</sup> Table 1.

**Table 1.** Physical and chemical properties of Ekranic Technosols from Zielona Góra.

Depth	TOC	Texture	CaCO <sub>3</sub>	pH-CaCl <sub>2</sub>	HA	TEB	CEC	BS
cm	%		%		cmol(+)-kg <sup>-1</sup> d.m.			%
Soils sealed with bitumen surface								
30–40	1.08	s*	1.30	7.3	0.10	6.68	6.78	98.56
40–60	0.35	s	1.50	6.9	0.35	6.33	6.68	94.73
60–100	0.11	s	0.40	6.8	0.29	2.23	2.52	88.67
100–130	0.16	s	0.00	7.1	0.19	4.97	5.16	96.36
130–150	0.08	s	0.00	6.9	0.20	2.18	2.38	91.50
20–80	1.50	s	0.70	7.2	0.23	7.47	7.70	97.08
80–150	0.87	s	0.00	7.1	0.31	6.11	6.42	95.21
Mean	0.59	–	0.56	–	0.24	5.14	5.38	94.59
SD	0.52	–	0.59	–	0.08	1.98	1.98	3.16
Soils sealed with concrete slabs								
05–10	0.72	s	0.60	7.2	0.14	7.16	7.30	98.05
10–100	0.65	s	0.00	7.2	0.22	7.57	7.79	97.21
100–150	0.16	s	0.00	5.8	0.58	2.62	3.20	81.94
5–8	1.08	s	0.40	7.2	0.12	11.89	12.01	99.00
8–50	0.59	s	0.00	7.0	0.33	9.49	9.82	96.64
50–90	0.36	s	0.00	7.3	0.15	6.21	6.36	97.64
90–120	0.29	s	0.00	7.3	0.19	6.48	6.67	97.19
120–150	0.21	s	0.00	7.4	0.17	6.12	6.29	97.26
Mean	0.51	–	0.13	–	0.24	7.19	7.43	95.62
SD	0.29	–	0.22	–	0.14	2.53	2.44	5.21
Soils sealed with concrete paving stone								
5–10	0.12	s	0.20	7.3	0.56	7.64	8.20	93.14
10–15	0.89	s	0.00	7.4	0.22	17.05	17.27	98.74
15–25	0.64	s	0.00	7.3	0.32	11.37	11.69	97.30
25–80	0.59	s	0.60	7.1	0.35	11.35	11.70	97.05
80–110	0.38	s	0.00	6.9	0.65	8.25	8.90	92.67
110–150	0.25	s	0.00	6.9	0.17	3.68	3.85	95.52
Mean	0.48	–	0.13	–	0.38	9.89	10.27	95.74
SD	0.26	–	0.22	–	0.17	4.12	4.09	2.21

\* s – sand

Heavy metals content in investigated soil profiles was low, in any cases below the thresholds values (TV) permitted in Poland for soils of traffic areas (soil group IV in Ordinance of the Minister of the Environment of Rep. of Poland, 01.09.2016 [22]). Maximum values for the Ekranic Technosols were respectively, for Cd 1.12 mg·kg<sup>-1</sup> (TV 15 mg·kg<sup>-1</sup>), Cu 38.6 mg·kg<sup>-1</sup> (TV 600 mg·kg<sup>-1</sup>), Ni 15.7 mg·kg<sup>-1</sup> (TV 500 mg·kg<sup>-1</sup>), Pb 56.8 mg·kg<sup>-1</sup> (TV 600 mg·kg<sup>-1</sup>) and Zn 154 mg·kg<sup>-1</sup> (TV 2000 mg·kg<sup>-1</sup>). In many cases the content of described metals was higher in the lower horizons of soil profiles, but it is hard to talk about the rule Table 2.

**Table 2.** The content of heavy metals in Ekranic Technosols from Zielona Góra.

Depth	Cd	Cu	Ni	Pb	Zn
cm	mg·kg <sup>-1</sup> d.m.				
Soils sealed with bitumen surface					
30-40	0.28	20.18	15.40	22.58	52.80
40-60	0.30	28.58	5.84	56.80	71.40
60-100	0.22	12.28	13.86	21.42	25.20
100-130	0.34	20.14	14.90	23.00	43.80
130-150	0.42	15.04	15.20	9.91	22.00
20-80	0.28	10.08	5.36	16.27	29.80
80-150	0.34	13.00	15.00	9.40	61.00
Mean	0.31	17.04	12.22	22.77	43.71
SD	0.06	5.90	4.21	14.86	17.55
Soils sealed with concrete slabs					
05-10	0.36	8.00	13.42	5.95	12.80
10-100	0.64	19.78	15.74	30.80	154.40
100-150	0.34	13.00	13.48	13.20	48.40
5-8	0.42	10.90	3.84	6.80	49.00
8-50	0.22	8.87	3.22	15.56	31.60
50-90	0.26	10.32	1.88	14.20	46.00
90-120	0.18	7.04	3.56	8.14	17.80
120-150	0.40	11.50	5.16	15.20	86.80
Mean	0.35	11.18	7.54	13.73	55.85
SD	0.13	3.72	5.28	7.39	42.95
Soils sealed with concrete paving stone					
5-10	0.40	13.68	12.62	7.00	24.80
10-15	0.38	38.60	12.80	20.29	40.00
15-25	0.36	15.48	4.80	35.80	85.00
25-80	0.26	8.10	3.26	7.24	16.40
80-110	1.12	23.06	10.24	19.20	116.60
110-150	0.26	15.14	2.44	10.00	70.60
Mean	0.46	19.01	7.69	16.59	58.90
SD	0.30	9.79	4.33	10.10	35.29

## 4 Discussion

The exponential increase in the number of cities inhabitants results in need for urban expansion and building densification. The growth of the cities results in seizure of large areas of land. Soils in urban areas show a significant mechanical transformation, that affect their physical, chemical and biological properties [21, 23]. Many areas within the cities are sealed with impermeable and semi-impermeable materials. In Zielona Góra the share of the Ekranic Technosols ranged from 13 to 15% in total area of the city, depending on city district [2]. Sealing form soil with impermeable materials such as

asphalt and concrete is mentioned as one of the main forms of mechanical degradation of urban soil. This kind of soil degradation strongly reduced permeability which effects in reduction of the infiltration of rainwater into the soil profile and interferes with gas exchange between the soil and the atmosphere.

The soil horizon below the technic surface has been mineral in the most of locations; the residual humic horizon occurrence has been noted rarely (3-10 cm thick). At a depth of 10 to 80 cm, the content of organic carbon ranged from 0.75 to 1.50%. In a consequence of land preparation for road construction purposes soils are truncated and the topsoil reach in organic carbon is transported to the other places. In effect lowering of organic carbon content in soil is observed. The low organic matter content in urban soils (urbanozems and ecranozems) can be explained other ways, by the disturbance of the soil/vegetation relationships [24]. However, changes between soil sealed with permeable and non-permeable material can be seen in the long term [3].

Sorption properties depend on the particle size distribution, organic matter content and the content of different artificial porous materials. CEC ranged from 2 to 17  $\text{cmol}\cdot\text{kg}^{-1}$  d.m. is typical for the most soils of Zielona Góra city and its surroundings.

One of the most commonly observed characteristics of Technosols is a presence of different artefacts, mainly construction rubble. Because of high carbonates content in the mixed rubble, pH values of soils in urban areas are normally higher than in city surroundings. All of examined soils show pH higher than these typical for agricultural or forest land in Zielona Góra surroundings (5.8–7.4 vs. 4.1–5.6). Soils sealed with concrete elements show higher reaction in the topsoil [1]. Frequently used technique of concrete element lay-out is locating them on special prepared sand-cement foundation. Additionally it is very rare situation cleaning the soil from rubble before the traffic area construction. An effect of this is unification of soil pH regardless of location and form of sealing. Lack of difference between the different Ekranic Technosols in the average pH values was described also by other researchers [1, 17].

The layers located directly below the pavements show a lower content of some heavy metals (mainly Cd, Cu, Pb, Zn) comparing to the deeper horizons. However, in some cases the opposite situation can be seen – the content of Zn, Ni and Pb can be relative higher. The described study does not detected significant differences in the heavy metals content under different technic surfaces. The presence of heavy metals in soil is an effect of different activities, natural and anthropogenic origin. Besides the mineralogical composition and rock weathering processes, many factors of heavy metals deposition are connected with water or air transport. Such movement determines the superficial distribution of trace elements in the soil profile. Many changes in such described causal chain are expected when the human impact is taken into account – mostly in a consequence of soil mixing, artificial layers forming and artefacts input. The heavy metal content in soils is also the result of time of impact.

Metals and metalloids unlike organics compounds are not degraded in the environment, which might occur even more dangerous when it comes to environmental safety. Huber with co-authors [25] show that presents of selected heavy metals can vary significantly in the runoff from traffic areas. Some research demonstrate that urban soil surface conditions have considerable influence on convective rainfall and that they are important in the chain of heavy metal distribution in the urban ecosystem [26]. Runoff from urban roadways can impact the quality of the environment, in the first place



surface waters and soils, after that the groundwater reservoir [27]. Some authors emphasize [28, 29] that non-permeable materials used for pavements may work as a natural filter for the contaminated rain water. This phenomenon can be linked with the sorption properties of the materials used for the technical construction [30].

## 5 Conclusion

1. Ekranic Technosols of Zielona Góra urban area are very poor, in most cases representing grain-size composition of sand. The material of these soils has been strongly modified during the pre-investment area preparation and process of building. As a result of the construction works, the soil material with good construction properties (bearing capacity, no swelling and shrinkage) was obtained.
2. The organic matter content is very low. Relatively higher content was revealed only in the horizons, situated directly under the technic surface, what is normal situation, due to the soil truncation before the road/pavement construction.
3. Physicochemical properties are not significantly different between soils representing sealing categories or changes can be seen in the longer term. Typical feature for these soils is high pH level what is result of building material admixture – constructional or waste. Many horizons show low sorption capacity due to the admixture of building sands and gravels or even artificial sand/gravel horizons construction.
4. Heavy metals were found in the tested samples in the quantities similar to the geochemical background of Zielona Gora urban area. This content can be regarded as ‘safe for the environment’.

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# The Technosols on 60–70 Year-Old Technogenic Deposits of the Lomonosov Moscow State University Campus

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**Abstract.** The complex of buildings of the main campus of the Lomonosov Moscow State University (LMSU) on the Leninskie Hills (Sparrow Hills) was constructed in the middle of the 20<sup>th</sup> century. In this paper we compare results of soil formation under different combinations of low intensity anthropogenic influences within an area of soils 60–70 years old, which were formed on similar technogenic deposits – ‘building grounds’. Pedogenesis is shown to have two main trends, postlithogenic and synlithogenic, depending on the rates of matter accumulation on the soil surface. Matter accumulation can lead to the formation of specific urban humus horizons that are eutrophic and calcareous. The climate warming and increasing humidity have resulted in intensive organic matter accumulation within areas, where leaf litter has not been removed and composts have been applied.

**Keywords:** Urban soils · Soil organic matter · Soil evolution  
Russia

## 1 Introduction

Modern urban environments are characterized by the active relocation of ground masses with the formation of new layers of technogenic deposits. Surfaces undergo long-lasting changes caused by intensive land use and the development of newly built-up areas. As a result, city soils generally tend to be quite young.

The complex of buildings of the main campus of the Lomonosov Moscow State University (LMSU) on the Leninskie Hills (Sparrow Hills) at the South-Western suburb of the city was constructed in the middle of the 20<sup>th</sup> century. Following the completion of the buildings, a Botanical Garden was established together with general land ameliorations within the LMSU campus. As a result, the site consists of a vast area with varying land use and soils 60–70 years old. Therefore, this allows for comparison of soil formation under different combinations of low intensity anthropogenic influences.

## 2 Study Site

Prior to the construction of the campus, the whole area of Leninskie Hills was occupied by rural settlements, fields and woodland patches. The native soils were classified as Albic Retisols (profile A-AE-E-Bt-BC-C) [1]. They are called sod-podzolic soils in the Russian tradition. This soil developed in a loamy parent material with predominantly Umbric humus horizon with 7–15 cm thickness, gradually going down to the light-colored Albic eluvial horizon having an irregular lower border with interfingering penetrating into illuvial Bt horizon having visible accumulation of clay. Sod-podzolic soils are predominantly formed on the not-stony mantle loams in the Moscow region. The area has been realigned several times during and after construction. Some layers of technogenic deposits have been formed at the surface from a mixture of natural soil material, natural sediments (from excavations) and different wastes (construction and household). Natural sediments are represented by moraine and mantle loam. Moraine age is synchronous with Alpine glaciation RISS 2. Works on soil remediation and landscape design were carried out after the construction phase.

The soils which were studied were formed on similar technogenic deposits – ‘building grounds’, from 0.3 to 3 m thick. Calcareous inclusions were very rare or absent within the surface layer, where modern pedogenesis takes place.

Currently, the territory of the campus includes a harmonious combination of buildings, roads of various sizes, lawns, planted trees and the botanical garden, which includes an arboretum (dendrarium), orchard, plots of cultivated plants, etc.

Land use was determined by the character of the human impacts. These include:

1. pollution from traffic and airborne solids from surrounding areas;
2. removal of fallen leaves (only partial since 2010 and not for 50 years in the Botanical Garden arboretum);
3. replacement of surface horizons and fertilizing of lawns by bedding composts;
4. periodic soil disturbances in connection with construction work;
5. sealing of soils by road surfaces;
6. the climate change resulting from the inclusion of the area into city territory, i.e., it is becoming warmer, from frigid and isofrigid to mesic soil temperature classes, with increased rainfall [2–4].

Studied soil pits were located in the Botanical Garden arboretum, on road-side lawns and under planted trees, altogether 20 pits (Fig. 1). The land management involved the complete removal of fallen leaves in the autumn except in the Botanical Garden arboretum. However, since 2011, only a partial removal of leaves has been practiced. The lawns have been regularly improved by additions of fertile composts.

## 3 Methods

Soil bulk density was determined in three replications in undisturbed core samples taken by a metal cylinder of known volume pressed into the soil. The bulk density was calculated by the ratio of dry mass to volume at the determined water content and/or the specified water tension [1]. Particle-size composition was determined in the field [5].



**Fig. 1.** Location of soil pits on the Lomonosov Moscow State University campus area.

Magnetic susceptibility of soil was measured with a KT-5 susceptimeter under natural conditions. Measurements were performed in five replicates for each horizon [6].

The pH of a 1:2.5 water suspension was determined potentiometrically. The carbonate content of soils was determined by the volumetric method with a calcimeter in two replications [7].

The organic carbon content was determined using the modifications of the Tyurin titrimetric method (dichromate oxidation). The group composition of soil humus (Cha/Cfa) was determined by use of the accelerated pyrophosphate method according to Kononova and Belchikova [8]. Organic carbon pools were calculated for the 0–30 cm, 0–100 cm and 0–150 cm layers.

Extraction of labile fractions of soil phosphorus and potassium was carried out by Machigin's method by solution of carbonate ammonium ( $\text{NH}_4)_2\text{CO}_3$  (1% (w/w) concentration) at a ratio of soil to solution 1:20 [7]. Standard quantitative methods – atomic absorption spectroscopy for potassium and photometric for phosphorus.

Exchangeable cations composition was investigated in 0.1 N  $\text{NH}_4\text{Cl}$ -ethanol extract after leaching of water-soluble compounds [7]. K and Na were determined by flame photometer, Ca and Mg by atomic absorption spectrometry.

## 4 Results and Discussions

The Botanical Garden's soils had a magnetic susceptibility of 0.5–0.1 SI, which is double or triple of that found in background soils. The road-side lawn soils had a magnetic susceptibility of 1–3 SI, which is comparable to mean values over the city. The rate of accumulation of airborne solid deposits in the soils studied varied from 15 to 50  $\text{g}/\text{m}^2$  per year, which corresponds to low and medium atmospheric loads within Moscow that are themselves 10–40 times higher than those outside the city [9, 10].

Macromorphologically, the results of 70-year-long pedogenesis were expressed in the formation of humus horizons. Micromorphologically, soil-forming processes were identified as follows: structuring of technogenic grounds due to their processing by soil fauna; vertical migration of soil organic matter and clay in the absence of carbonates; mineral weathering and decomposition of inclusions within soil; and the formation of calcareous and ferruginous pedofeatures.

Most soils of the study site can be classified as Technosols, according to the WRB [1]. In fact they can be subdivided into two groups depending on general pedogenetic trends.

The first group includes soils of typical postlithogenic pedogenesis and the A-AC-C profile, located within areas of low anthropogenic pressure. The description of a typical profile of this group of soils is shown below. According to WRB the soil was defined as Urbic Technosol (Siltic, Endogrossartefactic) (Fig. 2A).



**Fig. 2.** Urbic Technosols: A. - postlithogenic; B. and C. - sinlithogenic on the Lomonosov Moscow State University campus.

O\* (0–1) - Fragmentary litter composed of pine needles, small branches and remnants of cones.

AYur (1–16) - Slightly moist, greyish-brown (10YR 3/2) sandy loam, weak to moderate crumbly structure, many roots (grass roots in the upper part, and tree roots in the lower one), soft, friable, fine rock and brick fragments and few coarse ones, local effervescence with HCl; clear transition, even or slightly wavy boundary.

AYTCH1 (16–27) - Slightly moist, grey light brownish (2.5Y 5/4) sandy loam, blocky subangular to crumbly structure; very few roots; slightly firm; slightly compact; 10–20% fragments of brick and glass; few earthworm channels; no effervescence with HCl; clear transition by the decreasing number of earthworm channels, wavy boundary.

TCH1 (27–60) - Slightly moist, heterogeneous in colour: grey light brownish (2.5Y 5/3) with dark grey and reddish brown mottles (10YR 4/4), sandy loam, prismatic and blocky subangular structure, very few roots; hard and firm, clay-humus coatings on ped faces, charcoal, brick and stone fragments are common (20–30%), some of them effervesce with HCl; clear transition by colour, abundance of artefacts and density, wavy boundary.

TCH2 (60–100) - Slightly moist, light brown (2.5Y 4/4), sandy silty loam, prismatic and blocky subangular structure, no roots, firm and dense, many charcoal, brick and stone fragments (40–50%), strong effervescence with HCl.

\* Indices of the horizons according to [11] and can be correlated as follows: AYur – humus horizon with urban artifacts – Au, TCH – technogenic sediments – Cu.

The humus accumulation process resulted in a humified layer up to 30 cm deep (A+AC). Dense horizons of technogenic sediments are loosened under the action of macrofauna. Humus horizons are saturated with Ca and Mg (Table 1). Some humus horizons contain carbonates unlike the parent material. The accumulation of phosphorus is moderate, with most available phosphates being concentrated in the technogenic horizons.

**Table 1.** Properties of Urbic Technosols on the Lomonosov Moscow State University campus [4].

Horizon**	Depth, cm	Exchangeable cations, cmol (+)/kg					CaCO <sub>3</sub> , %	Available P <sub>2</sub> O <sub>5</sub> , mg/kg
		Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	∑		
1. MSU2 postlithogenic - Grey humus soil (partial removal of leaf litter)								
AYur	1–16	0.17	0.30	7.71	1.04	9.22	<1%	40
AYTCH1	16–27	0.17	0.14	12.73	0.78	13.82	n.d.	–
TCH1	27–60	0.14	0.05	10.02	0.68	10.89	n.d.	333
TCH2	60–100	–	–	–	–	–	<1%	39
2. MSU5 synlithogenic soil - Urbanozem (leaf litter removal, compost additions and intensive atmospheric deposition)								
URrat	0–6	0.41	1.17	19.50	1.52	22.60	2.0	29
UR1	6–41	0.33	0.26	10.57	0.89	12.05	3.2	8
UR2	41–50	–	–	–	–	–	1.7	13
TCH	50–100	0.72	0.43	14.26	0.69	16.10	<1	41
3. BG9 Reclaimed soil - Recreazem (regular compost additions and atmospheric deposition)								
RAT	0–12	0.54	0.42	16.43	1.53	18.92	<1	62
AY1	12–23	1.19	0.35	22.34	1.43	25.31	<1	–
AY2	23–37	–	–	–	–	–	<1	36
TCH	37–72	–	–	–	–	–	<1	42
[Pur.g]	72–90	–	–	–	–	–	n.d.	40

'n.d.' not detected; \*\* '–' no data

\*\* Indices of the horizons according to [11] and can be correlated as follows: AYur – humus horizon – Au, UR – urbic humus horizon – Au, RAT – peat-compost layer – A, P – arable horizon – Ap, TCH – technogenic sediments – Cu, BT – illuvial horizon of Albic Retisols – Bt.

The stratification of the surface horizons occurs in areas with the most active deposition of material onto the surface. The reasons for this may be different: long-term fertilization of soils; deposition of solids from the atmosphere and casual adding of peat or organic composts to the soil surface.



The second group includes soils with the synlithogenic trend of pedogenesis and comprises a greater diversity of soils: some of them have had an incrementally growing humus horizon due to compost additions (profile A1-A2-...-C), while others have had a specific urban humus horizon – Urbic (UR) (a kind of humus horizon) and have been termed as Urbostratozems [11]. Urbostratozems are formed within areas, where a significant rate of airborne dust deposition is combined with the occasional deposition of solid waste and possible additions of fertile composts. The description of a typical profile of this group of soils is shown below. According to WRB the soil was defined as Urbic Technosol (Eutric, Siltic, Mollic) (Fig. 2.B). The humus horizons are determined [11] as UR.

URrat\*\*\* (0–6) - Slightly moist, greyish and reddish brown (2.5Y 4/2), friable, mostly strong granular crumbly structure. Crumbs are angular, rather firm, and there are also earthworm casts and clusters of coprolites along fine roots, silty sandy loam. Many roots, plant residues are weakly decomposed. Weak discontinuous effervescence with HCl. Clear transition by the abundance of roots, colour, structure and number of artefacts; wavy boundary.

UR1 (16–41) - Slightly moist, heterogeneous in colour: from dark brownish grey to reddish brown grey (10YR 4/2, 4/3, 3/2); dark mottles are earthworm channels and coprolites. Rather firm, crumbly subangular blocky and granular structure with a trend to stratification. Peds are more firm than in the above horizon, coarse silty loam with sand admixture. The heterogeneity is seen as caused by the input of different substrates on the soil surface. Many roots (fine and coarse tree roots). Effervescence is medium and continuous. Many anthropogenic artefacts – construction and municipal wastes (>30%). Clear transition by colour, slightly wavy boundary.

UR2 (41–50) - Slightly moist, dark brown grey (10YR 4/2, 3/2, 2/2). Moderate to weak granular crumbly structure, more friable than the above horizon, dense tree roots, more abundant than above, many well decomposed plant residues. Silty sandy loam, very few artefacts, continuous effervescence with HCl. Clear transition by colour, abundance of roots and density, slightly wavy boundary.

TCH (50–100) - Slightly moist, but more moist than the above horizon, heterogeneous in colour: yellowish grayish brown (10YR 5/2, 5/3, 4/3, 4/4). Angular prismatic structure of several orders (from small to medium-size prisms), peds are firm. Loam with admixture of sand, few voids, (1–2 mm), dense. Fe-Mn segregations and iron ortsteins (nodules). Few roots, artefacts of construction wastes 10–20%, fine fragments of soft brick, charcoal, limestone in the fine earth. The colour heterogeneity is due to fragments of soddy-podzolic soil horizons. Weak effervescence of some artefacts.

\*\*\* Indices of the horizons according to [11] and can be correlated as follows: UR – urbic humus horizon – Au, rat – peat-compost material, TCH – technogenic sediments – Cu.

The Urbic horizons which developed over a period of 65 years were relatively thick (about 50 cm at the sites with preserved upper horizons), with a distinct tendency for horizontal splitting of structural units, high contents of artefacts of different sizes and well-developed processes of transformation of chemical properties. This has been formed concurrently with the parent material addition by the transformation of organomineral natural and/or artificial substrates. The UR horizons of the study site had the following features: Color Value <4 and Chroma 1–3; platy-blocky structure; the volume of (urban) artifacts of more than 20% in fine earth; alkaline to neutral pH; effervescence with 10% HCl; content of soil organic carbon (Corg.) of about 1–2%; the Cha/Cfa ratio of about 1:1; an increased Corg. pool as a result of large thickness of the

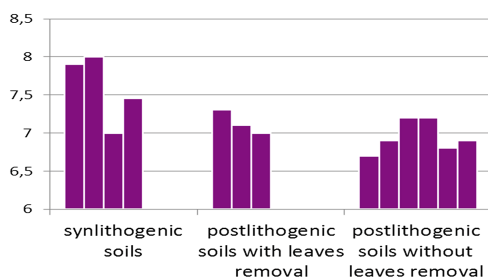


horizons; an increased amount of soluble compounds and a moderate accumulation of chemical pollutants.

There were also some buried soils and horizons, both natural and agriculturally transformed, preserved under the shallow technogenic deposits within the botanical garden.

According to the particle-size distribution, the natural soils and parent rocks were judged to be silty loams. Technogenic materials and horizons formed on such substrate have a sandy loam texture due to the large number of debris inclusions. The Urbic horizons of soils subjected to higher anthropogenic pressure near roads were sandy loams. According to bulk density measurements, soil compaction was insignificant. Bulk densities of humus horizons were 1.0–1.3 g/cm<sup>3</sup> [12].

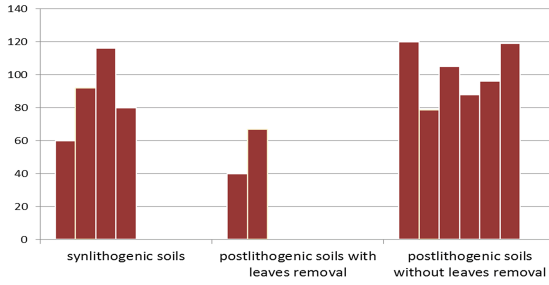
All the studied soils were characterized by eutrophication of their surface horizons due to depositions of airborne alkali salts and ice-melting agents incoming from roads. Soils with neutral to alkaline reaction developed on initially non-calcareous and weakly-calcareous parent materials, with their surface horizons containing up to 3% of carbonates. Most intensive influence of the city environment on the synlithogenic soils is the higher pH level (Fig. 3). The average soil pH level in Moscow city is about 7 [13]. This corresponds to the average pH level of atmospheric dust [10].



**Fig. 3.** pH of humus horizons on Lomonosov Moscow State University campus.

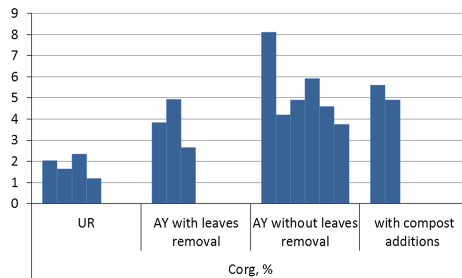
The soil organic carbon stocks of ranged from 40 to 120 t/ha within the 0–30 cm layer and from 50 to 250 t/ha within the 1 m layer (Fig. 4, Table 2). Synlithogenic soils were characterized by significant stocks of soil organic matter (SOM) because of their deep modern and buried humus horizons enriched in SOM. The biggest SOM stock (comparable to that in Phaeozems) was found in soils of the arboretum, where no leaf litter removal was carried out. In those soils SOM stocks were due to high contents of organic matter in upper horizons.

For young soils, SOM accumulation was the main pedogenic process. A general trend for the current formation of highly humified horizons was revealed. Depending on the leaf litter removal and biological activity of the soils studied, the contents of Corg ranged from 0.6 to 4% (outside the Botanical garden) to 4–7% (in the arboretum of the Botanical Garden and in the horizons of fertile compost) (Fig. 5). Without leaf litter removal in the arboretum of the Botanical Garden the soil horizons had a soil organic matter content of 10–14%. Horizons with organic matter accumulation under



**Fig. 4.** Corg pools (0–30 cm) in t/ha Lomonosov Moscow State University campus.

conditions of soil improvement through compost additions (during last 1–5 years) were characterized by a high organic matter level irrespective of the type of land use. The average level of organic matter contents in soils of Moscow city is 2–3%. Synlithogenic and postlithogenic soils, where leaf litter removal was carried out, had a similar level. Soils without leaf litter removal were characterized by more intensive SOM accumulation, probably related to climate warming and increasing humidity, which generally increases the bioclimatic potential for eutrophication of urban soils. The soil organic matter of the studied soils has different characteristics from those in native soils of the southern taiga belt, i.e., the SOM studied has features typical for more southern pedogenesis. However, a general ‘forest-type’ character of humus is preserved [14]. Due to climate change and eutrophication of soils the ratio Cha/Cfa increased in comparison to natural soils of the Moscow region. But this ratio in the studied soils corresponds to the average level for Moscow soils (about 1:1). It is only considerably higher in the compost horizons (Table 2).



**Fig. 5.** The content and quality of organic matter in different humus horizons Lomonosov Moscow State University campus.

Absorbance of humic acids also increases in all studied soils. Table 2 shows data indicating the predominant accumulation of humic acids in the profile of urban soils, which is untypical for their natural counterparts. The level of humus accumulation is higher in soils recultivated by subsoiling or fertilized with organic matter. There is an accumulation of organic matter due to fresh litter in the upper horizons of

postlithogenic Grey humus soil, a labile organic substances (humic and fulvic acids) are formed with low E-values coefficients in the upper horizon.

**Table 2.** Soil organic matter properties of Urbic Technosols [4] on Lomonosov Moscow State University campus.

Horizon**	Depth, cm	Corg, %	Cha/Cfa	0.001%HA E465nm,1cm	E4/6	Cha/Corg, %	Corg. pool, 0-100 cm, t/ha
1. MSU2 postlithogenic - Grey humus soil (partial removal of leaf litter)							
AYur	1–16	2.22	1.49	0.063	5.8	17.1	52
AYTCH	16–27	0.52	0.81	0.089	5.0	28.8	
TCH	27–60	0.39	0.90	0.025	4.9	23.1	
TCH2	60–100	0.36	–	–	–	–	
2. MSU5 synlithogenic soil - Urbanozem (removal of leaf litter, compost additions and intensive atmospheric deposition)							
URrat	0–6	6.96	3.52	0.082	5.8	18.7	143
UR1	6–41	0.69	1.36	0.087	5.3	23.2	
UR2	41–50	3.91	1.70	0.065	4.4	16.1	
TCH	50–100	0.70	0.40	0.045	5.3	5.7	
3. BG9 Reclaimed soil - Recreazem (regular compost additions and atmospheric deposition)							
RAT	0–12	4.89	1.04	0.083	5.5	29.2	246
AY1	12–23	1.63	1.02	0.085	4.4	30.1	
AY2	23–37	1.12	0.94	0.081	4.2	29.5	
TCH	37–72	0.56	0.92	0.043	4.1	21.4	
[Pur.g]	72–90	5.63	1.01	–	–	29.7	
[BTg]	90–115	0.10	–	–	–	–	

Humic acids lose their mobility with depth, with their partial condensation being likely within AYTCH horizon, which is expressed by an increase in the E coefficient values. The high values of Cha/Cfa ratio within the upper horizons of synlithogenic soils are caused by compost applications in combination with impeded downward migration of SOM due to its immobilization by calcium carbonates deposited from the atmosphere. The applied composts have different contents of Corg., which is reflected in the appearance of several peaks of Corg. distribution within the soil profile.

## 5 Conclusion

The general trends of soil development within the LMSU campus, where pedogenesis has not been interrupted by new additions of technogenic grounds which is now 60–70 years, are determined by a combination of low intensity anthropogenic impacts. There are depositions of inorganic materials onto the soil surface (airborne dust deposition, waste accumulation and compost addition) and accumulations of organic matter varying in volume and composition (with and without leaf litter removal, addition of

organic-rich composts and pollution by carbohydrates). The subdivision of pedogenesis into two main trends, postlithogenic and synlithogenic, is connected to the rate of mineral matter accumulation on the soil surface, which applies to the road-side locations and the areas, where soils have been improved by regular compost additions.

The accumulation of material on the surface leads to the formation and accretion of specific urban humus horizons, eutrophic and enriched by humus.

Soil chemical properties are determined by the parent material contains the fragments of alkaline construction waste and additions of compost. Atmospheric dust brings the high amount of alkaline and trace elements [10], that also leads to eutrophication of the surface soil horizons especially in sinlithogenic soils.

SOM accumulates in greater quantities than in natural southern taiga soils and has the characteristics typical for that of warmer regions:  $Cha/Cfa > 1$ , absorbance of humic acids  $> 0.08$ . This is especially noticeable for areas, where there is no leaves collection and compost additions.

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# Reflections on the Modern Soil Cover of the New Jerusalem Monastery: The History of Anthropogenic Landscape Transformation

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**Abstract.** The New Jerusalem Monastery is one of the largest cultural and historical monuments of Russia. A long history of anthropogenic transformation of the landscape has also changed the properties of soils. The territory inside the monastery walls has been exposed to the greatest transformation. The soils outside the monastery in the valley of the Istra River have undergone less anthropogenic transformation. We identified the main types of soils, and characterized their morphological peculiarities, and physical and chemical properties. Urbic Technosols on technogenic sediments are described in the different types of land uses: near the cemetery from the 17th century, under the apple tree orchard, and on the grassplot near the south wall of the monastery. The results of the study can be used to restore the monastery and historical landscape.

**Keywords:** Human impact · Technogenic deposits · Technosols  
Urban soils · Alluvial soils

## 1 Introduction

Many works have been devoted to the study of urban soils, both in Russia [1–4] and in other countries [5–13]. Moreover, the soils of monasteries located outside cities have been studied in the countryside [14, 15]. However, the soils of monasteries located in cities have scarcely been studied. Soils play an important ecological role in the city. In addition, they preserve the memory of the history of the development of the natural and anthropogenic landscape.

The purpose of this study was to study the main types of anthropogenic soils formed on the territory of the New Jerusalem Monastery. The following objectives were established: (1) to identify the main morphotypes of soils formed under different types of land use; (2) to study their morphological, chemical, and physical properties; (3) to establish the patterns of soil changes in relation to anthropogenic impact.

## 2 Material and Methods

The New Jerusalem Monastery is an object of federal significance<sup>1</sup>. This is one of the largest cultural and historical monuments of Russia. The New Jerusalem Monastery is located in the city of Istra, in the Moscow Region. It was built in 1656 according to the plan of Patriarch Nikon. The surrounding area of the monastery was significantly transformed based on the concept of “Russian Palestine.” The natural and cultural landscape of the monastery was to become an analogue of the “Holy Land” in Jerusalem. The monastery was one of the most popular centers of pilgrimage in the 19th century and at the beginning of the 20th century. Anthropogenic impact on the territory of the monastery has included several stages. The most significant of these were related to the construction and functioning of the monastery, although the beginning of agricultural development of the territory dates back to the Iron Age [16]. The monastery was built on a bend of the Istra River on a hill of natural origin (the second terrace above the floodplain). The hill is composed of moraine, fluvioglacial deposits, and various ages of alluvial sediments. From the surface they overlap with a cultural layer, with a thickness ranging from 0.2 m at the center of the hill to 7–8 m along its edges. The absolute height of the hill is 160.0–162.5 m. On all sides, except the east, the slopes of the hill have a steepness of 36–42°. The first terrace above the floodplain is of limited distribution, and it traverses the monastery hill from the north to the south-west. The floodplain of the Istra River, with a width of 100–250 m, stands out well in the relief. The slopes of the monastery hill are covered with woody vegetation. Part of the floodplain comprises a park (the former Gethsemane garden).

Investigations of the soil cover inside the walls and outside the monastery were conducted in 2012–2013 [17]. Soil profiles were described inside the walls of the monastery in relation to the different types of land uses: near the arborvitae avenue on the site of the cemetery from the 17th century (p. 1), under the apple tree orchard (p. 3), and on the grassplot near the south wall of the monastery (p. 2), on the north hillslope of the monastery from the Implementing tower to the course of the Kedronskiy flow (pp. 4, 5). Soil samples were taken from each site, and analyzed for soil properties such as  $\text{pH}_{\text{H}_2\text{O}}$ , total organic carbon, and exchangeable bases, using the Schollenberg method for acid soil, and Pfeffer’s method with the Molodtsov and Ignatova modification for neutral and alkaline soils. The content of mobile forms of phosphorus and potassium was analyzed according to Kirsanov’s method for acid soil and Machigin’s method for calcareous soil. Soil texture was determined by the pyrophosphate method. Mobile forms of heavy metals extracted from the soil were treated with ammonium acetate extract buffer at pH 4.8. The concentration of heavy metals in the extracts was measured by mass spectrometry with inductively coupled plasma in the ICP-MS 7500a.

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<sup>1</sup> New Jerusalem’s history, architecture and art museum was organized in 1920 within the precincts of the late “New Jerusalem” Resurrection (Voskresenskiy) monastery. It is one of the largest museums in the vicinity of Moscow. “New Jerusalem” Resurrection monastery is a unique phenomenon in Russian history and culture. The intention of its founder, patriarch Nikon (1605–1681), was really daring - to recreate the Holy Land of the Christians near Moscow. “Palestine” near Moscow was planned and realized as a grandiose architectural and landscape complex.

### 3 Results and Discussion

#### 3.1 Characteristics of Anthropogenic Soils: Soil Morphology and Properties

The territory inside the monastery walls has been exposed to the greatest transformation, concerning fills and strengthening for the slopes of the hill, the construction and repair of the monastery buildings, several fires, the destruction during the years of the Great Patriotic War, archaeological excavations, etc. As a result of this transformation, the natural soil cover has been completely destroyed and the natural ground has been covered by anthropogenic deposits over the different historical periods.

On the territory inside the monastery walls we investigated Urbic Technosols (Calcaric, Humic, Loamic) (p. 1) and Urbic Technosols (Calcaric, Humic, Hyperartefactic, Loamic) (p. 2)—on technogenic deposits [18]. The soil profile (p. 1) is divided into horizon A, densely permeated with roots, and an urbistratified Auk horizon with inclusions of brick fragments of different sizes and limestone (from depths of 9 cm). The content of artifacts is more than 20% of the horizon. Below are the technogenic deposits. Their upper layer is represented by a very dense, white, crushed limestone. The lower layers differ in terms of the abundance and size of inclusions of building materials (limestone fragments, bricks), as well as the presence of pebbles and boulders. Between the separate technogenic horizons, there are no soil formations. The technogenic horizons underlie stratified alluvial sediments. In the Urbic Technosols (Calcaric, Humic, Hyperartefactic, Loamic) at horizon Au2 there are up to 75% inclusions of different sizes of fragments of brick and stones. Based on the results of micromorphological studies, the upper horizons of the soils were characterized by a carbonate-argillaceous-humic composition of plasma—the highest biogenesisity presenting rich coprogenic zones—an aggregate of matter indicating the presence of a modern humic accumulative process.

Urbic Technosols (Calcaric, Humic, Loamic) on technogenic sediments were described in the apple tree orchard, which was newly planted on the territory of the monastery in 1970s (p. 3). The profile differed from those soils above, presenting a greater depth of stratification thickness necessary for the root system development of the fruit trees. The entire profile contains inclusions of artifacts (more than 20%). Urbic Technosols (Arenic, Eutric, Transportic) (p. 4) and Protoargic Arenosols (Colluvic, Technic) (p. 5) were formed on the steep slope side of the second terrace above the floodplain on allochthonous subsoil made up from outside to strengthen the walls of the monastery. The thickness of the filling layer, which included brick bars, amounted to 90 cm. The A horizon formed in its upper part. Below it was an underlying technogenic bed (p. 4) or buried subsoil (p. 5).

The texture of the A horizon of all the soil that formed on the filling layer was sandy loam (Table 1). The sandy proportion comprised 60–70%. The actual reaction of the anthropogenic soils is alkaline (pp. 1, 3), weakly alkaline (pp. 2, 4), or neutral (p. 5) (Table 2). This is due to the content of limestone in the soil profiles used in the construction of the monastery. Similar pH values are a characteristic feature of urban soils noted by many researchers [2–4]. This phenomenon is typical for anthropogenic soils of monasteries located in the countryside [14, 15]. This is a common property of



anthropogenically transformed soils, caused by the accumulation of domestic waste and construction debris.

The content of exchangeable calcium and magnesium in the upper horizons of anthropogenic soil from 8–15 cmol(equiv)/kg, decreased down to 3–4 cmol(equiv)/kg (Table 2). In the majority of soils the content of total organic carbon was low. In the upper horizons of the Urbic Technosols the content of total organic carbon was 1.8–3%. In the lower part of the soil profile the content of total organic carbon was less than 0.5%. The very high content of mobile phosphorus typical for all soils relates to the cultural layer. In Urbic Technosols (pp.1–3), the content of mobile phosphorus was 9–15 mg/100 g of soil. In p.1 and p. 2, this decreased down the profile. In p.3 it remained high and very high throughout the profile. The Urbic Technosols (Arenic, Eutric, Transportic) (p. 4) and Protoargic Arenosols (Colluvic, Technic) (p. 5) of the slope were characterized by a very high supply of mobile phosphorus throughout the profile. This may be due to the composition of the bulk material used to strengthen the slopes. An increased supply of mobile phosphorus is a characteristic property of urban soils, established in numerous studies [2, 4, 19]. The content of exchangeable potassium in most of the soils described was low and very low.

The anthropogenic soils were contaminated by heavy metals (Table 3). The content of mobile forms of zinc and cadmium achieved the maximum allowable concentration (MAC) in the soil of the garden, located within the monastery walls and created on transported soil. The excess of MAC of nickel, copper, zinc, and especially lead, was marked in the Urbic Technosols on technogenic sediments. The content of zinc and lead in Urbic Technosols formed on technogenic deposits achieved MAC. The Urbic Technosols formed near the cemetery from the 17th century were distinguished by the degree of pollution, significantly in excess of MAC for the content of nickel, copper, and zinc. Especially high concentrations of lead were found in this soil, significantly exceeding MAC. A decrease in the content of heavy metals with depth was clearly manifested. The soil contamination had a local character. It is necessary to take into account the quality of the man-made ground, which was used to create lawns. In addition, in the last few years, various types of equipment have been used for large-scale restoration work.

### 3.2 Characteristics of Alluvial Soils: Soil Morphology and Properties

Fluvic Cambisols outside the monastery walls in the valley of the Istra River present less anthropogenic transformation. Areas of the valley were employed for uses such as hay fields, gardens, and tillage. Hay making influenced changes in the biological cycle of substances. The soils retained their morphological characteristic features, but the result of the construction of the Istra reservoir in 1937, which entailed damming, disrupted the flood pattern, caused a reduction in the underground water table that worsened the signs of gleying in the soil, and stopped annual alluvial sedimentation. The soils studied were classified as Fluvic Cambisol (p. 6) and Gleyic Cambisol (p. 7). The soil cover was disturbed during the construction of various engineering structures in particular areas of the Bogoyavlenskaya Pustyn (the Cell of the Patriarch Nikon). During the period of the Patriarch Nikon, the hydrological regime of the soil was essentially changed as a result of the construction of a complex hydrological system,

**Table 1.** Particle size distribution in soils.

Horizon	Depth, cm	Content of the fraction (%): particle size (mm)						
		1,00–0,25	0,25–0,05	0,05–0,01	0,01–0,005	0,005–0,001	<0,001	<0,01
<b>Profile 1. Urbic Technosol (Calcic, Humic, Loamic)</b>								
A	0–8	44	22	16	4	6	8	18
Auk	8–21	52	19	13	5	4	7	16
Ckm	21–44	15	27	26	10	12	10	32
Cu	44–59	55	28	8	1	2	6	9
Cukm	59–82	43	17	21	6	4	9	19
C1	82–96	31	16	34	7	6	6	19
C2	96–110	28	19	35	6	6	6	18
<b>Profile 2. Urbic Technosol (Calcaric, Humic, Hyperartefactic, Loamic)</b>								
Au1	0–6	38	32	16	3	5	6	14
Au2	6–19	38	31	15	4	5	7	16
<b>Profile 3. Urbic Technosol (Calcaric, Humic, Loamic)</b>								
Aup1	0–6	16	20	35	7	9	13	29
Aup2	6–21	19	23	30	6	8	14	28
Cu1	21–58	34	26	23	5	5	7	17
Cu2	58–100	34	50	3	1	3	9	13
<b>Profile 4. Urbic Technosol (Arenic, Eutric, Transportic)</b>								
Au1	0–15	23	50	15	4	2	6	12
Au2	15–32	17	59	14	2	3	5	10
ACu	32–77	30	57	4	2	2	5	9
<b>Profile 5. Protoargic Arenosol (Colluvic, Technic)</b>								
Au1	0–10	30	35	20	4	5	6	15
Au2	10–52	32	30	26	3	4	5	12
Cuk	52–90	34	33	21	1	6	5	12
B1	90–145	37	55	2	1	2	3	6
B2	145–150	34	58	3	1	2	2	5
<b>Profile 6. Fluvic Cambisol (Loamic, Protocalcic)</b>								
A	0–5	20	15	41	9	7	8	24
Au	5–15	20	16	41	8	7	8	23
AuBh	15–33	14	14	51	7	8	6	21
Bh	33–51	28	17	41	5	5	4	14
Chm1	51–60	69	22	2	1	2	4	7
Chm2	60–85	68	17	2	4	3	6	13
R1	85–101	21	27	9	4	6	33	43
R2	101–116	23	29	10	4	5	29	38
<b>Profile 7. Gleyic Fluvic Cambisol (Aric, Siltic)</b>								
A1	0–3(7)	15	20	40	6	8	11	25
A2	3(7)–12(18)	12	19	44	5	9	11	25
AB	12(18)–28	4	21	50	7	7	11	25
B1	28–42	9	11	44	8	11	17	36
B2	42–63(67)	39	15	22	4	6	14	24
C	63(67)–117	74	19	2	1	1	3	5

**Table 2.** Chemical properties of soils.

Horizon	Depth, cm	pH <sub>H<sub>2</sub>O</sub>	Total organic C, %	Exchangeable bases, cmoll (equiv)/kg			Mobile forms, mg/100 g	
				Ca <sup>2+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup> + Mg <sup>2+</sup>	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O
Profile 1. Urbic Technosol (Calcic, Humic, Loamic)								
A	0–8	7,39	3,27	12,75	0,80	13,55	10,51	12,59
Auk	8–21	7,78	2,13	8,09	0,81	8,90	4,58	2,89
Ckm	21–44	8,48	0,51	8,96	0,02	8,98	3,00	3,41
Cu	44–59	9,71	0,15	3,87	0,02	3,89	3,00	3,53
Cukm	59–82	8,60	0,77	5,86	0,00	5,86	7,06	6,12
C1	82–96	8,37	0,52	4,10	0,00	4,10	8,11	3,30
C2	96–110	8,10	0,28	3,43	0,99	4,42	13,54	3,23
Profile 2. Urbic Technosol (Calcaric, Humic, Hyperartefactic, Loamic)								
Au1	0–6	7,24	1,80	8,7	1,26	9,96	14,7	14,55
Au2	6–19	7,45	1,06	7,26	0,9	8,16	9,76	8,83
Profile 3. Urbic Technosol (Calcaric, Humic, Loamic)								
Aup1	0–6	8,00	1,47	10,15	8,78	18,93	8,78	11,60
Aup2	6–21	7,79	0,96	8,87	4,81	13,68	4,81	6,36
Cu1	21–58	7,17	1,28	6,41	19,52	25,93	12,52	8,67
Cu2	58–100	7,91	0,23	4,38	7,13	11,51	7,13	4,27
Profile 4. Urbic Technosol (Arenic, Eutric, Transportic)								
Au1	0–5	7,19	0,77	6,61	3,26	9,87	11,53	12,33
Au2	5–32	7,20	0,74	5,08	1,64	6,72	9,76	4,68
ACu	32–77	7,17	0,24	3,58	0,3	3,88	10,87	3,53
Profile 5. Protoargic Arenosol (Colluvic, Technic)								
Au1	0–10	6,72	1,01	7,88	0,79	8,67	38,11	4,09
Au2	10–52	6,83	0,43	14,51	0,05	14,56	12,14	1,17
Cuk	52–90	6,51	0,10	5,85	0,41	6,26	24,02	1,51
B1	90–145	6,72	0,05	2,37	0,89	3,26	12,56	1,04
B2	145–150	6,69	0,09	2,76	1,04	3,8	11,45	1,01
Profile 6. Fluvic Cambisol (Loamic, Protocalcic)								
A	0–5	6,46	1,73	13,91	1,57	15,48	3,77	1,75
Au	5–15	6,41	1,71	14,32	1,55	15,87	3,88	2,35
AuBh	15–33	6,77	0,46	4,44	0,80	5,24	2,99	1,21
Bh	33–51	6,75	0,70	1,85	0,52	2,37	7,86	0,95
Chm1	51–60	6,80	0,16	1,11	0,37	1,48	4,99	0,62
Chm2	60–85	6,65	0,15	4,60	0,83	5,43	33,23	1,96
R1	85–101	6,96	0,66	21,45	2,67	24,12	–	–
R2	101–116	7,47	0,55	13,78	2,96	16,74	–	–
Profile 7. Gleyic Fluvic Cambisol (Aric, Siltic)								
A1	0–3(7)	6,00	2,59	20,13	1,64	21,77	21,55	25,74
A2	3(7)–12(18)	5,97	1,07	1,27	1,27	17,17	15,19	6,46
AB	12(18)–28	6,09	0,95	12,33	0,89	13,22	8,29	2,29
B1	28–42	6,10	0,45	16,85	1,03	17,88	5,52	2,84
B2	42–63(67)	6,10	0,19	13,69	0,98	14,67	1,66	2,01
C	63(67)–117	6,09	0,09	0,65	0,39	1,04	4,42	0,54

**Table 3.** The content of heavy metals and microelements in soils, mg/kg

Horizon	Depth, cm	Cr	Pb	Co	Ni	Cu	Zn	V	Mn	Sr
Profile 1. Urbic Technosol (Calcaric, Humic, Loamic)										
A	0–8	1,85	126,40	0,86	5,57	1,25	36,77	0,16	95,54	29,45
Auk	8–21	4,69	150,20	1,25	10,33	3,75	20,13	0,20	58,03	42,38
Ckm	21–44	3,44	12,23	1,39	12,75	1,04	2,51	0,11	39,02	59,55
Cu	44–59	0,67	0,87	0,09	0,78	0,45	0,69	0,04	15,72	10,63
Cukm	59–82	0,72	1,92	0,07	0,47	0,25	1,03	0,11	12,99	5,15
C1	82–96	5,52	0,19	0,12	0,72	0,48	2,99	0,07	35,46	4,74
C2	96–110	2,35	0,71	0,12	0,29	0,31	1,23	0,04	8,52	3,26
Profile 2. Urbic Technosol (Calcaric, Humic, Hyperartefactic, Loamic)										
Au1	0–6	1,04	163,90	0,42	2,54	2,85	15,86	0,27	73,34	17,88
Au2	6–19	1,49	200,70	0,48	3,84	6,68	13,92	0,36	45,59	23,86
Profile 3. Urbic Technosol (Calcaric, Humic, Loamic)										
Aup1	0–6	2,46	2,17	0,26	1,20	1,07	3,95	0,08	73,71	7,57
Aup2	6–21	0,77	3,30	0,09	0,56	0,51	1,85	0,03	42,25	4,74
Profile 4. Urbic Technosol (Arenic, Eutric, Transportic)										
Au1	0–5	1,59	54,01	0,26	1,32	0,89	5,46	0,20	48,31	10,17
Au2	5–35	1,44	20,50	0,12	0,61	0,75	2,61	0,13	25,53	5,77
Profile 5. Protoargic Arenosol (Colluvic, Technic)										
Au1	0–10	1,49	25,97	0,21	0,80	0,47	3,61	0,19	69,28	6,63
Au2	10–52	1,87	1,72	0,12	0,59	0,18	1,45	0,07	29,12	4,70
Cuk	52–90	1,86	0,55	0,11	0,34	0,20	0,88	0,06	9,68	2,86
Profile 6. Fluvis Cambisol (Loamic, Protocalcaric)										
A	0–5	0,69	3,36	0,23	0,33	0,20	0,93	0,12	51,12	2,86
Au	8–15	2,92	3,35	0,43	0,70	0,66	2,01	0,21	87,84	5,80
Profile 7. Gleyic Fluvis Cambisol (Aric, Siltic)										
A1	0–7	2,62	0,60	0,23	1,50	0,37	5,92	0,05	108,50	13,85
A2	3(7)–12(18)	2,53	0,59	0,17	1,35	0,30	2,82	0,03	80,43	12,43

which included a complex of partially interrelated systems of ponds and the “Kedronskiy flow,” which surrounded the monastery to the north, west, and south. Later, in the degradation of the monastery’s hydrosystem a main role was played by the highway engineering for the “Buzharovskoe roadway,” which cut through part of the monastery complex in the valley. The creation of the Gethsemane garden significantly affected the landscape: particularly the tree planting near the western walls of monastery (now the park area of the “New Jerusalem Museum”). The natural soils of the central floodplain and the first terrace rising above the floodplain partially have a predominantly sandy loam soil texture, characterized by the uneven distribution of proportions in soil profile resulting from the stratification of alluvial deposits (Table 1). Cambisols, characterized by a total organic carbon content of around 1.7–2.6% in the upper layers, sharply decrease in the soil profile; the pH is around 6, and the content of

exchangeable bases in the upper horizons is 15–21 cmol(equiv)/kg. The content of mobile phosphorus is very high in the soil profile. The Cambisols of the floodplain are not contaminated with heavy metals (Table 3).

## 4 Conclusions

The long history of anthropogenic changes in the landscape is reflected in the soil properties of the New Jerusalem Monastery. The natural landscape has undergone a radical change in the territory of the monastery hill. Within the monastery walls, the natural soil cover has been completely destroyed.

As a result of the transformation of the landscape, Urbic Technosols have formed on technogenic deposits under lawns and in the garden. On the steep slopes of the hill, sprinkled to strengthen the walls, Urbic Technosols and Protoargic Arenosols have formed on the ground. In this series, the thickness of the bulk of the fine-grained sequence of earth and the soil profile increases, depending on the functional use of soils. Anthropogenic soils are distinguished mainly by a light granulometric composition and low carbon content. They present stoniness due to the inclusion of construction and domestic debris, alkaline reaction, the high availability of mobile phosphorus, and local contamination with heavy metals—characteristic features of anthropogenically transformed soils.

Human intervention has changed the course of floodplain processes, represented in the development of Fluvic Cambisols. In 2009–2016, after extensive restoration works to reconstruct the architectural complex of the monastery, the primary target was to preserve the natural landscape of ecological and historical heritage, and the recreational natural anthropogenic landscape, without which the perceptual unity of the “Russian Palestine” would be impossible. Given the long-term development of tourism and pilgrimage to this historical place, it seems relevant to develop an appropriate infrastructure, which should be based on complex and comprehensive soil investigations.

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# Organic and Inorganic Contaminants in Urban Soils of St. Petersburg (Russia)

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**Abstract.** The study is aimed on assessment of soil contamination with organic and inorganic pollutants in areas with different land use type. A total pollution index ( $Z_c$ ) was calculated in order to assess soil contamination level according to 4 categories. A total of 8 metals were analyzed including Pb, Cd, Cu, Zn, Ni, As, Hg. Multiple excess of maximal permissible levels in soils of residential and industrial sites were found. Obtained  $Z_c$  values refers soils to high health risk category. A total of 15 priority polycyclic aromatic hydrocarbons (PAHs) were analyzed. Measured total PAHs and benzo(e)pyrene concentrations ranged from 0,06 to 3,77 mg/kg between different land uses with a maximum for residential areas. A slight positive correlation between Pb and benzo(e)pyrene concentrations in soil was found. Applied statistical method revealed significant differences in levels of HMs and PAHs, between land uses. A benzo(a)pyrene equivalency approach was used to assess health risk posed to humans due to soil contamination with PAHs.

**Keywords:** Urban soils · Contamination · Heavy metal · Organic pollutants

## 1 Introduction

St. Petersburg is a large industrial and transport center located at the eastern coast of the Baltic sea. It is the second largest industrial, transport and the first large marine and tourist center in Russia, situating close to the European Union, and thus the most important strategic center in Russia. Inland waters cover about 10% of the city. Total area of the city covers 1439 km<sup>2</sup>, 10% of which are dedicated to inland waters. Total population according to Rosstat data is 5 225 700 people. St. Petersburg is the administrative center of the North-West Federal District of Russian Federation, having highly developed industry and road density with extremely high traffic, a major seaport, providing gate to the Europe and other parts of the world.

The ecological state of the city is driven by emissions from numerous industries, railways, cargo and passenger seaport and heavy traffic highways, including Ring road with Western Speed Diameter. Large diesel and gasoline vehicle fleet includes 20 221 buses, 217 738 trucks and 1 638 183 cars, as of 2015 [1, 2]. A huge amount of operating petrol stations currently includes 397 stations. Industries of the city include high-capacity, resource- and power-consuming ecologically dangerous works.

Emissions to the air from stationary and mobile (transport) sources are dominant factor of soil contamination in the city due to atmospheric deposition. Control of air pollution is carried out by the automatic air monitoring system of the city including 12 automatic stations in different part of the city. In 2015 according to collected data total emission into the air from both the stationary and mobile sources has reached 521.0 thousand tons of chemicals, including particulate matter (PM) – 3.1 thousand tons, sulfur dioxide (SO<sub>2</sub>) – 4.4 thousand tons, carbon oxide (CO) – 379.4 thousand tons, nitrogen oxides (NO<sub>x</sub>) – 61.4 thousand tons, hydrocarbons (CH<sub>x</sub>) – 22.3 thousand tons, volatile organic compounds (VOC) – 49.2 thousand tons and 1.2 thousand tons of other pollutants [2]. 91.9% of emissions are accounted to the transport activity.

Soils of St. Petersburg are characterized by a different genesis and various degree of disturbance – from technosols of the historical center to seminatural albeluvisols of city parklands. Soils of the sites with high anthropogenic pressure are characterized by modified soil profiles, with inclusion of debris and other anthropogenic artifacts, and have a medium to a strong degree of surface littering, low projective cover of plants and signs of chemical contamination [11].

Soil ecological monitoring in St. Petersburg has been started since 1991 under the order of Committee for Nature Use, Environmental Protection and Ecological Safety of St. Petersburg (further reference - Committee for Nature Use). Survey of soil contamination is conducted to the moment at the expense of variety of funding sources, with a main contribution of the Committee for Nature Use, with a sampling network of 200 × 200 m covering already an area of about 830 km<sup>2</sup>, which includes the main residential and industrial zones and areas of prospective development. List of priority pollutants includes heavy metals (HMs) and metalloids (As), persistent organic pollutants (POPs – dioxins, polychlorinated biphenyls, organochlorine pesticides), aromatic hydrocarbons (BTEX – benzene, toluene, ethylbenzene, xylene) as well as hazardous organic compounds such as polycyclic aromatic hydrocarbons (PAHs – benzo[a]pyrene, benzo[k]fluoranthene, benzo[b]fluoranthene, benzo[g,h,i]perylene and others). Importance of soil contamination control is based on increasing of the potential health risks (carcinogenic and non-carcinogenic), posed to children and adults due to chronic exposure [3]. It is to be noted that exposure magnitude and dose received from soil contamination are different between the age categories. Children are more susceptible to soil contamination due to higher exposure magnitude [4, 5]. Thus the ecological state of urban soils especially at residential and recreational areas of the city needs to be under control.

Therefore, this study is aimed on assessment of anthropogenic load on urban soils of different land use scenarios in St. Petersburg determining the total concentrations of organic (benzo[a]pyrene; sum of PAHs) and inorganic (HMs) pollutants in soil.

## 2 Materials and Methods

Study area covered industrial, residential and recreational land uses of the Primorsky, Vasileostrovsky and Kirovsky administrative districts of St. Petersburg. Potential sources of soil contamination affecting HMs and PAHs levels in soil here are high traffic activity (Western highway and Primorsky prospect), steel and chemical



industries (Kirovsky engineering plant, Baltiysky shipyard plant, varnish factory “Kronos”), thermal-power-stations (“North-Western”) and other industries. A total of 135 grab topsoil samples were collected diagonally from 25 m<sup>2</sup> sampling plots [10].

Determination of PAHs in soils was carried out by reverse-phase high-performance liquid chromatography (HPLC). A total of 15 individual PAHs were analyzed. Data on the HMs content in soil was obtained via flame atomic absorption spectrophotometry method. Total concentrations of Pb, Cd, Cu, Ni, Zn, As and Hg were analyzed examined. Total soil pollution index ( $Z_c$ ) was calculated in order to assess health risk, according to the following equation:

$$Z_c = n(K_1 \times K_2 \times \dots \times K_n)^{1/n} - (n - 1)$$

Where,  $n$  – is a number of analyzed elements;  $K_1 \dots K_n$  – ratio of actual concentration of the element to its soil background (regional or clarke).

Health risk level is assessed according to 4 categories in order of increasing numerical value of the index:  $Z_c < 16$  – low;  $16 < Z_c < 32$  – moderate;  $32 < Z_c < 128$  – high;  $Z_c > 128$  – extremely high.

Obtained data were treated with STATISTICA 10.0 software, providing mean values with standard deviations e.g. “ $a \pm b$ ”. The normality of the data set was verified using a Shapiro-Wilk normality test. The null hypothesis is formulated as follows: “The sample being analyzed is derived from a general population having a normal distribution.” If the obtained probability of error  $P$  is less than an accepted level of significance (for example, 0.05), the null hypothesis is rejected. Obtained  $P$  values ranged between 0,07 and 0,09, suggesting the normal distribution of analyzed groups of data. Fisher’s least significant difference (LSD) post hoc test was used to verify significance of differences among the compared groups of data after the ANOVA being conducted. Differences were considered to be significant at  $P < 0.05$ .

### 3 Results and Discussion

Results of HM and PAH analysis are shown in Table 1. Measured sum of PAHs values ranged from 0.17 to 3.77 mg/kg between different land utilization types. Maximal concentration was revealed in Kirovsky district between all studied land uses (2.28–3.77 mg/kg). Soils of industrial and residential zones of Vasileostrovsky district reach high total PAHs concentrations as well, but at the same time soils of residential zone are characterized by higher PAHs level (3.02 mg/kg) than industrial (2.04 mg/kg). There is no standards on the total PAHs content in soil in Russian Federation, regulation is provided only for benzo[a]pyrene, which is equal for all land use and soil types – 0.02 mg/kg (MPC, GN 2.1.7.2041-06, 2006). Comparing with German soil guideline value of 1.0 mg/kg for sum of PAHs in soil, it can be concluded that all studied soils in Kirovsky and Vasileostrovsky districts, excepting recreational zone of Vasileostrovsky district, do not conform to standard limit. Benzo[a]pyrene concentrations have similar distribution pattern as total PAHs. Practically all studied soils have shown concentrations exceeding maximal permissible concentration. Benzo[a]pyrene portion counts

**Table 1.** Heavy metals and PAHs concentrations in urban soils, mg/kg of air dry soil

	Pb	Cd	Cu	Ni	Zn	As	Hg	BaP	$\sum$ PAHs
Kirovsky district									
Industrial	296,40 ± 11,41	0,91 ± 0,09	74,00 ± 6,18	89,00 ± 8,04	343,00 ± 22,79	7,11 ± 1,08	2,57 ± 0,29	0,84 ± 0,06	3,77 ± 0,52
Residential	126,70 ± 3,61	0,69 ± 0,11	59,10 ± 5,21	61,90 ± 5,93	96,00 ± 9,47	4,91 ± 1,03	1,86 ± 0,22	0,58 ± 0,11	2,32 ± 0,17
Recreational	82,04 ± 5,57	0,52 ± 0,09	64,00 ± 7,02	72,10 ± 5,66	71,30 ± 6,22	5,74 ± 0,38	2,05 ± 0,21	0,46 ± 0,06	2,28 ± 0,29
ANOVA, <i>P</i>	<b>0,03</b>	<b>0,05</b>	<b>0,04</b>	0,06	<b>0,04</b>	<b>0,05</b>	<b>0,05</b>	<b>0,03</b>	<b>0,03</b>
Vasileostrovsky district									
Industrial	237,12 ± 49,63	0,64 ± 0,07	53,00 ± 7,27	74,20 ± 11,15	301,40 ± 51,24	6,30 ± 0,97	2,70 ± 0,52	0,46 ± 0,09	2,04 ± 0,63
Residential	101,30 ± 23,51	0,63 ± 0,07	23,20 ± 2,34	40,00 ± 6,39	204,00 ± 36,19	6,10 ± 1,12	1,53 ± 0,53	0,70 ± 0,12	3,02 ± 0,74
Recreational	120,01 ± 34,08	0,49 ± 0,06	20,00 ± 3,08	33,70 ± 4,28	80,00 ± 9,21	5,98 ± 1,14	1,10 ± 0,53	0,11 ± 0,01	0,53 ± 0,09
ANOVA, <i>P</i>	<b>0,02</b>	<b>0,04</b>	<b>0,04</b>	<b>0,05</b>	<b>0,04</b>	<b>0,05</b>	<b>0,05</b>	<b>0,02</b>	<b>0,02</b>
Primorsky district									
Industrial	147,00 ± 25,52	0,79 ± 0,17	52,00 ± 3,11	17,20 ± 2,33	147,00 ± 15,86	6,10 ± 1,64	2,43 ± 0,73	0,11 ± 0,01	0,56 ± 0,08
Residential	22,70 ± 3,02	0,42 ± 0,05	25,50 ± 2,68	22,80 ± 1,95	116,90 ± 25,49	5,60 ± 5,57	1,30 ± 0,33	0,02	0,17 ± 0,06
Recreational	19,10 ± 1,39	0,36 ± 0,12	22,30 ± 9,29	12,20 ± 0,94	51,20 ± 15,40	4,10 ± 0,35	0,37 ± 0,09	0,04 ± 0,01	0,21 ± 0,03
ANOVA, <i>P</i>	<b>0,03</b>	<b>0,05</b>	<b>0,04</b>	0,06	<b>0,04</b>	<b>0,05</b>	<b>0,05</b>	<b>0,03</b>	<b>0,03</b>
SGV*	32,00	0,50	33,00	20,00	55,00	2,00	2,10	0,02	1,0**

\*SGV – soil guideline values according to Russian legislation GN 2.1.7.2041-06 (2006)

\*\* - soil guideline value for the sum of PAHs according to German legislation BBodSchV (1999) [6].

up to 30% from the sum of PAHs in studied soils which evidently shows predominant accumulation of this substance [10].

Heavy metals concentrations in soils of industrial and residential zones between all Districts were found to be higher than permissible levels. Measured total Pb concentration in soil of industrial zone in Kirovsky district exceeded MPC (32.0 mg/kg) for nine times reaching the value of 296.4 mg/kg. Soil of Kirovsky district is generally characterized by higher HMs level comparing with Vasileostrovsky (moderate) and Primorsky (supposed to be the cleanest). However obtained values of total pollution indices refers all studied soils to the high health risk category with except for soil of recreational zone of Primorsky District, which applies to the low health risk category (Table 2).

**Table 2.** Evaluation of health risk according to Zc categories

	Zc	Zc health risk category
Kirovsky district		
Industrial	121,14	High
Residential	87,01	High
Recreational	81,80	High
Vasileostrovsky district		
Industrial	117,37	High
Residential	64,97	High
Recreational	47,28	High
Primorsky district		
Industrial	97,10	High
Residential	48,82	High
Recreational	14,24	Low

Application of ANOVA statistics revealed significant differences between the concentrations of both organic and inorganic contaminants in urban soils and land use types of the area. The most significant differences were found for lead and benzo(e)pyrene levels in soil between industrial along with residential and recreational land uses with P values ranging from 0.02 to 0.03. Possibilities of ANOVA for other contaminants in soils were also bellow the significance level  $P = 0.05$ .

Correlation analysis between lead and benzo(e)pyrene concentrations in soils of the residential land use showed a slight positive relationship ( $r = 0.69$ ), considering that accumulation of these two contaminants is associated with the same sources. Though correlation between HMs and PAHs concentrations in other areas of study was not observed, we suggest that found relationship can testify the dominance of pyrogenic sources of soil contamination [10].

Health risk related to soil contamination with PAHs was assessed using BaP equivalents [4, 6, 7, 10]. The calculated  $BaP_{eq}$  of the of the PAH sum in investigated soils ranged from 0.44 to 0.66  $mg \cdot kg^{-1}$  dry soil [10]. The maximal  $BaP_{eq}$  levels of the

$\sum$ PAHs were found in industrial and residential areas – 0.55 and 0.66 mg·kg<sup>-1</sup> correspondingly. The soils of parks showed levels of BaP<sub>eq</sub> of the  $\sum$ PAHs with an average value of 0.44 mg·kg<sup>-1</sup>. Obtained data on the values of the BaP<sub>eq</sub> are several times higher than reported in a number of studies [4, 8, 9].

Finally, obtained BaP<sub>eq</sub> were compared with SQG values for the combined route of exposure respecting to particular land use [3]. The acceptable level of incremental lifetime cancer risk (ILCR) of  $1 \times 10^{-6}$  corresponds to BaP<sub>eq</sub> concentrations in soil below the 0.6 mg·kg<sup>-1</sup> (for each land use). The reported BaP<sub>eq</sub>'s of the  $\sum$ PAHs in studied urban soils were above 0.6 mg·kg<sup>-1</sup>. These soils may probably pose a significant risk to human health from carcinogenic effects of PAHs, even in urban park-land areas [10].

## 4 Conclusions

Results of the study showed that soils of the studied urban areas of different land use are characterized by different loads of PAHs and HMs. The highest levels of total 15 PAHs content were fixed in residential and industrial land uses. The general distribution patterns of PAHs between studied sites clearly indicates the common PAHs sources. A slight positive correlation between lead and benzo(e)pyrene concentrations in soil was detected. Statistics results (ANOVA) showed significant differences in HMs and PAHs concentrations in studied urban soils, suggesting the significance of the land use factor on distribution of the pollutants in soils.

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# Impact of Building Parameters on Accumulation of Heavy Metals and Metalloids in Urban Soils

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**Abstract.** The influence of urban development parameters on the pollution of soil cover with heavy metals and metalloids (HMMs) has been assessed. The residential area of the Ulan-Ude city was chosen as an object of the study. The greatest impact of the building patterns on the HMMs emission ( $Z_d$ ) was identified in an area with a radius of 150 m. Contamination of soil cover with HMMs has been observed with an increase in the total and average building area, i.e. in the building density, and in proximity of buildings to the sampling point. Integral soil pollution by HMMs ( $Z_c$ ) is 1.6–2.0 times higher for the cases with high surface area of buildings and their proximity in prevailing NW and SW wind directions. The impact of sorption properties of the soils on the HMM content is more pronounced due to their low buffer capacity.

**Keywords:** Soil cover · Urban development · Building geometry  
Mechanical barrier · Pollution · Heavy metals and metalloids

## 1 Introduction

The quality of the urban environment is determined by the allocation of pollution sources, in addition, the influence of relief, urban development features and also meteorological factors, which control the diffusing and concentrating ability of the atmosphere [1, 2]. Urban districts, especially with high-rise buildings, represent a complex system of surfaces with a different slope gradient, located at different levels and blown by air fluxes. Buildings greatly alter wind patterns in the surface layer of the atmosphere. In areas with high rise and high density developments, wind velocity sharply decreases, what leads to contamination of urban environment [3–7]. Along the major highways the “canyon effect” occurs [3, 8]. Such effects create a considerable heterogeneity of the pollution in urban areas.

The aim of this paper is to determine the impact of building parameters on accumulation of heavy metals and metalloids (HMMs) in urban soils of residential area. To achieve this aim, we took samples of snow and surface soil horizons, determined the total contents of the HMMs in snow solid fraction and soils, defined physical and chemical properties of surface soil horizons. Then, with the help of geoinformation and statistical analysis, we confirmed the influence of urban relief on the quality of the

atmosphere and determined the radius of impact zone using the snow and defined (in this radius) the impact of building on the HMMs accumulation in soils.

## 2 Materials and Methods

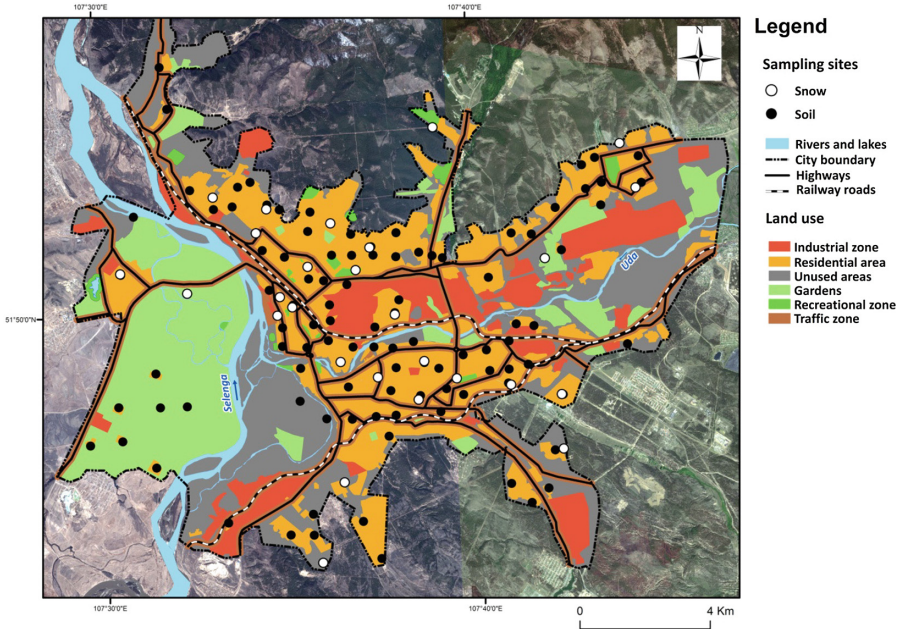
The object of the study is Ulan-Ude, a city with a population of over 400 thousand people located in the Ivolginsky-Uda intermountain basin, drained by the Selenga river and its right tributary, the Uda river [9, 10]. Its climate is severely continental with the prevailing western winds. The various topographic patterns and composition of parent rocks as well as anthropogenic impact cause the variability of soil cover. Mechanically transformed soils, with modified structure of the soil profiles, include urbanozems, ekranozems, necrozems and culturozems. Chemically transformed soils incorporate industrizems and intruzems. According to the classification proposed in [11], the urban soils are characterized by low buffer capacity. They have relatively low level (on average 5.8%) of physical clay (particles less than 0.01 mm in diameter), being formed on light textured parent rocks and man-made deposits. The pH values changes from alkaline (8.5) to weakly acidic (6.1) in the sandy soils of the outskirts areas. The average humus content is low (2.5%).

Ulan-Ude is included in the priority list of the cities with air pollution index (API)  $\geq 14$  and has 35 potential pollution sources (plants for repair of locomotives and wagons, rolled metal products, aircraft and shipbuilding, etc.) [12]. The main contribution to air pollution is made by a coal-fired thermal power plant and vehicle emissions [9, 13].

Soil-geochemical survey of the soil cover in the residential area of Ulan-Ude was conducted in summer of 2014. One hundred six mixed (with 3 duplicates) soil samples from the surface (0–5 cm) horizons were taken (Fig. 1). Samples were collected at grid points with grid size equal to 1000 m in the outskirts areas and 700 m in the central part of the city. The pollutant's fallout rates were evaluated using the data of snow survey conducted in winter of 2014, as a result, 27 samples were collected (Fig. 1). Eleven background soil samples and 4 samples of snow were taken in the reference sites, located 20–30 km to the south-west and to the east of the city. The solid and liquid phases of snow were separated by filtration.

The total contents of the HMMs in the snow solid fraction and in soils were determined by ICP-MS and ICP-AES analyses using “Elan-6100” and “the Optima-4300 DV” equipment (Perkin-Elmer, USA). Conventional methods were applied to define the properties that affect soil ability to fix pollutants (pH, humus content, texture, the contents of Fe, Mn, Al oxides). The priority pollutants in the soil and snow covers were identified using enrichment  $EF = C_{urb}/C_{ref}$  and fallout  $FF = D_{urb}/D_{ref}$  factors relative to reference (background) values  $C_{ref}$ ,  $D_{ref}$  [14]. Fallouts  $D_{urb}$  of HMMs were derived from their concentrations in the solid fraction of the snow  $C_{urb}$  and the daily dust load  $P$ . The total geochemical load on soil or snow cover was evaluated using integral index of pollution  $Z_c$  and emission  $Z_d$ , respectively. They were calculated as  $Z_c = \sum EF - (n-1)$ ;  $Z_d = \sum FF - (n-1)$ , where  $n$  – the number of chemical elements  $EF$  or  $FF > 1.0$ ,  $n = 14$  [14].





**Fig. 1.** Map of land-use zones in the city of Ulan-Ude with snow and soil sampling sites

The contours of buildings were obtained from the OpenStreetMap database [15]. The heights of buildings ( $H$ ) were determined by visual interpretation of GeoEye-1 satellite image (2015) using the database 2GIS [16]. The area occupied by the individual buildings ( $S$ ) was determined by a special tool for calculating the geometry (*Calculate Geometry, Area*) in the software package ArcGIS 10.0. The distance ( $L$ ) from the sampling points to the buildings was measured using a distance tool (*Generate Near Table*), which allowed also to identify the directions of the lines connecting the sampling points and the buildings.

Building parameters were determined in the zones with different radius (50, 100, 150, 200 and 250 m) where the central point was represented by a sampling point (Fig. 2). To select the optimal radius we used the data derived from the snow survey. It corresponded to the distance at which the correlation between dust  $P$  or the HMM  $Z_d$  fallout and the building parameters reached the maximum. The building parameters were averaged ( $\bar{S}$ ,  $\bar{L}$ ,  $\bar{H}$ ) and summed ( $\Sigma S$ ) for each sampling point using one-way ANOVA analysis of variance. In addition, parametric statistics were calculated for 4 major sectors (directions) of the impact zone.

To describe the geochemical heterogeneity of soil cover in relation to building parameters and a complex of soil factors, the method of regression trees (SPlus package) was used. This approach allows to predict the levels of pollutants in soils with different combinations of factors, and to assess their significance [17, 18].



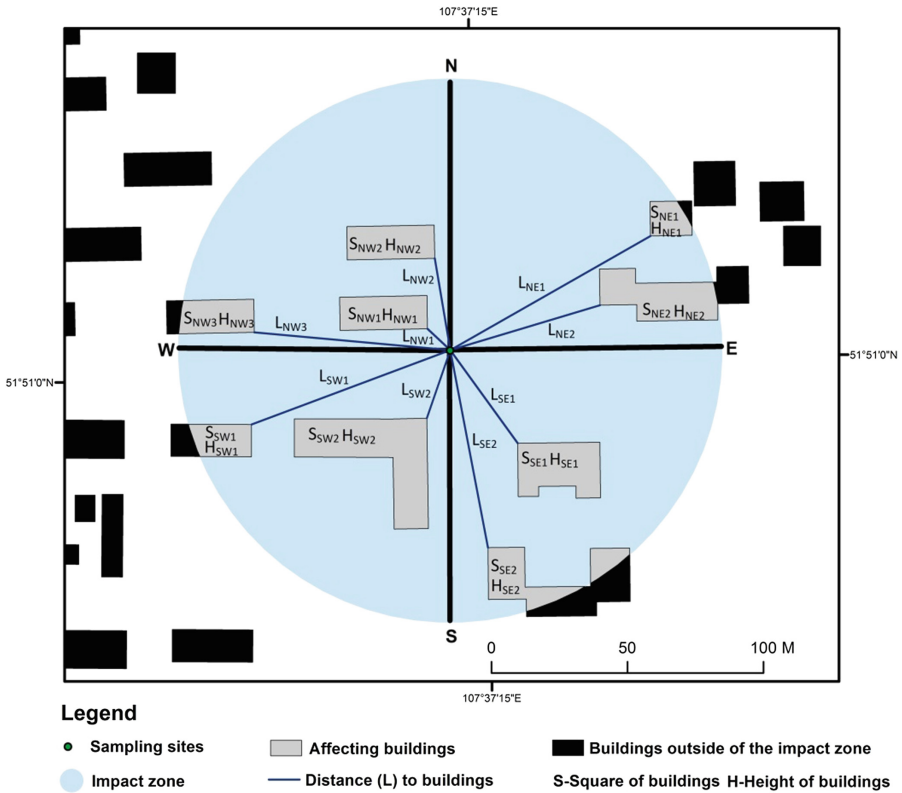


Fig. 2. Example of determining the building parameters in a zone with a radius of 100 m

### 3 Results and Discussion

#### 3.1 Features of Snow Contamination and Determination of the Impact Zone Radius

For all radius of the impact zone, the daily dust load  $P$  and the integral index of emission  $Z_d$  increased with the growth of the building area and a decrease in the distances to the building (Table 1). The height of the buildings was not as important factor, as low-rise (two- or one-storied) buildings dominating in the city. The increase of this parameter caused a slight rise of dust pollution of snow cover. The greatest impact of the building patterns was identified in an area with a radius of 150 m in the south-west and north-east sectors which corresponded with the highest repeatability of the south-west winds in winter [19].

Similar results were obtained in other cities. In Hong Kong, high density residential developments caused low air quality because of wind stagnation and blockage and the heat island effect [3, 5]. In Guangzhou, a correlation between building density and dust load was also positive ( $r = 0.64\text{--}0.68$ ) [7]. The results of international consulting company Ramboll Environ confirmed a positive correlation between building height and

**Table 1.** The Spearman rank correlation coefficients between daily dust load  $P$ , integral index of emission  $Z_d$  and building parameters.

Building parameters	Correlation with $P$					Correlation with $Z_d$				
	Radius of the impact zone, m					Radius of the impact zone, m				
	50	100	150	200	250	50	100	150	200	250
$\bar{L}^*$	-0.51 (1)		-0.55 (2)	-0.56 (2)	-0.51 (2)		-0.53 (3)	-0.50 (2)	-0.48 (2)	-0.44 (2)
$\bar{L}_{total}$			-0.55					-0.56		
$\bar{S}^*$	0.52(1)		0.58(2)	0.45(2)	0.57(2)			0.56(2)	0.43(2)	0.51(2)
$\bar{S}_{total}$			0.51	0.43	0.44		0.46	0.55	0.40	
$\bar{H}_{total}$			0.40	0.44	0.43					
$\Sigma S^*$	0.61 (1)					0.56 (1)				

Note: This table presents only statistically significant values ( $P = 0.05$ ;  $n = 27$ ). \*Across major directions: SW (1), NE (2), SE (3).

air quality [6]. According to Ramboll Environ findings, “skyscrapers or other prominent buildings alter the wind flow through a city and increase air pollution on city streets”.

### 3.2 The Building Impact on the Accumulation of HMMs in Soils

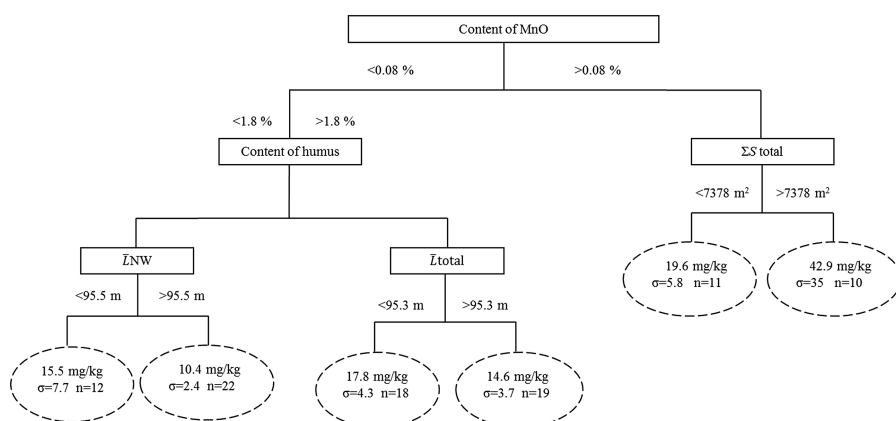
The priority pollutants of soils in Ulan-Ude are antimony (Sb), lead (Pb), tin (Sn), cadmium (Cd). In some districts of the city, near industrial enterprises and along major highways, geochemical anomalies of molybdenum (Mo), nickel (Ni), wolfram (W), zinc (Zn), copper (Cu), chromium (Cr), and bismuth (Bi) were also identified [20]. Multivariate regression analysis showed the influence of the building parameters on the accumulation of almost all studied HMMs (Table 2). With the dominance of low-rise buildings in the city the main factor was their average area ( $\bar{S}$ ): its growth led to an increase in topsoil concentrations of Cd (by 3.1 times), W, Bi, Zn (1.5–1.6), As, Sb, Mo, and Sn (1.3–1.4). With the increasing total area ( $\Sigma S$ ) the levels of Cd, Pb, Cu and Mo increased by 1.4–2.2 times (Fig. 3). The vicinity of the buildings to a sampling point in the northwestern sector contributed to the fallout from the atmosphere and accumulation in soils of Bi, Zn, Cu; their concentrations increased by a factor of 1.3–1.5 (Fig. 3). The exception was building density in northwestern sector and vicinity of the buildings in southwestern sector, which growth decreased concentrations of Cr, Zn, and Bi by 1.3–1.6 times. A probable reason of such impact is initially low content of Cr, Zn and Bi in technogenic material of places with high building density in northwestern sector and vicinity of buildings in southwestern sector. Alternatively, this can be explained by the relative arrangement of the emission sources of these elements and artificial relief features, which protect the soil from the atmospheric Cr, Zn and Bi fluxes. However, such influence of development was not confirmed by results in the previous subsection and extensive literature.

Integral soil pollution with HMMs ( $Z_c$ ) was 1.6–2.0 times higher in the areas with high surface area of buildings and their proximity in prevailing NW and SW wind directions. The impact of sorption properties of the soils on the HMM content was more pronounced due to their low buffer capacity. The growth of  $Fe_2O_3$  and humus contents led to a significant increase in the accumulation of almost all of HMMs (Table 2).

**Table 2.** The impact of building parameters and sorption properties of soils on accumulation of HMMs and integral pollution index  $Z_c$  of topsoils in Ulan-Ude.

Factors	Cd	Pb	Sn	Sb	Zn	Cr	As	Cu	Mo	W	Bi	$Z_c$
$\bar{S}$	1 + SW		2 + NE	3 + SW 4 + SE	3 + NE		4 + SW		3 + SE 4 + SW	2 + NW	4 + SE	4 + SW
$\Sigma S$	3+	2 + NW 3 + NE				2 - NW		2+	1 + SW			
$\bar{L}$					1 + SW 3 - NW			3 - NW 3-			2 - NW 3 + SW	3 - NW
$Fe_2O_3$			2+	1+		1+	1+		3+	1+		2+
Clay							2,3+			2+		
Humus	2+	1+	1,3+	2+	2+			2+	2+	3+	1,3+	1,4+
MnO						2+		1+				

Note: Ranks from 1 to 4 show a decrease in the factor significance, and the signs “+” or “-” define positive or negative correlation, respectively. If the building parameters influence the accumulation of pollutants in a certain sector of the impact zone, it is specified by letters. The process of splitting in regression trees stops if n becomes less than the predetermined value. Statistical significance of differences between means in terminal nodes was verified using t-test.

**Fig. 3.** Example of regression tree for the Cu content in soil

## 4 Conclusion

The snow survey confirmed barrier effect of development. The greatest impact of the building patterns on the HMMs emission ( $Z_d$ ) was identified in an area with a radius of 150 m. This affect caused contamination of urban soil cover with HMMs. The content of Cd, W, Bi, Zn, As, Sb, Mo, Sn, Pb, Cu increased with the growth of average and total building area i.e. density of development. Accumulation of Bi, Zn, Cu additionally depended on proximity of buildings to the sampling point. The influence of height was not significant due dominance of low-rise buildings in the Ulan-Ude city. Integral soil pollution by HMMs ( $Z_c$ ) was 1.6–2.0 times higher for the cases with high surface area of buildings and their proximity in prevailing northwestern and southwestern wind directions. The exception in this investigation was building density in northwestern sector and vicinity of the buildings in southwestern sector whose growth decreased concentration of a few elements in soils. Further research is needed to explain this finding.

We recommend conducting similar investigations in high-rise and high-density cities with increased buffer capacity of soils. Possibly, in these cases more considerable results will be obtained.

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# Microfungal Community Composition and *Alternaria* Phytotoxic Effect in the Lead Polluted Urban Soil

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**Abstract.** The present study is devoted to investigate the effect of high lead contamination on the soil microfungal composition of the urban forest. The investigation was performed for the urban forest soil contaminated by following concentrations of lead: 80, 800, 8,000 and 80,000 ppm. The experiments revealed high resistances of *Alternaria* and *Fusarium* fungi to Pb contamination of urban soil. Simultaneously was determined the relatively low tolerance of soil *Penicillium* microfungi along lead concentration gradient (up 80 to 80,000 ppm). Moreover, the phytotoxic effect of *Alternaria* microfungi cultivated on high-lead contaminated soil (80–8,000 ppm) was assessed. Obtained results showed the significant impact of lead concentrations (>80 ppm) on the phytotoxicity of *Alternaria*. Decrease in germination of pea seeds and average root growth was more than 85% in the high lead contaminated soils in comparison to the control sample.

**Keywords:** Heavy metals · *Alternaria* phytotoxic effect · Urban soils  
Microfungal community composition

## 1 Introduction

Heavy metals (HM) contamination is one of the global environmental problems. Along with the direct harmful effects, HM characterized with indirect consequences for the environment [1]. One of the impacts is the change of soil microfungal community' composition [2, 3]. The HM contamination of soils leads to the increasing of HM-resistant fungi in microbial community and therefore changes the amount of fungi metabolic products – mycotoxins [4–6].

Mycotoxins are the toxic secondary metabolites produced by fungi and are capable of causing disease and death in both humans and animals. The mycotoxins' effect to plants (phytotoxicity) in HM contaminated soils is primarily related with the changes of soil physical and chemical properties, including decrease in pH, redox potential and enhanced decomposition of organic matter [3, 7]. The phytotoxic effects are characterised with reduction of seeds' germination rates, reduction of growth etc [3].

Urban soils are one of the most HM contaminated soils due to affects from anthropogenic activities [8, 9]. Globally average concentration of lead in urban soils is about 100 ppm, with some soils having total lead in excess of 1,000 ppm [1, 10]. The HM effect on microfungal community composition of urban soils is poorly investigated [11–13]. Studies of the microfungal composition in polluted urban soils also allow to find out the HM resistant fungi and hence to assess the possibilities of using it in bioremediation programs [4]. The research questions are addressed to: (1) what is the impact of various lead concentration on composition of microfungal community of urban soil? (2) what is the phytotoxic effect of mycotoxins produced by *Alternaria* fungi along the gradient of soil lead contamination?

## 2 Materials and Methods

The study was carried out in the model experiment with Albeluvisols polluted by various concentration of lead: 80, 800, 8,000, 80,000 ppm. Albeluvisols were collected from 0–10 cm layer of forests urban soil located in the North of Moscow (55°49'59"N; 37°33'3.7"E, Russia). Lead was applied in acid-soluble form ( $\text{Pb}(\text{CH}_3\text{COO})_2 \times 3\text{H}_2\text{O}$ ) as more spread in urban soils.

Microfungi were isolated by dilutions of soil samples with various lead concentration in sterile water (1:100) with subsequent plating on solid Czapek's agar media containing streptomycin to suppress growth of bacteria. The plates were incubated (25 °C, 7 days). Fungi genus identification was based on the determination of the morphological features (mycelium types, structure of reproductive organs) by direct microscopy method.

Moreover, the phytotoxic effect of *Alternaria* genus was identified. Bekker media was used for the isolation of the fungi. *Pisum sativum* was planted on the isolated in the pure culture *Alternaria* fungi. In other words, the plants were grown on the media of the fungal exudates and were impacted by fungal mycotoxins. Plants were exposed in fungi exudates for 18, 36, 54, 72, 90 and 108 h. Simultaneously plants' growth was performed on the control sample with distilled water. The *Alternaria* fungi phytotoxic effect was assessed by measuring the growth rate of test-plant (length of the roots, germination rate of seeds).

Statistical analysis of the data included the t-student test and regression (significance level 0.05), it was performed in the R-studio software.

## 3 Results

### 3.1 Composition of Soil Microfungal Community

Studies of fungi cultivated from lead contaminated urban soil showed significant differences in the composition along lead concentrations gradient (Table 1). Soil fungi - *Alternaria*, *Fusarium*, *Penicillium* were able to grow in the presence of lead contamination. Other fungi could not be identified. In the uncontaminated soil with trace content of lead (control) the fungi *Penicillium* was dominated. However, *Penicillium*

content decreased on average two times under the increasing lead concentration up to 80,000 ppm. *Penicillium* showed relatively low tolerance to lead contamination in comparison to other fungi.

**Table 1.** Composition of microfungal community (%) of soil polluted by various Pb concentrations.

Pb ppm	Fusarium	Penicillium	Alternaria	Other fungi
Control	NA	55 ± 3.2	10 ± 0.5	35 ± 2.1
80	NA	50 ± 2.8	19 ± 0.8	41 ± 2.3
800	22 ± 1.2	41 ± 2.2	20 ± 1.4	17 ± 0.9
8,000	30 ± 2.2	36 ± 1.6	26 ± 1.2	8 ± 0.6
80,000	38 ± 2.1	26 ± 1.4	26 ± 1.2	10 ± 0.6

The *Fusarium* fungi dominated in the soil with the highest lead concentration, however it was not possible to identify in uncontaminated soil. The dominance of the fungi within high lead concentrations indicates the resistance of *Fusarium* to lead contamination. The *Alternaria* content was increasing on average 2.6 times along the soil lead concentration gradient. It was identified that the *Alternaria* percentage did not change with increasing Pb concentration in the range of 8000–80000 ppm and was equal to 26%.

Therefore, *Fusarium* and *Alternaria* microfungi isolated from the high lead contaminated soil showed the high resistance to pollution and perhaps are able to perform the bioremediation functions.

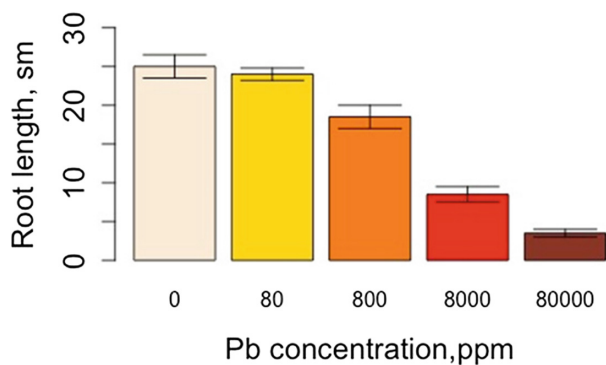
### 3.2 Phytotoxic Effect of *Alternaria* Microfungi

Stable phytotoxic effect of mycotoxins produced by *Alternaria* was revealed in the variant where fungi isolated from the soil with Pb concentration equal and higher 800 ppm (Fig. 1). Pea seeds were grown on fungal exudates isolated from the soil with the Pb concentration 80,000 ppm are characterized with the shortest length of the roots –3.5 mm, which is 7 times less than in control sample –24 mm. Significant relationship between soil Pb concentration and average root length was found during the experiment ( $R^2 = -0.81$ ). Exudates of fungi isolated from soils with the 80 ppm lead concentration did not change the length of pea roots and remains similar to the control sample. Although the *Alternaria* content was stable in microfungi composition in conditions of lead concentration above 800, the phytotoxicity of the exudates increased exponentially.

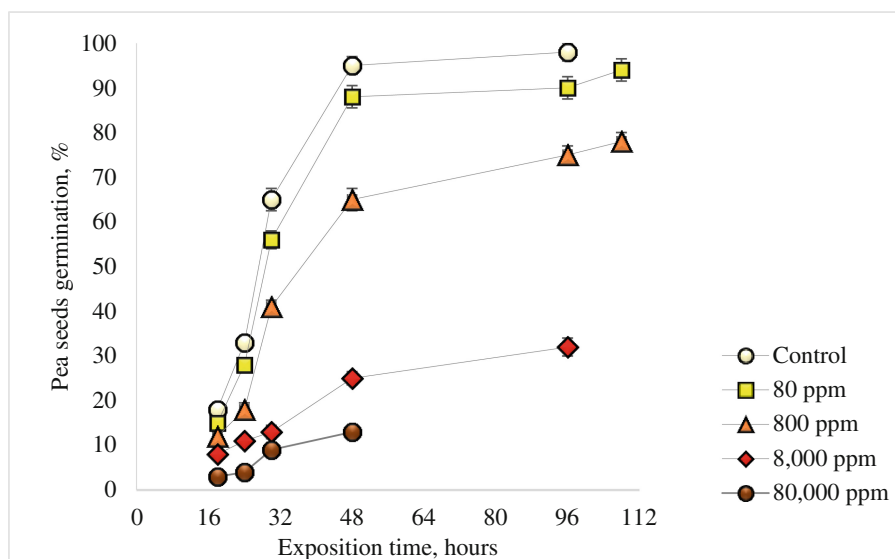
Pea seeds cultivated on *Alternaria* exudates in dynamics showed differences in germination rate characteristics. Germination rate for all samples was highest in 24–30 h, except samples with 8,000 ppm concentration of lead (Fig. 2). Also was found inhibition of germination rate for all samples containing Pb.

The obtained results revealed possibility of using microfungi in bioremediation programs in the urban soils with Pb contamination up to 800 ppm due to the lack of stable phytotoxic effects.





**Fig. 1.** Phytotoxic effects of *Alternaria* microfungi isolated from the soil polluted by various Pb concentrations on Pea roots length.



**Fig. 2.** Pea seeds germination on the exudates of *Alternaria* isolated from the soil with the various Pb concentrations depending on exposition time.

## 4 Conclusions

During the study the influence of lead contamination exceeding 80 ppm on the microfungi community composition was determined. The significant changes of the *Fusarium*, *Alternaria* and *Penicillium* microfungi content was found. *Fusarium* and *Alternaria* microfungi isolated from the high lead contaminated soil showed resistance to pollution. Phytotoxicity of *Alternaria* isolated from soil with high Pb concentrations

(800–80,000 ppm) was observed through decrease of pea root length and germination energy rate of the seeds.

The identified patterns allow to model response of microfungi community composition and phytotoxic effect of *Alternaria* at wide range of soil lead contamination. The obtained results also confirmed with the studies of microfungi ability to resist and hence to remove toxic metals from polluted sites as they are able efficiently accumulate heavy metals from external environment [4, 5]. The ability to perform the bioremediation functions by efficiently accumulation of heavy metals in microfungi on lead contaminated urban soils is of great importance.

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# Removal of Heavy Metals and Metalloids in an Industrial Stormwater Treatment System

SIMS Metal Management, Bronx, NY, USA

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**Abstract.** This study examines the efficiency and process of metals and metalloids removal from the runoff by an innovative stormwater capture and treatment system at the SIMS Metal recycling site in New York City. This system is one of the very early pilots of stormwater management systems in New York City, and uses a combination of natural and engineering approaches (e.g., filtration capacity of soils and patented engineering designs). The runoff, with particulate and dissolved metals, metalloids and hydrocarbons, were directed into a vegetated field with engineered soil and mulch. The spatial distribution of metals and metalloids within the soil (soil surface and soil columns) and groundwater quality (water in the StormChambers and pumped to the surface) were evaluated. Even with less than 30 cm of topsoil, the system removes metal and metalloid contaminants efficiently.

**Keywords:** Stormwater · Contaminant · Metal recycling · Treatment

## 1 Introduction

As urbanization accelerates throughout the world, stormwater management is becoming a more and more pressing issue. The expansion of impervious surfaces led to the large volume of stormwater runoff, often contaminated, into water bodies in and around the City. This threatens public health and ecological systems, and is often one of the main causes of the water quality problem in urban areas [1].

The Sims Metal Management Municipal Recycling in the Bronx (New York City of USA), formerly known as Sims Hugo Neu until a 2005 buyout, has successfully recycled hundreds of tons of metals and plastics daily for the industrial and commercial sectors [2] (Fig. 1). The size of the site is about 6.4 acre. However, as the majority of the site was covered by impervious concrete, the facility was frequently flooded during storm events (on average New York City has 45 storm events each year, or about 115 cm depth). As a result, about 6.4 million gallons of runoff, with metals, hydrocarbons, suspended solids, and other pollutants, are discharged directly into the



**Fig. 1.** Birdseye view of the SIMS metal recycling site.

adjacent Bronx River each year. This poses a long standing threat to water quality and the health of human and ecosystems in the area.

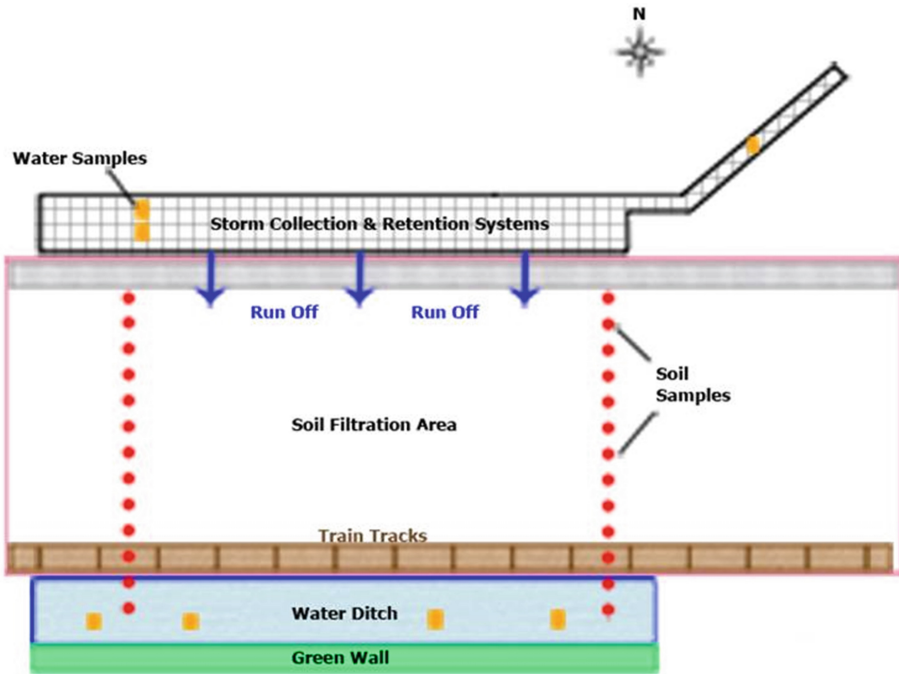
In 2009, The Gaia Institute, led by Dr. Paul Mankiewicz, helped design an innovative stormwater runoff capturing and treatment system. This is one of the very early pilots of the stormwater management systems (later also called low impact development systems, or green infrastructure systems) in New York City. This project was the first-ever zero-discharge industrial retrofit of a material handling facility in the city or state of New York [2].

Presently, the stormwater travels through a system of native plant meadow soil columns, an infiltration conveyance system, an evaporative wall, a created wetland, and five rows of underground detention/infiltration system consisting of 240 StormChambers and 15 SedimenTraps [2]. The structural gravel support layers under the concrete work pad also acts for water storage and water table flow. The top 30 cm is a mix of gravel and sandy soil covered by about 10 cm of mulch. Underlying gravels constitute the base of an abandoned railway.

This study was conducted to examine the performance of such a system for intercepting runoff and capturing the metal and metalloid contaminants. Soil and water samples from different areas and depths of the system were collected and analyzed, as well as some other physical and chemical characteristics that can help document the fate and transport of these contaminants.

## 2 Methods

Soil samples were collected at the surface (0–5 cm) along two transects (Fig. 2) in order to examine the runoff transport of contaminants from the impervious area to the infiltration area. Soil samples were also collected at six depths of a soil pit to understand the vertical movements of contaminants in the soil column. The soil samples were then dried and sieved. The <2 mm fraction was acid digested following US EPA method 3050B (Acid digestion of sediments, sludges and soils) [3]. Heavy metal and metalloid determination followed US EPA method 6020A (Inductively coupled plasma – mass spectrometry) [4].



**Fig. 2.** Schematic site map showing basic layout and sampling locations

Water samples were collected from four wells tapped into storm chambers which are about 6 feet deep and from a ditch by the green wall (Fig. 2). The ditch is fed by groundwater continuously pumped to the green wall powered by solar panels. Water samples were filtered and acidified on site, and then analyzed for heavy metal and metalloid concentrations at the Brooklyn College Environmental Sciences Analytical Center following US EPA method 6020A. The pH and salt content of well water and surface water were also measured on site at the time of sample collection with portable pH meter and conductivity meter, respectively.

### 3 Results and Discussions

#### 3.1 Spatial Variations of Heavy Metals and Metalloids in Soils

Soil heavy metal and metalloid contents showed large spatial variations, and for some metals the values differed by two orders of magnitude (Fig. 3a). Many of the metals were enriched compared to common soils. For example, Zn concentration was as high as 10,000 mg/kg and the maximum Pb reached nearly 3000 mg/kg. Background soil at the site has Zn and Pb concentrations in the range of 10–20 mg/kg. The New York State Soil Cleanup Objective criteria for Zn and Pb are 10,000 mg/kg and 1000 mg/kg respectively for commercial land uses [5].

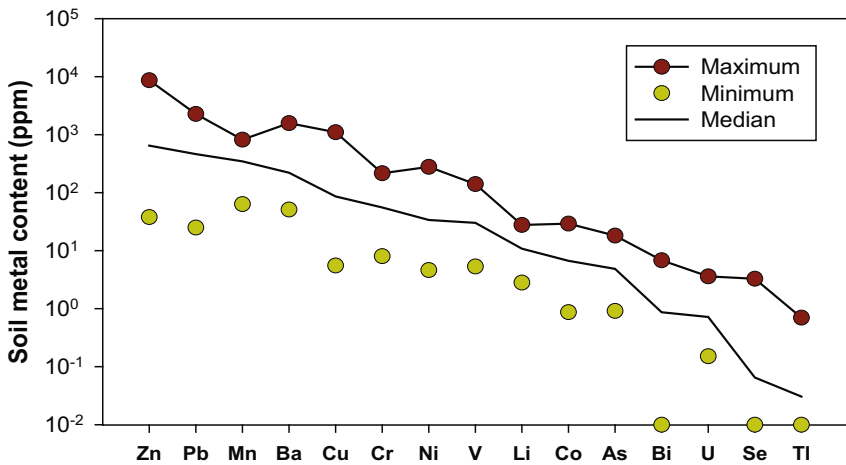


Fig. 3a. Range of metal and metalloid concentrations in topsoil samples.

In the mulched unplanted area situated over soils and gravels, Pb content decreased quickly and significantly from near the paved area (closest to where the recycled materials are stored) to the green wall (Fig. 3b), agreeing with the runoff overflow direction. Runoff carries metal-containing particles and dissolved metals, which were captured by topsoil while the runoff flows across the soil infiltration area (Fig. 2). The quick drop of metal concentrations along the flow path suggested that the majority of the metals were captured in the vicinity of the inflow. In the planted area where sand covered the gravels (note: the area was not mulched), Pb content was generally low. This is likely due to the fact that this area is relatively higher, and much less runoff had flowed into or flooded this area.

Figure 4 shows a typical soil profile in the soil infiltration area. The top 30 cm is a mix of gravel and sandy soil covered by about 10 cm of mulch. The underlying substrate was mostly gravel – reflective of its past land use as a rail yard. The depth profiles of Pb, As, Cr, Cu and Li are shown alongside the soil profile. In general, soil

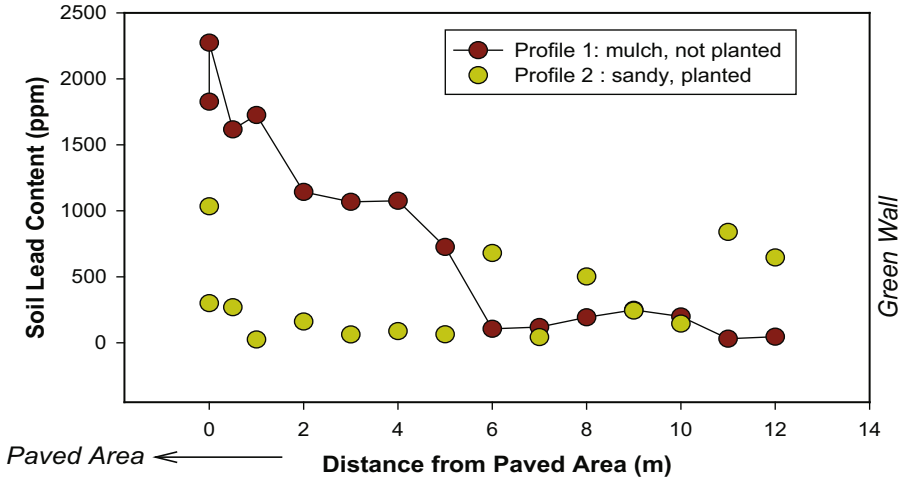


Fig. 3b. Pb concentrations in soil samples along two profiles (see Fig. 2)

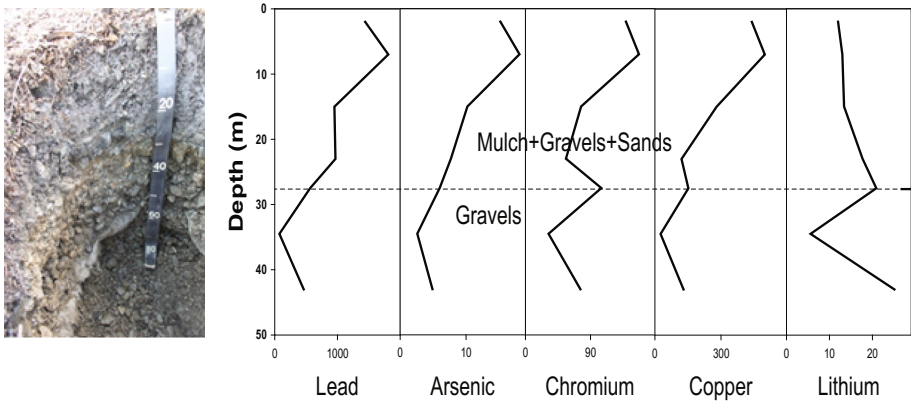


Fig. 4. Depth profile of Pb, As, Cr, Cu and Li in the soil filtration area.

metal or metalloid contents decreased quickly with depth, suggesting that the top soil horizon has effectively retained contaminants. This is especially true for Pb, As and Cu.

It is widely recognized that most heavy metals are bound with particulates. Iron and Al oxides and oxy-hydroxides, which are present ubiquitously, are ideal adsorbents for many heavy metals and metalloids. In the runoff from a metal recycling facility like SIMS, there also could be pure metal particles from recycled materials. Such particles can easily settle down into soil where runoff slows down on entering the infiltration gallery of the constructed soil columns. The relatively small soil pore spaces can allow infiltration and natural but efficient filtration of contaminant-bearing particles. Furthermore, dissolved metals and metalloids can be adsorbed by Fe- and Al- oxyhydroxides and clay minerals [6]. Mulch is also known to bind metals from runoff and



stabilize it in the soil [7]. At about 25–30 cm depth where the organic-rich, dark layer meets the gravels, an interesting redox front was apparent. The redox front has high Cr, Cu and Li – suggesting these dissolved metals are sequestered within this layer through redox reactions.

### 3.2 Water Quality

The total salt concentrations in the well water samples ranged 390–1620 ppm, comparing to the Bronx River with salinity of 8000 ppm. Because this site is adjacent to the Bronx River, a brackish water body that connects to the Atlantic Ocean, it is not surprising that the groundwater here is slightly salty. Tides can periodically recharge the groundwater immediately next to the river. Water pumped from the groundwater to irrigate the green wall had 1200 ppm and 1440 ppm salinity. The higher than groundwater concentrations may be due to surface evaporation over time, or to extraction of salt from a peat layer of the old salt marsh underlying the pump heads.

The pH of five well waters ranged from 7.0 to 8.2, while two stream water measurements yielded pH of 7.7 and 7.9, respectively. These values are very similar to the Bronx River water with pH of 7.7. All the water samples are slightly basic, a condition that favors the chemical precipitation and adsorption of heavy metals and metalloids rather than dissolution. It also indicates that the potential for leaching of heavy metals and metalloids from topsoil is very low. Urban runoff has often been found neutral to slightly basic [7]. The relatively higher pH is likely a result of concrete pavement which neutralizes the slightly acidic rainwater.

It should be noted, however, that the well water all had very strong odor resembling that of H<sub>2</sub>S which most frequently occurs under strong reducing conditions. The salty seawater has high levels of sulfate, which can be reduced to H<sub>2</sub>S if sulfur reducing bacteria are present. The well water samples all became very turbid shortly after being collected, suggesting that high populations of microbial communities were present. These bacterial communities, however, were not characterized in this study. Surface stream water was clear, free of odor, and with low turbidity and low total dissolved solids, and would appear to present no obvious health concern.

Concentrations of metals and metalloids in the well water samples and in the surface stream water samples were compared to levels in the Bronx River water (Fig. 5). Water samples from neither wells nor the stream (the constructed surface ditch) contain significantly higher metal concentrations than the levels found in Bronx River (their levels are often slightly lower). This clearly suggests that on one hand contaminants had been effectively filtered by the soil horizon and were not leached into the groundwater, and on the other hand the percolated water no longer poses a threat to the water quality of the Bronx River. This was demonstrably not the case before the stormwater capturing project was implemented.

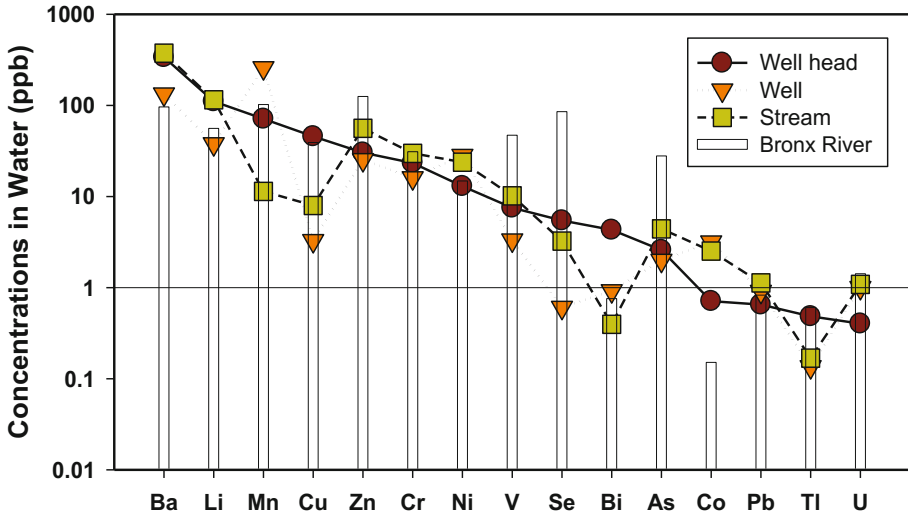


Fig. 5. Concentrations of metals and metalloids in well water, stream water and Bronx River water.

## 4 Conclusions

Urban runoff often contains pollutants that are threats to water quality, human health and ecological sustainability. At the SIMS metal recycling site, heavy metals had been a concern for Bronx River as millions of gallons of stormwater runoff from the site were directly discharged into the river each year. Through the construction of a stormwater treatment system, where runoff is filtered through a constructed soil column before entering groundwater which flows and discharges into the Bronx River, contaminants are effectively managed, providing a clean freshwater source, and eliminating a long term threat to the Bronx River ecosystem.

Soil is an effective natural filter, the largest such biogeochemical matrix in terrestrial environments. Particulates can be effectively removed by soil filtration – in this study the particulate-bound contaminants are trapped within the top 10 cm of the soil. Dissolved contaminants can also be removed by sorption and chemical precipitation processes in soil, which were evident in the soil column studied here, in particular the interesting redox layer between the soil layer and the gravel layer. The filtered water had no elevated contaminant levels comparing to Bronx River water. It should be noted that there is a compromise between filtration rates (for maximum water retention for stormwater capture) and efficiency for contaminant removal. Engineered soil horizons can be developed to optimize infiltration rates and contaminant removal. Further studies are needed to increase understanding regarding the C, N dynamics and metal retention in various engineered soil systems.

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# Analysis of Carbon Stocks and Fluxes of Urban Lawn Ecosystems in Moscow Megapolis

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**Abstract.** Urbanization results in irreversible transformations of vegetation and soils. Urban lawn is an important part of urban ecosystems, providing several principal ecological functions, including participation in global carbon cycle. Carbon stocks and fluxes in urban lawns are diverse due to the different functional uses (residential, recreational areas, etc.), and different morphogenetic and physico-chemical properties of soil and their components. The research was focused on C stocks and fluxes in urban lawns to assess their function in regulating atmospheric air composition. Soil CO<sub>2</sub> emission and CH<sub>4</sub> fluxes (summarized for summer period); soil organic C (SOC); below and above-ground biomass were studied. Carbon emission by soil respiration and C sequestration in biomass were considered to estimate C balance.

**Keywords:** Carbon stocks and fluxes · Urban lawns · Urban forest  
Root and aboveground biomass · Methane

## 1 Introduction

Moscow is one of the biggest megapolis globally. The city area contains built-up areas and infrastructure objects as well as different green zones such as urban lawns. City lawns perform important ecological functions, which importance will increase with on-going urbanization. The participation in the global carbon (C) cycle estimated by C fluxes and pools in soils and biomass is one of the integral criteria to assess the ecological functional of urban lawn ecosystems [1–4]. The high spatial diversity caused by different land uses such as residential, recreational, industrial production zones, and by variation of morphogenetic and physico-chemical properties of soils and their components make it more difficult to estimate C balance [3, 5–7]. Also, high dynamism of lawn ecosystems properties in particular C fluxes necessitates to carry out the monitoring researches to assess their ecological functioning [8–10].

The research was focused on C stocks and fluxes in urban lawns to assess their function of regulating atmospheric air composition. The following parameters were studied: soil CO<sub>2</sub> emission (summarized for a year and growing season), soil CH<sub>4</sub>

fluxes (summarized for summer period); soil organic C (SOC); below and aboveground biomass. C emission by soil respiration and C sequestration in biomass were considered to estimate C balance.

## 2 Materials and Methods

The research sites located at the Russian State Agrarian University in the North of the Moscow city and included plots with similar vegetation cover but different functional uses, varying in management and anthropogenic load. High level of anthropogenic load was represented by lawns of the Central parterre (P-Wops) (N55°83'32; E37°55'05) and Golf course (S-CEM) (N55°83'88; E37°56'83). A standard level of anthropogenic load was represented by ornamental lawns in the territory of the meteorological Observatory (L-St) (N55°83'62; E37°55'44) and Park (St) (N55°83'25; E37°54'85) [11].

Soil CO<sub>2</sub> fluxes were measured by infrared gas analyzer Li-820. The measurements were carried out every 15 days in the afternoon from 10 to 13 h. Soil CH<sub>4</sub> fluxes were measured by the exposition chambers (Patent RU2518979C1) method with subsequent gas samples analysis in the gas chromatograph twice a month (June-August). Air temperature, soil moisture and temperature were observed in parallel to flux measurements (soil hydrometer Thetaprobe HH2 and soil thermometer Checktemp 1). Aboveground and root biomasses were collected three times a month. Soil chemical properties (C-organic content, pH, P and K content) were determined by standardized methods the GOST 26484-84, R54650-2011, 2610-91, 26107-84, 26213-91 [12, 13].

The grass stands of the studied plots were dominated by cultivated grasses, except the meadow urban ecosystems (L-St), which consisted of native grasses with the sowing of cultivated cereals (Table 1) [8, 14]. An average plot size was about 50–100 m<sup>2</sup>. Soil and biomass were sampled in three replicates inside each plot.

**Table 1.** Characteristics of studied urban lawns.

Year	Grass stands	Vegetation coverage, %	Number of stems per m <sup>2</sup>
Meteorological Observatory (L-St)			
2014	Native grasses with a predominance of timothy grass (lat. <i>Phleum pratense</i> ), red fescue (lat. <i>Festuca rubra</i> ), bluegrass (lat. <i>Poa pratensis</i> )	94 ± 3	10114 ± 60
2015		96 ± 2	10345 ± 143
Park (St)			
2014	Cultivated grasses with a predominance of red fescue (lat. <i>Festuca rubra</i> ), bluegrass (lat. <i>Poa pratensis</i> ) and daisy (lat. <i>Bellis perennis</i> )	97 ± 3	10350 ± 101
2015		98 ± 2	10408 ± 105
Central parterre (P-Wops)			
2014	Bluegrass (lat. <i>Poa pratensis</i> ) and bent grass (lat. <i>Agrostis tenuis</i> )	98 ± 2	11150 ± 108
2015		98 ± 2	11305 ± 111
Golf course (S-CEM)			
2014	Sorts of red fescue (lat. <i>Festuca rubra</i> ) and bluegrass (lat. <i>Poa pratensis</i> )	99 ± 1	14535 ± 113
2015		100 ± 0	15989 ± 117

The following subtypes of urban soils were identified at the research plots (based on the classification by Prokofieva et al., 2011): ‘recreazems’ – for at the L-St plot, ‘culturozems’ – at the St and P-Wops plots, and ‘constructozems’ – at the S-CEM plots (Table 2) [12, 13, 15].

**Table 2.** Chemical characteristic of soil on studied plots

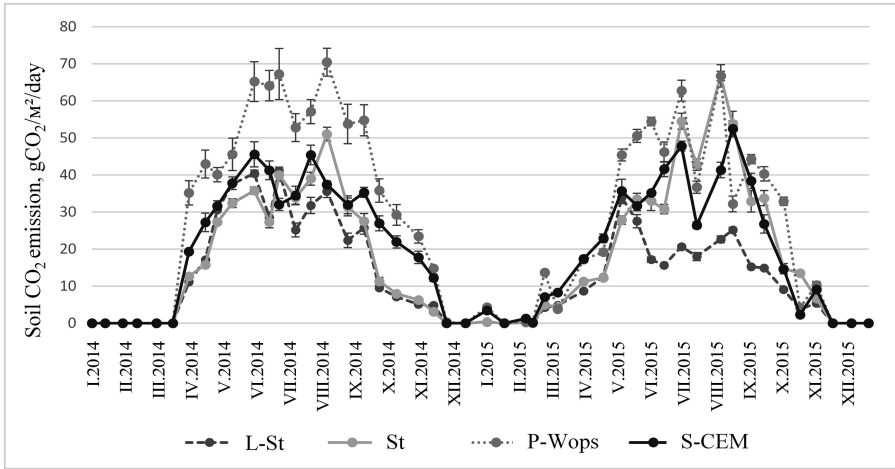
Plots (subtype of urban soil)	Hori-zon	Depth, cm	pH (KCl)	Corg., %	K <sub>2</sub> O, mg/kg	P <sub>2</sub> O <sub>5</sub> , mg/kg	N, %
L-St (recreazems)	AY	0–26	6,61 ± 0,10	1,92 ± 0,05	102,6 ± 1,0	110,3 ± 3,8	0,23 ± 0,02
	EB	26–55	6,43 ± 0,09	1,13 ± 0,02	82,4 ± 2,3	91,9 ± 4,9	0,13 ± 0,01
	B	55–97	5,94 ± 0,08	0,89 ± 0,05	83,2 ± 1,3	115,6 ± 4,5	0,09 ± 0,01
	Bt	97–150	5,67 ± 0,11	0,45 ± 0,04	63,7 ± 2,8	104,3 ± 3,4	0,05 ± 0,01
St (culturozems)	AYur	0–22	6,80 ± 0,09	2,12 ± 0,08	117,5 ± 2,7	112,7 ± 1,6	0,25 ± 0,02
	U <sub>1</sub>	22–61	6,77 ± 0,13	1,25 ± 0,03	96,2 ± 2,9	97,9 ± 3,5	0,14 ± 0,01
	U <sub>2</sub>	61–81	6,17 ± 0,14	1,18 ± 0,01	91,6 ± 2,5	95,1 ± 1,8	0,12 ± 0,02
	U <sub>3</sub>	81–108	5,87 ± 0,13	1,01 ± 0,04	90,2 ± 2,1	91,5 ± 2,1	0,11 ± 0,01
	Bt	108–150	5,47 ± 0,11	0,84 ± 0,05	71,2 ± 1,6	105,0 ± 2,3	0,08 ± 0,01
P-Wops (culturozems)	Ai	0–32	6,71 ± 0,09	3,95 ± 0,09	113,0 ± 0,9	118,3 ± 2,1	0,41 ± 0,03
	U <sub>1</sub>	32–104	6,54 ± 0,04	1,93 ± 0,04	83,3 ± 2,5	84,5 ± 2,8	0,20 ± 0,02
	U <sub>2</sub>	104–127	6,26 ± 0,04	1,13 ± 0,03	70,1 ± 2,1	82,2 ± 3,3	0,12 ± 0,01
	EB	127–150	6,10 ± 0,03	0,61 ± 0,03	54,2 ± 2,1	104,5 ± 3,0	0,08 ± 0,01
S-CEM (constructozems)	RAT	0–24	6,72 ± 0,08	2,83 ± 0,13	100,5 ± 4,7	113,8 ± 2,8	0,35 ± 0,04
	TCH	24–55	6,13 ± 0,08	1,54 ± 0,16	85,3 ± 4,9	99,3 ± 6,6	0,16 ± 0,02
	Bt	55–105	5,94 ± 0,17	0,87 ± 0,08	69,4 ± 5,9	81,4 ± 1,6	0,08 ± 0,01
	BC	105–150	5,63 ± 0,14	0,43 ± 0,05	42,7 ± 1,8	63,1 ± 3,2	0,05 ± 0,01

### 3 Results and Discussion

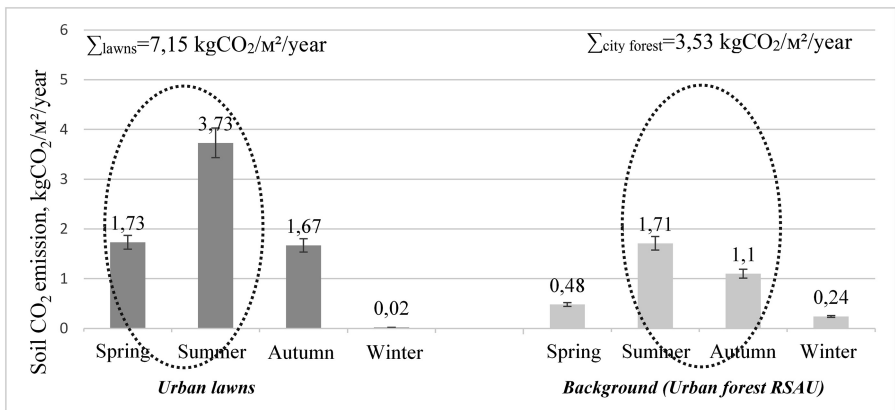
As an undisturbed background was assessed the site of the Urban forest adjacent to the study area. The average annual carbon emission in the process of soil respiration was 0,96 kgC/m<sup>2</sup>/year. Significant seasonal dynamics of C fluxes was observed for all investigated plots. We observed the highest soil CO<sub>2</sub> emission in summer periods (June to August) with maximal values of 50,3 and 64,7 gCO<sub>2</sub>/m<sup>2</sup>/day obtained for the P-Wops in June 2014 and 2015 respectively, and the minimal values of 33,1 and 19,3 g CO<sub>2</sub>/m<sup>2</sup>/day obtained for L-St in July 2014 and 2015 respectively (Fig. 1). Seasonal dynamics of CO<sub>2</sub> emissions was positively correlated with soil temperature ( $R = 0,81-0,86$ ;  $p > 0,01$ ).

The largest flow of carbon dioxide was measured during the summer (3,73 kg/m<sup>2</sup>), which represented 47,8% of the annual CO<sub>2</sub> emissions. In autumn, the flow was smaller. Thus, the value of the total flux decreased in a series of summer>spring>autumn>winter. The patterns shown for the background site were different. The values of the total flux decreased in the series summer>autumn>spring>winter (Fig. 2).

Comparing seasonal dynamics of CO<sub>2</sub> emission for lawns with different anthropogenic load revealed that the highest CO<sub>2</sub> fluxes (8,63 kgCO<sub>2</sub>/m<sup>2</sup>/year) was recorded for lawn urban ecosystem with a high level of anthropogenic load. Comparing annual



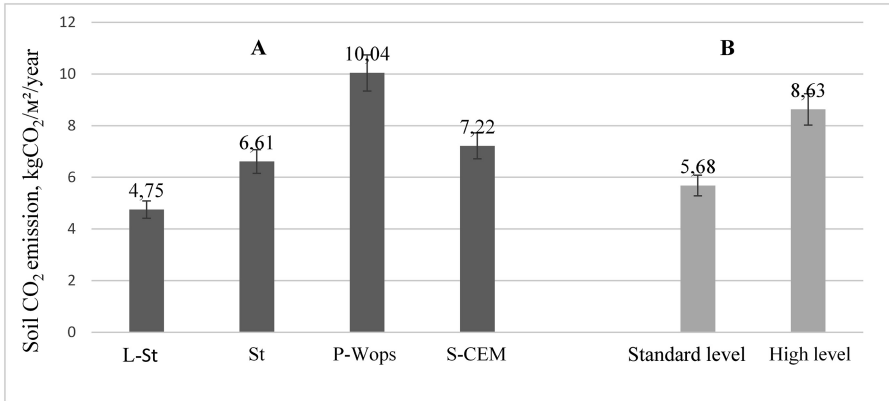
**Fig. 1.** Seasonal dynamic of CO<sub>2</sub> fluxes in studied urban laws with different types



**Fig. 2.** Total emission of CO<sub>2</sub> in a year in studied urban lawns with different seasonal distribution of total values

CO<sub>2</sub> emissions by type of lawn urban ecosystems revealed that the maximal 10,04 kgCO<sub>2</sub>/m<sup>2</sup>/year was measured at the P-Wops and the minimum 4,75 kgCO<sub>2</sub>/m<sup>2</sup>/year at the L-St plots (Fig. 3).

These differences in carbon dioxide emissions can be attributed to two factors, which determine the flow value for various types of ecosystems: the content of organic substances and the mechanical impact [3, 5]. The maximum SOC concentrations of 4% were obtained for P-Wop plots, for which the highest annual CO<sub>2</sub> emission was also reported. The minimum value (1,92%) was observed in meadow urban ecosystems (L-St), which corresponds to the minimum value of CO<sub>2</sub> emissions per year. A positive correlation between annual emissions of CO<sub>2</sub> emission and SOC in soil was found (R = 0,92; p > 0,01). The minimal mechanical disturbance of the soil cover that was



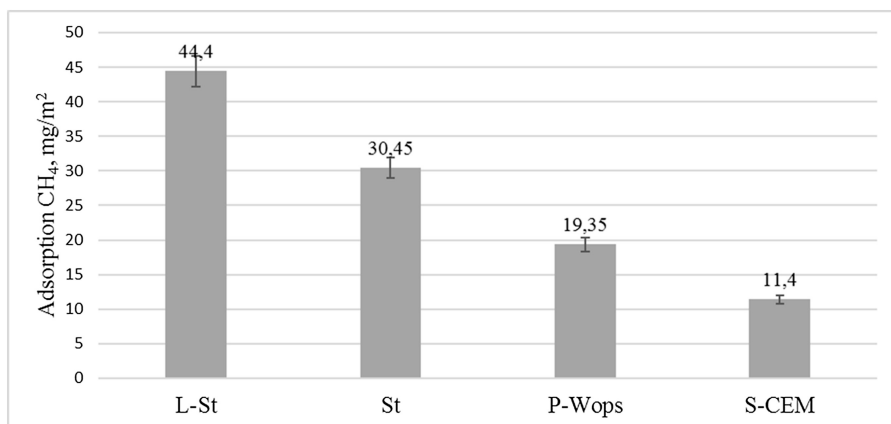
**Fig. 3.** Total emission of CO<sub>2</sub> in a year in studied urban lawns with different types (A) and levels of anthropogenic load (B)

observed in the urban ecosystems with the standard anthropogenic load level (no machining, rolling, etc.) was characterized by minimal flow of carbon dioxide, whereas the maximum value was observed in the variants with periodic mechanical irregularities of the soil surface (P-Surface and C-Surface). Therefore, the CO<sub>2</sub> emission was also related to the intensity of anthropogenic load and lawn management (Fig. 3).

In contrast to CO<sub>2</sub>, CH<sub>4</sub> adsorption by the studied soils was shown in average for the year with the highest adsorption in the least disturbed sites. The highest adsorption of CH<sub>4</sub> during the study period (June-August) was observed in lawns of the meadow type – 44,4 mg CH<sub>4</sub>/m<sup>2</sup>, and the smallest in sports (11,4 mgCH<sub>4</sub>/m<sup>2</sup>) (Fig. 4). However, at some periods during the year when humidity was high the CH<sub>4</sub> emission was obtained with a positive correlation between soil moisture ( $R = -0,78$ ;  $p > 0,05$ ). This process can be explained by the fact that an increase of the soil moisture decreases the oxygen concentration in the soil air, that increases anaerobic niches, which are occupied by methanogens [16, 17].

Carbon sequestration in the studied lawns was measured based on the biomass growth. The maximum gain of the ground biomass was observed in May at all study sites, while the maximum increase was observed in the sports turf urban ecosystems with high level of load ( $222,7 \pm 7,2 \text{ g/m}^2$ ), and the minimum in the meadow with a standard level load ( $155,2 \pm 12,4 \text{ g/m}^2$ ). The minimum increase on all types of studied urban ecosystems was observed in August. Maximum average values of grass growth during the growing season were observed on urban ecosystems with high load level ( $779,9 \pm 12,4 \text{ g}$ ), that was more than the growth of herbs with a standard operational load level ( $482,4 \pm 15,2 \text{ g}$ ) by 61.7%. This can be explained by the difference in the maintenance and operation. In urban ecosystems with a high level of treatment, frequent mowing, regular watering and mechanical tillage (aeration, combing) contribute to the activation of growth of the ground and root biomass due to the optimal conditions of soil moisture and air supply. Lawns with a standard load levels differ with rare mowing, watering and lack of machining [8].





**Fig. 4.** Total of adsorption CH<sub>4</sub> in studied urban lawns (June–August)

Reduction of the root biomass and, as a consequence, minimum connectivity of sod were observed in all studied areas after the winter period. The maximum losses were observed on urban ecosystems meadow type ( $93,4 \pm 5,9 \text{ g/m}^2$ ), the minimum - on sports ( $13,9 \pm 1,6 \text{ g/m}^2$ ). For all types of the studied lawns, root biomass decreased in July, which was associated with summer herbs depression [14]. A positive correlation between the increase in above-ground and root biomass was established ( $R = 0,74$ ;  $p > 0,05$ ).

Carbon balance was estimated based on the comparison between CO<sub>2</sub> emissions from soil and C sequestration in biomass. Flows of CH<sub>4</sub> were not taken into account, because their contribution was negligible. For all the plots, the flow of carbon into the atmosphere prevailed over the fixation with the difference between the flow and absorption ranging from 10,9 to 2,31 kgC/m<sup>2</sup> per year. The greatest carbon losses were observed at the plots with lawn parterre (P-Wops), where they amounted to 2,74 kgC/m<sup>2</sup>/year, whereas the lowest - in the meadow (1,29 kgC/m<sup>2</sup>/year) (Table 3).

It was also revealed a significant prevalence of carbon emissions for areas with a high level of operational load. This is due to the fact that on these areas regular mechanical tillage occurs (aeration, vertical cutting, and rolling), which largely affects soil cover and ground vegetation [8, 14].

To analyze the influence of soil temperature and soil moisture on the emissions of carbon dioxide a regression analysis was carried out [18].

Two regression equations were calculated and allowed to predict the soil CO<sub>2</sub> flux for lawn urban ecosystems with different levels of anthropogenic load.

For the standard level of anthropogenic load, as a result of regression analysis, it was found that soil moisture is an insignificant factor. On the basis of this equation,

**Table 3.** Comparative analysis and assessment of soil carbon emissions in studied urban laws average for the year.

Plots	Emissions C $\uparrow$ , kgC/m $^2$	Fixation C $\downarrow$ , kgC/m $^2$		Carbon balance C $\uparrow$ -C $\downarrow$
		Aboveground biomass	Root biomass	
L-St	1,29	0,17	0,03	1,09
St	1,80	0,22	0,06	1,52
P-Wops	2,74	0,31	0,12	2,31
S-CEM	1,96	0,33	0,18	1,45

69% of the variation in the soil CO $_2$  flux ( $R^2 = 0,69$ ,  $p < 0,01$ ) can be predicted. The equation operates in the range of soil temperatures 0 to 25 °C. The regression equation for these urban ecosystems is as follows:

$$P[\text{gCO}_2/\text{m}^2/\text{day}] = 2,17 + 1,66T[^\circ\text{C}] \quad (1)$$

For the increased level of anthropogenic load, it was found that moisture and soil temperatures are reliable factors. On the basis of this equation, it is possible to predict 61% of the variation in the soil CO $_2$  flux ( $R^2 = 0,61$ ,  $p < 0,01$ ). The equation operates in the range of soil temperatures 0–25 °C, and soil moisture 5–70%. The regression equation for these urban ecosystems is as follows:

$$P[\text{gCO}_2/\text{m}^2/\text{day}] = 20,67 + 1,59T[^\circ\text{C}] - 0,24W[\%] \quad (2)$$

Considering the influence of the lawn urban ecosystems type and the level of operational load on CO $_2$  emissions a variance analysis was made (total CO $_2$  emission for two years of research) (Table 4) [18].

**Table 4.** Results of variance analysis (two years of research).

Level anthropogenic load	CO $_2$ , kg/m $^2$
Standard	11,35 $\pm$ 2,03 <sup>b*</sup>
High	17,25 $\pm$ 3,09 <sup>a</sup>
*Values with different letters (a, b) differ significantly ( $p \leq 0,05$ ), Student's test; n = 3	
Types of urban lawn ecosystems	CO $_2$ , kg/m $^2$
P-Wops	20,07 $\pm$ 0,23 <sup>a*</sup>
S-CEM	14,43 $\pm$ 0,21 <sup>b</sup>
St	13,20 $\pm$ 0,17 <sup>c</sup>
L-St	9,50 $\pm$ 0,20 <sup>d</sup>
*Values with different letters (a, b, c, d) reliably ( $p \leq 0,05$ ) differ for each type of urban lawn ecosystem separately (ANOVA, Tukey criterion); n = 3	

The results of variance analysis showed a significant spatial diversity of urban lawn ecosystems in the study area, not only in terms of operational load, but also in the type of specialization.

## 4 Conclusion

Significant spatial diversity in the structure of lawn urban ecosystems located in the north of the Moscow metropolis was revealed. Such urban ecosystems differ in terms of functional use, level of management and type of urban soils. There are recreation soils of the meadow urban ecosystems, cultivated urban soils of the landscape gardening urban ecosystems and constructed soils of the sport urban ecosystems. The results of one year-round monitoring of atmospheric air composition showed that all the investigated urban ecosystems are the source of CO<sub>2</sub>, since the predominance of emissions over carbon uptake in terrestrial and root biomass for all the studied sites was revealed. It is important to note that the urban ecosystems with higher level of management emit in average 34% of CO<sub>2</sub> more than their counterparts. Therefore, we showed that urban soils have a high potential to emit carbon contribute to climate change and this effect will likely increase in future considering on-going urbanization.

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# Abandonment of Arable Lands Triggers the Recovery of Native Vegetation and Organic Carbon Content in Soils

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**Abstract.** Fast growth of urban population during the last century led to massive abandonment of arable lands near big cities due to the outflow of rural population. After withdrawal, former arable lands undergo a process of self-restoration, and there are some periods of natural succession of vegetation and soils. This study was aimed to estimate the changes in plant biodiversity and organic carbon content in soils during postagrogenic evolution of former arable lands in various bioclimatic zones of the European part of Russia. The chronosequence studies were carried out in southern taiga (Albeluvisols, Kostroma region), zone of deciduous forest (Phaeozems, Moscow region), and steppe zone (Chernozems, Rostov region). Each chronosequence included arable, abandoned lands of different ages, and native (forest or steppe) cenosis. The content of organic carbon ( $C_{org}$ ) and total nitrogen ( $N_{org}$ ) was determined in mixed soil samples (0–20 cm layer). Total species richness (TSR) was used to quantify the biodiversity of plant communities. It was shown that the withdrawal of soils from agricultural use resulted in some alterations in species composition, increase of biodiversity, and a gradual recovery of native vegetation attributed to the bioclimatic zone. The highest values of TSR were observed in abandoned lands of 13, 15, and 30-yr old under grasslands. A notable increase in  $C_{org}$  content in the upper part of former arable layer was observed during the postagrogenic evolution for all bioclimatic regions. However, the tendency was more pronounced for postagrogenic soils in northern bioclimatic zones in comparison to southern ones: Albeluvisols > Phaeozems > Chernozems. Thus,  $C_{org}$  content in Albeluvisols under forest was 4.7 times higher than in arable soil. The same ratio ( $C_{org}$  in native cenosis:  $C_{org}$  in arable) for Phaeozems and Chernozems comprised 2.3 and 1.4, respectively.

**Keywords:** Succession of vegetation · Biodiversity  
Arable and abandoned lands · Organic matter · Self-restoration

## 1 Introduction

Fast growth of urban population during last century led to massive abandonment of arable lands near big cities due to the outflow of rural population. In the 1990s in Russia, large areas of the arable lands were abandoned due to the depression in agriculture and moving of rural population to urban territories [1]. After withdrawal, former arable lands undergo a process of self-restoration, and there are some periods of natural succession of vegetation and soils [2]. The dynamics of the species composition of plant cover through the postagrogenic succession appreciably varies among the bioclimatic zones [3].

Changes in plant cover always accompany the removal of soil from agricultural use and its conversion to native vegetation, and affect the content and reserves of organic matter in the topsoil [4–7]. The restored native vegetation and postagrogenic soils become a sink of atmospheric carbon [1, 7]. The average rate of carbon accumulation in soils due to conversion of arable land into grasslands or forest plantations is 33–34 g C/m<sup>2</sup> per year [8]. The average rate of carbon sequestration in the former arable soils of Russian Federation during the first 20 years after their removal from agricultural use is estimated to be more significant, reaching  $105 \pm 10$  g C/m<sup>2</sup> per year [7]. A negative exponential relationship was revealed between the rate of carbon accumulation in the soil during postagrogenic evolution and the age of abandoned lands [9]. Thus, the recovery of natural vegetation on former arable lands could significantly affect the biogeochemical cycle of carbon, increasing the carbon (C) sink in postagrogenic ecosystems and mitigating climatic changes. Therefore, the assessment of ecological potential of lands withdrawn from agricultural use is of great interest nowadays especially in the context of global climate change.

The most important processes that lead to an increase of organic carbon pool in soil are: (1) input of organic residues to the soil, (2) enrichment of deeper soil layers by organic matter (OM) due to the increasing of belowground phytomass and active perturbation of soil by soil fauna, and (3) formation of organic-mineral complex protecting OM [8, 10, 11]. Carbon accumulation in the soil also depends on the intensity of decomposition of the newly incorporated OM and OM already being present in the soil [12, 13]. An increase in respiratory activity and microbial carbon during the restoration of natural plants is a general tendency observed during the remediation of arable soils after the cessation of agricultural use [11, 14].

This study was aimed to estimate the changes in plant biodiversity and organic carbon content in soils during postagrogenic evolution of former arable lands in various bioclimatic zones of the European part of Russia (southern taiga, deciduous forest, and steppe).

## 2 Objects and Methods

The chronosequence studies were carry out in (1) Kostroma region (south taiga, Albeluvisols), (2) Moscow region (deciduous forest zone, Phaeozems), and Rostov region (steppe zone, Chernozems). In Kostroma region (Manturovo district, 58°10'N, 44°28'E), the chronosequence included (Table 1): an arable sown by oat, abandoned

lands of 8-, 15-, and 35-yr old, and a mixed secondary forest ( $\sim 100$  years). In Moscow region, study plots belonged to the Experimental Field Station of the Institute of Physicochemical and Biological Problems of Soil Science of the Russian Academy of Sciences ( $47^{\circ}27'N$ ,  $39^{\circ}35'E$ ) and consisted of: an arable under fallow, abandoned lands of 6-, 15- and 30-yr old, and a secondary linden-aspen forest ( $\sim 65$  years). The abandoned lands of 15- and 30-yr old are periodically mowed and thus reforestation did not occur on these plots. In Rostov region, the chronosequence was located in the Agrobiological Station of the Southern Federal University ( $54^{\circ}20'N$ ,  $37^{\circ}37'E$ ) and included: an arable sown by winter wheat, abandoned lands of 10-, 15-, 26-, and 81-yr old. The last plot presented climax stage of postagrogenic succession (or fully recovered steppe cenosis).

**Table 1.** General characteristics of vegetation on the arable and postagrogenic soils in the various bioclimatic zones

Albeluvisols loamy (southern taiga zone)					
Period after abandonment	Arable land	8 years	13 years	35 years	$\sim 100$ years
Plant community	Oat	Meadow with the dominance of cereal grass	Developed 5–8-yr willow forest with grass cover	Bilberry aspen-birch forest	Moss-bilberry spruce-birch forest
Phaeozems loamy (deciduous forest zone)					
Period after abandonment	Arable land	6 years	15 years	30 years	65 years
Plant community	Current fallow	Ruderal herbaceous grass	Cereal-herbaceous grass	Cereal-herbaceous meadow	Maple-linden-aspen forest
Chernozems (steppe zone)					
Period after abandonment	Arable land	10 years	15 years	26 years	81 years
Plant community	Wheat	Legume-cereal-motley grass	Cereal-legume-herbaceous grass	Herbaceous-cereal meadow	Herbaceous-feather grass steppe

Total species richness (TSR) was used to quantify biodiversity of plant communities. TSR-value represented the number of all plant species growing in the plots, including trees and shrubs. Geobotanical observation of the study plots in Moscow and Kostroma regions was carried out in the beginning of July when grass vegetation was characterized by the highest biodiversity. Geobotanical observation in Rostov region was carried out in September. At this period, spring vegetation has completely disappeared, and thus it was difficult to correctly estimate the TSR. We used the name of the plant association from Lopes de Gerenyu et al. [11].

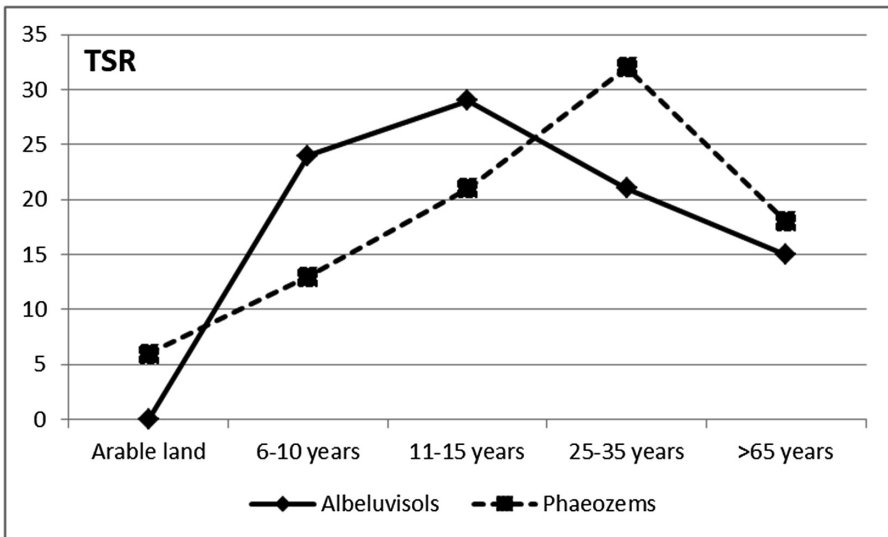
The content of organic carbon ( $C_{org}$ ) and total nitrogen (N) was determined in the mixed soil samples collected from former arable layer (0–20 cm) using an automatic CHNS analyzer (Leco, USA). The graphs show mean values and a standard error (SE) for three analytical replications.

### 3 Results and Discussion

After withdrawal former arable lands undergo a processes of self-restoration leading to the formation of a natural type of ecosystem attributed to a bioclimatic zone [3, 15, 16]. Initially, during the first 3–5 years, former agricultural lands pass through the ruderal stage (Table 1). Further restoration of the plant community during postagrogenic evolution and the period for full recovery of natural vegetation depended mainly on the bioclimatic conditions of regions.

In middle and southern taiga, the typical quasi-climax spruce forests (green-blue-cowberry, bilberry, mixed-grass) are formed on former arable lands after 170–180 years of postagrogenic evolution (Lyuri et al. 2010). In the zone of deciduous forests, recovery of climax vegetation (broad-leaves forests) might occur ca. 80–100 years after withdrawal of cultivation. In the forest-steppe, the formation of climax vegetation (a mixed-grass steppe) takes the shortest - at least 50–60 years [1].

Our studies showed that TSR-values increased from arable plots to natural cenosis and reached their highest values in 13-, 15-, and 30-yr old abandoned lands, which are the richest plant communities (Fig. 1). However, the renewal of woody vegetation during the postagrogenic evolution led to a decrease in species richness, due to the complete disappearance of photophilous vegetation under the closed forest canopy.

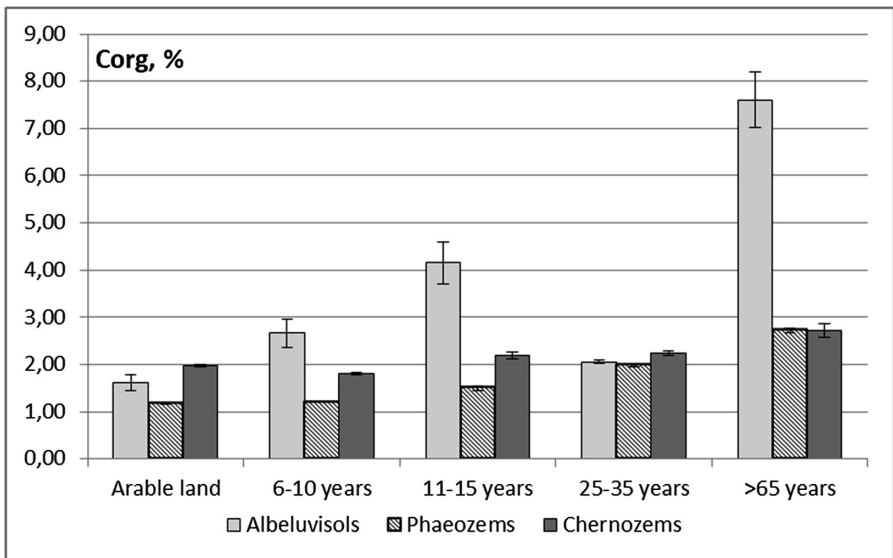


**Fig. 1.** Dynamics of the total species richness (TSR) of plant community in southern taiga and deciduous forest zones during postagrogenic evolution (x-axis corresponds to time after arable land abandonment).

Evolution of plant communities during postagrogenic evolution inevitably affects the main soil properties resulting in the recovery of soil structure and fertility as well as carbon and nitrogen accumulation, especially in the former arable layer [2, 17]. We also



observed a notable increase in  $C_{org}$  content in the upper part of former arable layer during the postagrogenic evolution for all bioclimatic regions (Fig. 2). However, this tendency was more pronounced for postagrogenic soils in northern bioclimatic zones in comparison to southern ones: Albeluvisols > Phaeozems > Chernozems. Thus,  $C_{org}$  content in Albeluvisols under forest was 4.7 times higher than in arable soils. The same ratio ( $C_{org}$  in native cenosis:  $C_{org}$  in arable) for Phaeozems and Chernozems comprised 2.3 and 1.4, respectively. It was considered that low carbon stocks in the cultivated soils are caused by low input of fresh organic matter due to annual removal of yield. After withdrawal of arable soils from agricultural use, plenty of weeds begin to develop during the first years after abandonment and later natural cenosis is formed due to native plant succession. As a result, the amount of fresh organic material input to the soils (leaves, grass litter, roots, etc.) considerably increased after cessation of cultivation, and  $C_{org}$  accumulated in the former arable layer, especially in its upper part (0–10 cm).

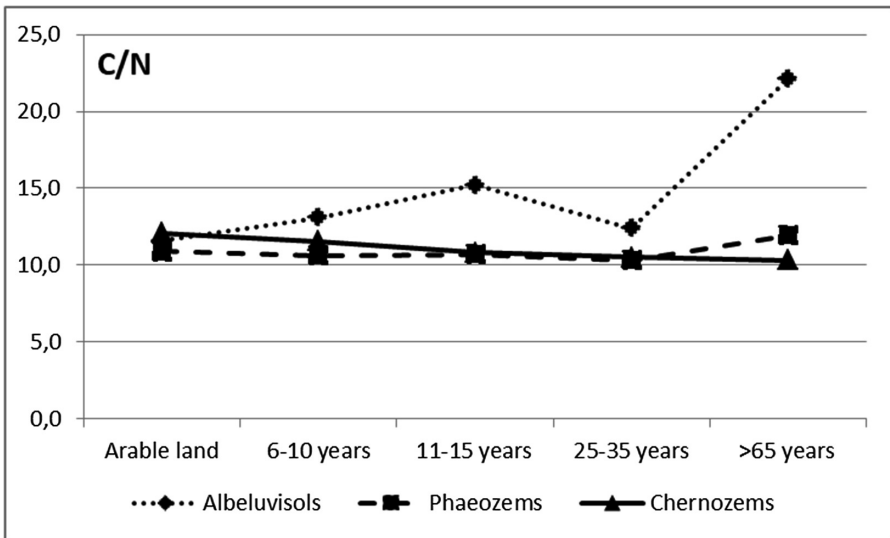


**Fig. 2.** Organic carbon content ( $C_{org}$ ) in abandoned lands of different age in various bioclimatic zones of the European part of Russia (0–20 cm layer).

Although rate and direction of the ecosystems recovery are mainly determined by their zonal localization, such factors as the initial land use and the degree of anthropogenic transformation of arable lands before abandonment, as well as the nature of the input of organic substrates to soils can substantially affect the process of soil recovery. This could explain our findings that the tendency of increase in  $C_{org}$  content is weakened in the order Albeluvisols > Phaeozems > Chernozems or from northern to southern bioclimatic zones. The most significant increase in the content of  $C_{org}$  in Chernozems was observed only in final stages of succession, apparently due to high stability of OM in Chernozems to degradation caused by their cultivation [2, 16, 18, 19].

The postagrogenic evolution of soils in south taiga and undergoing process reforestation might cause not only accumulation of  $C_{org}$ , but also eluviation of OM in Albeluvisols. Due to this, some  $C_{org}$  depletion of OM was observed in the upper part of the soil profile (under organic layer) after 35 years of abandonment of former arable Albeluvisols in comparison with the 13-yr period. However, in secondary spruce-birch forest, carbon enrichment of the upper part of the mineral horizon increased again due to the formation of powerful litter. The content of  $C_{org}$  here reached  $7.6 \pm 0.6\%$  due to the presence of coarse humus litter compounds, which were mixed with the mineral matrix of the upper soil layer owing to the activity of the mesofauna. Similar changes in  $C_{org}$  content were also observed at the final stages of natural reforestation during postagrogenic evolution of Phaeozems in Kursk region [20].

The enrichment of the organic matter with nitrogen (or C to N ratio, C/N) changed in former arable lands during the recovery of natural vegetation as well (Fig. 3). The C/N ratio in 0–20 cm layer increased substantially in post-agrogenic Albeluvisols only. The changes in the C/N ratio in Phaeozems and Chernozems were negligible. It is considered that humification of plant residues is more intensive and nitrogen is included more actively in specific aromatic humus compounds in southern soils (Phaeozems, Chernozems) compared with northern ones (Albeluvisols) [21].



**Fig. 3.** The C to N ratio (C/N) in abandoned lands of various bioclimatic zones of the European part of Russia (0–20 cm layer)

## 4 Conclusions

Massive abandonment of arable lands near big cities is often caused by an outflow of rural population to the urban lands. This process might strongly affect carbon biogeochemical cycle, carbon sequestration in soils, and climate changes via feedback. Due to the cessation of agricultural use, natural succession of vegetation and soils is triggered that causes growth in biodiversity and gradual recovery of climax plant communities in each bioclimatic zone. The input of large amount of fresh organic matter to the former arable lands resulted in a notable increase in  $C_{\text{org}}$  content in soils during their postagrogenic evolution. In forest cenoses, the accumulation of organic matter in the former arable horizon causes the formation of a litter layer during the early stages of postagrogenic succession, and sod horizon forms at the final succession stage. A notable increase in  $C_{\text{org}}$  content in the upper part of former arable layer was observed during postagrogenic evolution for all bioclimatic regions. However, the tendency was more pronounced for postagrogenic soils in northern bioclimatic zones in comparison to southern ones: Albeluvisols > Phaeozems > Chernozems. At the same time, the most significant increase in the content of  $C_{\text{org}}$  in Chernozems was observed only at final stages of succession due to the high stability of OM of Chernozems to degradation caused by their cultivation.

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# Dynamics of Soil Organic Carbon of Reclaimed Lands and the Related Ecological Risks to the Additional CO<sub>2</sub> Emission

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**Abstract.** The total global emission of CO<sub>2</sub> from soils is recognized as one of largest fluxes in the global carbon cycle and changes in the approach of reclamation of quarries could have a large effect on the concentration of CO<sub>2</sub> in the atmosphere and environmental sustainability of ecosystem. CO<sub>2</sub> production and sequestration are underestimated for mining areas of Russian North-West. Therefore, investigation of soil organic matter content and quality was conducted on examples of reclaimed postmine lands of Russian North-West. Long-term monitoring data on soil restoration on reclaimed dumps of open quarries in the Kingisepp area of phosphorite mining are discussed. An application of <sup>13</sup>C NMR spectroscopy for investigation of humic substances has revealed very low levels of compositional variability within the soil age. High alifaticity rate has been considered to be indicative of a higher availability of soil organic matter to mineralization.

**Keywords:** Soil organic matter · CO<sub>2</sub> emission · Recovery of quarry Phosphorite mining

## 1 Introduction

During the recent decades, the world has witnessed an ever-growing concern towards global warming resulting from greenhouse gases, for example carbon dioxide (CO<sub>2</sub>). In preparation of Paris Agreement, countries submitted national plans that spell out their intentions for addressing the climate change challenge after 2020. Targets and actions for reducing greenhouse gas emissions are core components. Land use types have a substantial effect on CO<sub>2</sub> emission of individual countries in 2025 - 2030 and are associated with substantial uncertainties [1]. The potential soil carbon sequestration ability of human affected and managed ecosystems roughly the same as the total historic carbon losses assumed at 55 to 78 Gt, however the attainable soil C absorption capacity is only 50 to 66% of the possible ability. In the light of sustainability policy of soil carbon sequestration is examined and cost-efficient. Sequestration of carbon governs transmission of atmospheric CO<sub>2</sub> into long-lived pools holds it safely consequently it is not instantly reemitted. Thus, soil C sequestration implies growing soil organic carbon (SOC) and soil inorganic carbon (SIC) stocks through land reclamation.

The global soil carbon pool assessed as about 2500 gigatons (Gt) includes about 1550 Gt of soil organic carbon and 950 Gt of soil inorganic carbon. The soil C pool is 3.3 times the size of the atmospheric pool (760 Gt) and 4.5 times the size of the biotic pool [1]. Mining and quarry exploration results in fundamental changes in all landscape up to its full destruction. These abandoned pits, without soil and vegetation cover, become a large and persistent source of atmospheric CO<sub>2</sub> due to reduced vegetation productivity and various soil processes.

In view of the increasing of concentration greenhouse gases in the atmosphere, there is a strong need to investigate the processes of dynamics of soil organic matter of recultivated lands.

One of the negative consequences of mining is the high CO<sub>2</sub> emission, this is especially true for carbonate rocks. CO<sub>2</sub> emission to the atmosphere is conditioned by both weathering of carbonates and soil basal respiration, in the development of soil and vegetation, emissions of carbon dioxide changes to its sequestration, the level of the latter process can be gauged by the content of organic carbon in the soil. The study was conducted on the territory of the phosphorite mining quarry. The role of the former mining complexes on regulation of carbon stock and carbon dioxide emission were assessed in this context by the number of evaluation and instrumental methods. In addition, we believe that recovery of woody plants could be preferred on quarries because it is potential sources of recalcitrant biomacromolecules in soil and it may contribute stabilization of CO<sub>2</sub> into soil organic matter.

That is why the work is aimed to investigate the quantitative composition of soil C on reclaimed dumps of open quarries in the Kingisepp area of phosphorite mining.

## 2 Materials and Methods

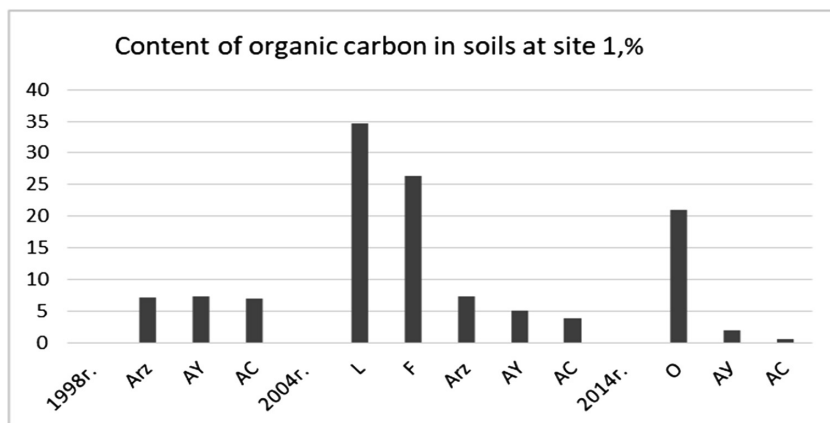
The study area is located in the Kingisepp area of phosphorite mining. The Kingisepp phosphorite deposit was developed in the early 1960s, and phosphorites have been intensively mined in this area since the 1970s [2]. Reclamation of quarry was carried out by following scheme: dense spoilbanks with high content of stones were covered by two types of substrata – friable carbonate loams without organic carbon and friable carbonate loams with admixture of turf. During the first stage of the reclamation, the surface of the dumps was leveled to an inclination of 2–6° and loose stripping rock was applied onto the large rock debris. These flat surfaces were revegetated with use of seedlings of *Picea abies* (L.), *Larix sibirica* Ledeb, *Pinus sylvestris* L. Seedlings were planted on the dumps in rows up to 4 m apart; the space between the trees varied from 0.7 to 2.0 m. The vegetation cover between the tree rows was restored in the natural way. On these plots was established during monitoring surveys in 1998, 2004 and 2014 yrs. The area of the examined plots was 20 × 20 m. On the first plot initial substrate is characterized by mixture of peat and heaped rocks (the Histic material content is up to 30%, gravimetric). The Norway Spruce was planted here. The second and third plots are characterized by heaped rocks with high stone fraction content in the superficial layer. Larch and pine were planted during reclamation implementation on the second and third plots correspondingly. At the time of the first observation in 1998, the period of overgrowth of the first plot was 19 yrs, the second - 15 and the third - 10 yrs. Soil is

replantozem. Soil samples were taken between the tree lines under the abandoned restored gross plants. Fine earth were grounded and sieved from soil samples, the total carbon content, pH and the bulk elemental composition were analyzed by routine methods. Qualitative and quantitative composition of humic acids extracted from soils of different periods of ripening was investigated by solid state  $^{13}\text{C}$ -NMR- spectroscopy method. This method is a valuable tool for the characterization of soil organic matter and humification processes in soils [3]. Preparations of humic acids were isolated according to the scheme. The humic acids were extracted with 0.1MNaOH (soil:solution = 1:10) under nitrogen gas. After 24 h of shaking, the alkaline supernatant was separated from the soil residue by centrifugation at 1516 g for 20 min and acidified 6 M HCl to pH 1. The supernatant was separated from the precipitate by centrifugation at 1516 g for 15 min. The humic acids were then redissolved in 0.1 M NaOH and shaken for 4 h under  $\text{N}_2$ , the suspended solids were removed by centrifugation. The solution was acidified 6 M HCl to pH 1, and the humic acids were separated by shaking overnight in 0.1 M HCl/0.3 M HF (solid/solution = 1:1). Next, they were repeatedly washed with deionised water until pH was reached 3.

Before alkaline extraction, soil samples were decalcified with sulfuric acid. Ash content of preparations determined gravimetrically did not exceed 5%. For preparation of humic acids  $^{13}\text{C}$  NMR solid-state spectra were recorded on a pulsed NMR spectrometer Bruker Ultra\_Shield\_500. The spectrum data were quantified by Fourier transformation. Depending on the chemical structure of the substance under the influence of the magnetic field, the atoms in the molecule resonate at different frequencies [2]. The atom resonance frequency offset is converted to a chemical shift magnitude, since its value is extremely small it is measured in parts per million (ppm). Identification of structural fragments was carried out by chemical shift intervals according to references [4–6]. It should be noted that the approaches to the interpretation of the chemical shift intervals on the NMR spectra are mildly different, but in general they are similar. The ratios of carbon contained in various structural components were determined. The degree of aromaticity was calculated as the ratio AR/AL (%), where the signals from aromatic structures were summed over the regions 105–164 and 183–190 ppm, from aliphatic structures were 0–105 and 164–183 ppm.

### 3 Results

The content of organic carbon, and, respectively - humus, was maximum in the upper soil layers and decreased downward along the profile. The richest in the amount of  $\text{C}_{\text{org}}$  is the litter of a thirty-five years old replantozem on a peat-mineral mix under a spruce, probably this is due to the long period of overgrowing and the best level of decomposition of organic compound (Fig. 1). By comparison the results of 2014 with earlier ones, the share of organic carbon in the lower layers in this area during the period 1998–2014 is decreasing. It should also be noted that, according to the results of the post-hoc test, differences in carbon content in 1998 and 2014 on the first site were not reliable. On the second and third sites, on the mineral substrate without peat, the carbon content in the upper organogenic layers significantly decreased for the specified time, in contrast to the lower mineral horizons. In general, the content of soil organic carbon under the pine



**Fig. 1.** Soil C<sub>org</sub> content (%) in different soil horizons at site 1.

and larch is not significantly different on the first site with admixture of peat (under *Picea abies* (L.)) organic carbon content of mineral horizons decreases (Fig. 1).

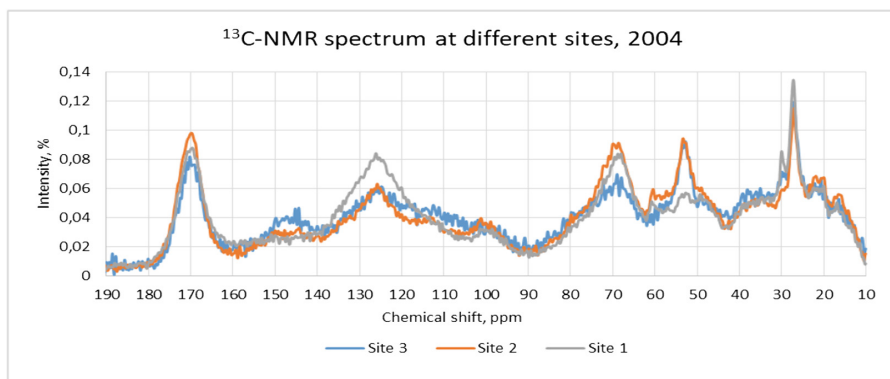
<sup>13</sup>C NMR spectroscopy data obtained for 6 HA preparations of different age soils (19, 25 and 35 yrs.) allow one to judge the stability of the carbon skeleton of macromolecules in time and to assess the similarity of the structural composition of HA under trees studied. Extraction yields of HA were calculated as the percentage of carbon recovered from the original soil sample used for extraction. The yield of HA, extraction yield was 0.2-1.0% of the initial dry fine soil weight. The analysis of molecular structure preparations of HA showed that in all samples there was a predominance of aliphatic carbons over aromatic (Table 1).

**Table 1.** Portion of aromatic and aliphatic carbon groups in total content of, HA % (2004 and 2014 yrs.).

Group	Site 1		Site 2		Site 3	
	2004	2014	2004	2014	2004	2014
Aromatic	36	33	28	33	35	34
Aliphatic	64	67	72	67	65	66

Examples of <sup>13</sup>C-NMR spectrum of HAs, of studied soils, are shown on Fig. 2. Comparison of spectrums of soil with 10 years difference in age showed no any evident and differences in portion of functional groups and molecular fragments. The distinct peak in the 23–32 ppm region, representing CH<sub>2</sub> alkyl structures was observed in all the spectrums. Biochemically recalcitrant SOM fractions are enriched with alkyl carbon structures and resist decomposition due to intrinsic molecular properties. Figure 2 also demonstrated a smaller peak in the methyl group (51 ppm) and carboxyl C regions at all samples.





**Fig. 2.**  $^{13}\text{C}$ -NMR spectrum of humic acids at three studied sites.

The ratios of structural fragments groups of HA remained almost unchanged since 2004 to 2014 (Table 2). It might be indicated the stability of humic acids in time and served as indicator of relative stabilization of soil organic matter under reclamation.

Webster et al. [7] proposed to calculate the ratio of the peak area in the spectrum of 0–52 (Alkyl-C) to the spectrum 52–108 (O-alkyl-C) in order to judge the decomposition degree of the organic matter. The higher this parameter, the higher the decomposition degree of organic compounds. The values of this indicator are presented in

**Table 2.**  $^{13}\text{C}$ -NMR section integrals (percent of total carbon) for key carbon structures (Clarified correctly what presented?) of soil humic acids in studied sites for 2004 and 2014 yrs.

Resonance region, ppm	Functional groups and molecular fragments	Site 1		Site 2		Site 3	
		2004	2014	2004	2014	2004	2014
10–27	alkyl, methyl, $-\text{CH}_2-$ units	11,1	10,4	12	12,4	11,6	11,9
27–32	$\text{CH}_2$ alkyl structures in transconformation	5,59	6,79	4,56	5,54	5,07	4,38
32–50	quaternary carbon CH carbons	11,2	12,6	11,5	11,3	12,2	10,7
50–70	methyl group resonance region of aliphatic, aromatic ethyl ethers, aminoacid carbons, methyl esters of carboxylic groups	14,9	15,2	17,8	15,8	15,2	14,8
70–100	C–H bonds, secondary alcohols, other carbon atoms bound to oxygen	12,5	15	14	14,3	13,7	13,7
100–108	cellulose anomeric carbon and hemiacetal carbon	2,97	3,89	3,89	3,77	3,78	3,65
108–135	protonise aromatic carbon, bridgehead	20,2	15,5	15,6	15,9	17,4	14,7
135–150	alkyl aromatic	6,02	6,43	5,83	6,96	7,2	9,65
150–170	aromatic C of phenol, phenol esters	9,32	9,5	8,46	8,63	8,47	10,2
170–190	carboxyl group, amidic carbonyl	6,18	4,71	6,41	5,4	5,43	6,39

**Table 3.** The ratio of Alkyl-C/O-alkyl-C

Site 1		Site 2		Site 3	
2004	2014	2004	2014	2004	2014
1,01	0,97	0,92	0,96	0,98	0,92

Table 3. In the samples studied, the indicator is almost the same in all areas, and in 10 years it has not changed much.

## 4 Discussion

We determined the content of total carbon in the soil, we believe that its origin is mainly organogenic, nevertheless the presence of mineral forms of these compounds cannot be denied. The latter is confirmed by the relatively high content of carbon and nitrogen in the mineral horizons. The problem of determining the carbon content inherited from the rock is far from being resolved, it can be not only the carbon of the peat mixed into the rock, but also the carbon of the kerogenous origin.

Perhaps significant decrease of the C content in the upper horizons of 2 and 3 sites is due to a decrease in the role of grassy vegetation and an increase in the proportion of coniferous litter in the litter, the decomposition of which proceeds more slowly. The reduction of SOM in mineral horizons due to mineralization and humification processes contributes to increasing the rate of enrichment of atmospheric concentration of CO<sub>2</sub>. But at the same time the succession of gross community to forest leads to the intensive accumulation of forest floor and organic matter. On other plots without fertilization by organic amendments organic carbon content slowly increases due to vegetation formation.

Due to inherent biochemical stability of natural aliphatic biomacromolecules might be increased the terrestrial storage of atmospheric carbon dioxide. Usually this type of bio(macro)molecules, for example, waxes, terpenoids and glycerides arise from plants, animals and microorganism. It should be noted that aliphatic components also could be formed in surface during non-enzymatic polymerization of low-molecular-weight lipids.

Additionally, samples showed a signal at 68 ppm, indicating the presence of methyl esters of carboxylic groups. Furthermore, the signal at 125 ppm for studied sites is characteristic of protonise aromatic carbon. Such long lived molecules derived from tissues of plants promote stabilized aliphatic hydrocarbons to soil organic carbon. The chemical shift in the range from 0 to 50 ppm corresponds to the resonances of aliphatic carbon structures [7]. According to some researchers the presence of aliphatic structures could be interpreted as the result of a large contribution of vegetable origin substances (wax, cutin, phospholipids, fatty acids) and the products of microorganisms' vital activity in humification processes [8, 9]. At all sites both in 2004 and in 2014, this range includes the main resonance peaks. This region could be described in more detail if it is divided into intervals 10–32 ppm (H-, C- substituted aliphatic fragments that belong to the most active and mobile compounds alkyl nature) and 32–50 ppm

(CH<sub>2</sub>-alkyl structures - the most stable media of alkyl compounds). The distinct peaks that can be observed on all spectra in the 20–30 ppm range correspond to the carbon resonance of alkyls, 23, 26 and 29 ppm are linear chains of hydrocarbons, 30 ppm are longitudinally stretched aliphatic structures containing polymethylene groups [6–9]. In 2004, the long linear chains of hydrocarbons were the most pronounced in all spectra, by 2014 some peaks from this range have lost their intensity. According to a number of studies, in the case of forest soils demonstrating peaks in the range of alkyl structures, the genesis of humic acids is due precisely to the accumulation of plant derivatives, rather than products of microbial metabolism [7, 10]. No significant peak is observed in the second spectral region of 32–50 ppm, this range corresponds to carbon protons and short branched aliphatic chains with terminal CH<sub>3</sub> groups [6].

On the second and third sites in both years of observation (at the first it is more explicitly in 2014), peaks in the 50–60 ppm range are distinguished. A number of authors believe that this range corresponds to aliphatic parts of lignin molecules - degradation products of coumarine, synapic and coniferyl alcohols [11, 12]. According to earlier publications this is the area of resonance of amino acids [13, 14]. In all samples studied, peaks are observed in the 64–73 ppm region, which characterizes O- and N-substituted aliphatic “carbohydrate” fragments. A fairly wide spectrum of 108–170 ppm corresponds to typical aromatic structures. The maximum area of peaks among aromatic fragments accounts for the range of 108–135 ppm (protonated aromatic carbon). A distinct peak in the region of 128 ppm at the first site under the spruce in 2004 and the less intense peaks of this range at other sites may characterize the H and C-substituted aromatic structures, presumably by the type of substituted phenylpropane. Chukov [15] believes that most likely it is single aromatic rings linked to the rest of the molecule via aliphatic chains. The distinct peaks in the 167–170 ppm region, which are clear in all samples, is the range of the resonance of the aromatic carbon of phenols and ethers. Analysis of the humic acids molecular structure showed that in all samples aliphatic groups prevail over aromatic groups. According to the received opinion, the development of humic acids is associated with an increase in the proportion of benzoic aromatic fragments and a decrease in aliphatic ones [16]. At the same time, some researchers point to that during the succession of the soil-vegetation cover and the change of grassy communities to forest soils, the proportion of aliphatic fragments of humic acids increases [17]. Also, the upper soil horizons of forest communities are characterized by an increased content of alkyl carbon structures in comparison with grassy ones.

High similarity of amount of functional groups and molecular fragments at different sites could be caused by predominance woody species. As is known, tree species as well as underground parts of plants have high proportions of alkyl C, as opposed to grassy species [17].

## 5 Conclusions

The pedogenesis and soil development rate is closely related to the reclamation practice, applied on the territory of pot mining areas and soil organic matter accumulation/stabilization processes are the key driving factors in soil restoration.

Amendment of reclaimed soils by peat (histic) material result in intensification of organic-mineral interactions, soil aggregation and formation of crumb structure. After 20 years of soil restoration the stabilization of soil organic matter became evident from the data of molecular compositions of the humic substances, arised from  $^{13}\text{C}$  MNR spectroscopy. The results of qualitative and quantitative analysis of humic acids have revealed a low level of change in the carbon skeleton in time, as well as the similarity of humic acid composition under different plant communities. Appearing of the stable forest canopy on reclaimed plots provide the stable input of humification precursors and result in stability of molecular composition of the humic substances. It has been established that aliphatic compounds, which are contained in needles in large numbers, greatly outnumber aromatic compounds. From these facts, one may conclude that litterfall plays a crucial role in the processes of humus formation.

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# Comparative Study of Soil Respiration Partitioning Methods for Herbaceous Ecosystems

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**Abstract.** Soil CO<sub>2</sub> efflux is a complex flux composed of autotrophic and heterotrophic sources of the CO<sub>2</sub>. To correctly estimate whether soil is and will be acting as a sink or a source for atmospheric CO<sub>2</sub>, these two principal components should be studied separately. This is because they respond differently to biological and environmental drivers. Studies which compare partitioning methods of soil CO<sub>2</sub> in one single study using unique measurement equipment are lacking instead.

In this study we attempted to compare three partitioning methods of soil CO<sub>2</sub> efflux: mesh exclusion, combined SIR and regression method and to choose the most appropriate for herbaceous ecosystems (e.g. grasslands and urban lawns). Mesh exclusion and combined SIR demonstrated comparable results in determination of autotrophic and heterotrophic contribution to CO<sub>2</sub> efflux and the methods were defined as suitable. Regression method necessitates ulterior improvements prior application in herbaceous ecosystems.

**Keywords:** Soil respiration · Partitioning · Root-derived respiration  
Microbial-derived respiration · Grasslands · Lawns

## 1 Introduction

Soil CO<sub>2</sub> efflux is a complex flux which integrates growth and maintenance respiration of autotrophic roots and organisms living in the root-affected zone (hereafter as autotrophic respiration), and SOM and plant-debris decomposition by soil microorganisms, and CO<sub>2</sub> production by soil fauna (hereafter as heterotrophic respiration) [1–3]. The dynamic of different components of soil CO<sub>2</sub> efflux is controlled by different biotic and abiotic factors, such as temperature, water availability, photosynthetic activity, plant phenological development [4]. While the activity of soil heterotrophs is tightly related to changes in soil temperature, root and rhizosphere respiration depends

mainly on the amount of assimilates supplied from aboveground [5, 6]. In constantly growing urban areas, soils are additionally exposed to a variety of anthropogenic-associated stressors like compaction, pollution, acidification, salinization with unknown effect on individual components of this flux [7, 8]. To carefully predict future changes in soil CO<sub>2</sub> efflux, we need deeper understand the performance of its individual components in changing environment.

To date, a variety of methods have been proposed to separate individual components of soil CO<sub>2</sub> efflux. Hanson et al. [9] reviewing partitioning methods and results quantified a contribution from autotrophic component to vary in a range of 10–90%. Considerable variation is due to diversity of ecosystems and potential biases associated with application of different techniques and/or various time scales. There are still no studies which compare the suitability of the partitioning methods for herbaceous ecosystems (e.g. natural and semi-natural grasslands, urban lawns) in one single study using unique measurement equipment. The objectives of this study were (1) to compare estimates of root and microbial contribution to soil CO<sub>2</sub> efflux obtained by three different partitioning methods in a grassland ecosystem; (2) to evaluate possible methodological shortcomings associated with an accuracy of estimation of single components of soil respiration.

## 2 Material and Methods

### 2.1 Site Description

The study was conducted in Amplero - a Mediterranean grassland site located in central Italy at 900 m asl. The average temperature in the site is 10 °C and average precipitation - 1365 mm. The site is subjected to a regular mowing – once a year and the rest of the growing season is used for the cattle grazing.

### 2.2 Methods Description

Were chosen three partitioning techniques potentially suitable for application in ecosystems with herbaceous cover: (1) mesh exclusion technique, an improved version of widely used root exclusion method, consisting in physical separation of autotrophic and heterotrophic fluxes [4, 10]. The novelty of this method is in the possibility of using small pore size meshes which allow the movement of bacteria, rhizodeposits and other substances through the mesh while excluding roots, maintaining by that environmental conditions similar to the exterior soil; (2) combined SIR method which unites soil substrate-induced respiration and component integration methods [11, 12]. This method consists in the quantification of the enlargement factor -  $k_{mic}$ , corresponding to an increase in microbial respiration which is limited in easily available C substrates, in response to glucose addition; (3) regression methods, based on the assumed linear relationship between root biomass and amount of CO<sub>2</sub> respired by roots and rhizosphere microorganisms. The amount of CO<sub>2</sub> derived from microbial decomposition of SOM corresponds to the y-intercept of the regression line between root biomass and total CO<sub>2</sub> efflux from soil [13, 14].

The experiment lasted for two years. Mesh-exclusion method was applied in both years. In the first year it was confronted with combined SIR results and in the second year – with the results obtained by regression method. Partitioning plots for mesh exclusion and combined SIR methods were installed in the very beginning of the growing season in the first measurements year ( $n = 8$ ). Soil CO<sub>2</sub> efflux from all plots was measured with infrared gas analyzer (EGM-4, PP-System, USA). Measurements were done with bi-weekly frequency for mesh-exclusions method and three times during the growing season – for the other two methods. Regression method requires a collection of the root material beneath the soil efflux measurement points ( $n = 9$ ). Roots were collected to a depth of 20 cm, without distinguishing between live and dead roots. All roots belonged to a class of the fine roots (<2 mm in diameter).

### 3 Results

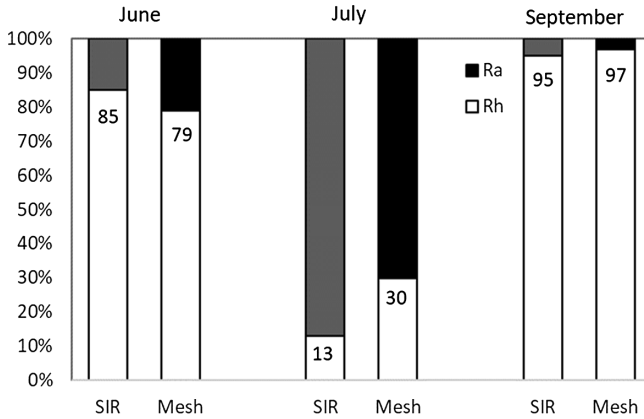
#### 3.1 Mesh- Exclusion vs. Combined SIR Method

The contribution of heterotrophic component estimated by mesh-exclusion method over the first growing season varied in the range of 21%–98%, with an average value of 72% (data not shown). In June, July and September, simultaneously with measurements by mesh-exclusion method but on the separate plots, we added a glucose solution to the soil with and without roots in order to quantify  $k_{mic}$  and estimate root and microbial contribution by combined SIR method. Soil flux components estimated by two methods demonstrated similar seasonal pattern (Fig. 1). In June and September, no differences were observed in autotrophic and heterotrophic respiration estimated by two techniques. Both methods were congruent in absolute prevalence of heterotrophic component in soil CO<sub>2</sub> efflux. Soil temperature was 23 and 18 °C and soil water content –26 and 21% respectively in June and September. In July, combined SIR approach demonstrated three-fold higher contribution of autotrophic respiration (13% vs 30%), although both methods were congruent in general rise of autotrophic contribution. Decline in heterotrophic contribution was associated with the onset of the summer drought and heat (soil water content dropped to 7% and soil temperature reached 34 °C). These results demonstrate a major sensitivity of soil microorganisms to environmental stressors in comparison to roots.

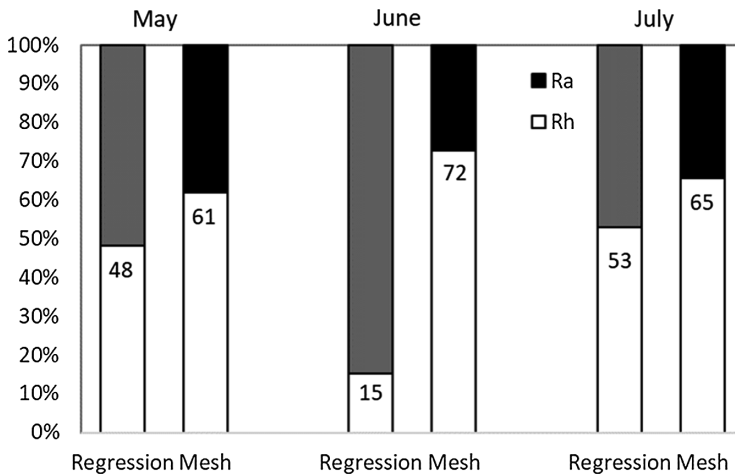
#### 3.2 Mesh- Exclusion vs. Regression Method

Partitioning of soil CO<sub>2</sub> efflux in the second experimental year is shown in Fig. 2. Heterotrophic contribution as estimated by mesh-exclusion method varied in this year from 31% to 91% with an average contribution of 68% (data not shown). Regression method constantly overestimated autotrophic flux in confront to mesh exclusion method (Fig. 2). Regression curves, obtained after plotting of the total CO<sub>2</sub> efflux vs. changes in belowground biomass were generally characterized by low values of R<sup>2</sup>, varying from 0.1–0.6 and often the obtained correlations didn't result significant.





**Fig. 1.** Partitioning obtained by mesh-exclusion (Mesh) vs. combined SIR (SIR) methods in Amperlo site. Results are shown in % of autotrophic (Ra) and heterotrophic (Rh) contribution to total CO<sub>2</sub> efflux.



**Fig. 2.** Partitioning obtained by mesh-exclusion technique (Mesh) vs. regression approach (Regression) in Amperlo site. Results are shown in % of autotrophic (Ra) and heterotrophic (Rh) contribution to total CO<sub>2</sub> efflux.

## 4 Conclusions

Among the applied methods, two, mesh exclusion and combined SIR, showed similar results in the absolute magnitude of partitioned fluxes (data not showed) and in relative contribution of the components to the total flux (Fig. 1). These methods are very different in the theoretical and methodological background so that the congruency in the results could be a good sign of their suitability and reliability for herbaceous

ecosystems like grasslands and lawns. Although regression approach was nominated in the review of partitioning methods [3] as the most universal, clean (not associated with soil disturbance) and suitable for a wide range of ecosystems, its applicability for herbaceous ecosystems is questionable in the current methods version. The particularity of the herbaceous ecosystems is that the most of belowground biomass is in the fine root form, characterized by a greater variation in root specific activity contrary to coarse roots, which constitute the majority of belowground biomass in forests [12]. Increase of the replicate number could improve the method sensitivity. Another improvement may consist in considering non structural C content of roots (soluble sugars) instead of bulk root biomass alone. This is because structural C fixed in the root cell walls and comprising the major root C pool is hardly utilized to fuel root respiration expensis [15]. It should also help to overcome the problem of the presence of the dead roots in the collected root sample. At a current state we don't recommend this method for flux partitioning in grasslands and lawns.

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# Seasonal and Annual Variations in Soil Respiration of the Artificial Landscapes (Moscow Botanical Garden)

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**Abstract.** Cities emit 30–40% of total greenhouse gases emissions and are responsible for 45–70% of total energy-related CO<sub>2</sub> emissions. CO<sub>2</sub> fluxes in cities consist of a complex balance of biogenic and anthropogenic sources. Despite the evidence that biogenic urban CO<sub>2</sub> fluxes can be important, we still know little about the magnitude of the urban biogenic CO<sub>2</sub> flux. Our study included two main tasks: (1) estimation of annual carbon dioxide efflux by urban forest soils the case of the Botanical Garden arboretum (Lomonosov Moscow State University) and the assessment of its seasonal dynamics; (2) to identify the factors responsible for the annual and seasonal variations of soil respiration. Studies were carried out on the two stationary plots with plantations of *Picea obovata* (spruce) and *Carpinus betulus* (hornbeam) from 2014 to 2017 years (starting in October). Annual CO<sub>2</sub> flux depending on the year and type of plantation was from 1750 to 3180 g CO<sub>2</sub> m<sup>-2</sup> yr<sup>-1</sup>. Summer period (when the soil temperature at 10 cm depth was above 10 °C) was more than half the annual soil CO<sub>2</sub> efflux. In the seasonal aspect, the role of abiotic factors (soil temperature and moisture) in the dynamics of soil respiration is different. Soil temperature plays a key role in the dynamics of soil respiration during the mid-seasons (spring and autumn). When the soil temperature reaches 10 °C, its role decreases, the soil moisture becomes the determining (limiting) factor. In the winter, early spring and, possibly, late autumn periods, other factors and processes may be leading, such as soil freezing-thawing, pronounced gas diffusion and dissolution.

**Keys words:** Botanical garden · CO<sub>2</sub> flux · Seasonal dynamic  
Soil moisture · Soil respiration · Soil temperature · Urban forest

## 1 Introduction

Soils play an important role in climate regulation, particularly through the sequestration of atmospheric carbon and its storage within major carbon sinks [1, 2]. About 25% of atmospheric carbon dioxide comes from the transformation of organic matter in the soil, which contains twice as much carbon as in the atmosphere, and three times more than in the vegetation [3, 4]. As the result of irrational use, soils can be a major source

of carbon dioxide emissions [5]. A decrease in carbon storage in the soil affects the concentration of atmospheric CO<sub>2</sub> [5].

In recent years, more attention has been dedicated to study the role of cities in global climate change. Cities emit 30–40% of total greenhouse gases emissions [6, 7] and are responsible for 45–70% of total energy-related CO<sub>2</sub> emissions [8]. In contrast to natural ecosystems, CO<sub>2</sub> fluxes in cities consist of a complex balance of biogenic and anthropogenic sources [9]. Attempts to quantify the role of urban areas on the global carbon budget have focused largely on inventories of emissions, from estimates of fossil fuel consumption [10, 11]. It is considered that the urban carbon cycle is entirely driven by fossil fuel emissions. However, the magnitude of the biogenic CO<sub>2</sub> efflux for urban environment is still uncertain. Soil respiration is one of the important sources of the biogenic CO<sub>2</sub> efflux. Soil CO<sub>2</sub> emission (respiration) of urban and suburban areas have been measured in temperate zone [12–18]. While the most of these studies were either spatially or temporally limited. In turn, most soil surveys regarding to carbon cycle assessment do not include urban areas, instead delineating them as partially empty space in regional soil monitoring systems [19, 20]. Most soil carbon studies have focused on agricultural and natural ecosystems [21–23].

Currently in the world, there are about 2300 botanical gardens and arboreta, which are centers of floristic and geobotanical research, public environmental and education. In Russia there are 99 botanical gardens, most of which belong to the universities, as well as agricultural, forestry and medical institutions [24]. Botanical gardens in the cities are unique artificial ecosystems in which, due to continual investment of resources, it is possible to partially offset the negative impact of the urban environment and create a high level of biodiversity.

Our study included two main tasks: (1) estimation of annual carbon dioxide efflux by urban forest soils the case of the Botanical Garden arboretum (Lomonosov Moscow State University) and assessment of its seasonal dynamics; (2) to identify the driving factors of the annual and seasonal variations of soil respiration.

## 2 Materials and Methods

### 2.1 Site Description

The Botanical Garden of the Lomonosov Moscow State University (MSU) is located 800 meters south-west from the edge of the high right bank of the Moscow River (55.708°N, 37.526°E). The Botanical Garden was founded in October 1950. Arboretum covered an area about 10 hectares, planted more than 20,000 trees and shrubs 700 species. Because of the significant soil disturbance during the construction of the MSU main building, it was necessary to carry out work on remediation of topsoil in Botanical Garden. Significant amounts of lowland peat were used for this purpose. In some places peat was mixed with the upper layer of the ground. Later, during the first 10–20 years lowland peat and mineral fertilizers were added annually onto the soil surface to increase soil fertility [25].

Moscow has a humid continental climate with severe winters, no dry season, warm summers and strong seasonality. In Moscow the average annual air temperature is 5 °C

and annual precipitation is 689.2 mm. The parent material is silty clay and loam with low permeability, which lies on the moraine. Soils of MSU Botanical Garden differ from other urban soil and from south taiga soils near Moscow. Soils of MSU Botanical Garden are characterized by high fertility and relatively slightly contaminated [25]. Soils of the studied sites can be classified as Technosols or Anthrosols [26].

## 2.2 Field Measurements

Soil CO<sub>2</sub> emission were measured on the two stationary plots with plantations of *Picea obovata* and *Carpinus betulus* from 2014 to 2017 years (starting in October). Each plot was about 200 m<sup>2</sup>. Carbon dioxide efflux (respiration, Rs) from the soil surface was measured by the closed chamber technique [27, 28] in a triplicate at each plot by infrared gas analyzer DX6210 (accuracy of 0.002%). Measurements were carried out every 1–2 weeks between 13<sup>00</sup> and 15<sup>00</sup> h. We avoided post-rain measurements to prevent rapid transition of the soil respiration rate during observations.

Air and soil temperatures were measured at each plot all year round six times per day with Thermochron ibutton™ data loggers (Dallas Semiconductor Corporation, TX, USA) (resolution 0.5 °C, accuracy ±1 °C). Air temperature was measured at 1.5 m above the ground. Soil temperature was determined at 2, 10, 20, 40 and 60 cm depth. Soil volumetric water content at the 0–10 cm depth (W<sub>10</sub>) was measured simultaneously with the Rs adjacent to the chamber with FieldScout TDR 100 Soil Moisture Meter (resolution 0.1%, accuracy ±3.0%).

## 2.3 Soil Chemical and Physical Analysis

Sampling was carried out from each horizon of soil profiles at studied sites with soil auger (Eijkelkamp Company). The pH<sub>w</sub> was measured by potentiometer method (soil: water = 1:2.5). The soil organic carbon was analyzed by dichromate oxidation [29]. The moisture content of the soil samples was determined by gravimetric method.

# 3 Results and Discussion

## 3.1 Soil Chemical and Physical Properties

In studied sites the litter thickness was not exceed 0.5 cm. Morphological, physical and chemical soil properties at various depths (horizons) are given in Table 1. Soils are characterized by a high content of organic carbon in the upper horizon (from 3.9 to 8.4%) decreasing along the soil profile depth. The pH ranged from 6.9 to 7.7.

Soils of all plantations are characterized by similar annual temperature regimes. The soil average annual temperature varies very slightly with depth and it is about 7 °C. The observed nonsignificant differences of soil temperature of two studied plantations are attributed to varying in projective cover degree, canopy density, as well as the depth and duration of snow cover. Soil freezing in winter was limited to the upper 10–20 cm. Soils were in the frozen state only one or two months [30].

**Table 1.** Soil morphological, chemical and physical properties of the sites with plantations of *Picea obovata* (spruce) and *Carpinus betulus* (hornbeam).

Site	Depth, cm	Color	Texture	Structure	Artifacts, rock fragments	Organiccarbon, %	pH <sub>w</sub>	GW*, %	Bulk density, g cm <sup>-3</sup>
Spruce	0.5–8	7.5YR2.5/2	Sandy loam	Very fine – fine subangular blocky	–	8.40	6.9	32.9	0.8
	8–20	7.5YR4/4	Sandy loam	Fine subangular blocky	Single fine gravel	5.45	7.2	18.1	1.1
	20–38	7.5YR5/3, 6/3	Silty loam	Fine angular blocky	Small pieces of brick and coal	2.77	7.4	19.8	1.4
	38–60	7.5YR4/4	Loam	Coarse angular blocky	//-//, fine gravel	0.69	7.7	14.7	1.4
Hornbeam	0.5–18	7.5YR2.5/2 (8/1)	Silty loam	Medium subangular blocky	Carbonate, brick	3.89	7.2	33.2	0.9
	18–34	7.5YR3/2, 3/4	Loam	Coarse angular blocky	Single carbonate, brick	2.83	7.0	18.3	1.2
	34–60	7.5YR4/6	Loam	Very coarse platy	–	0.19	7.3	15.3	1.2

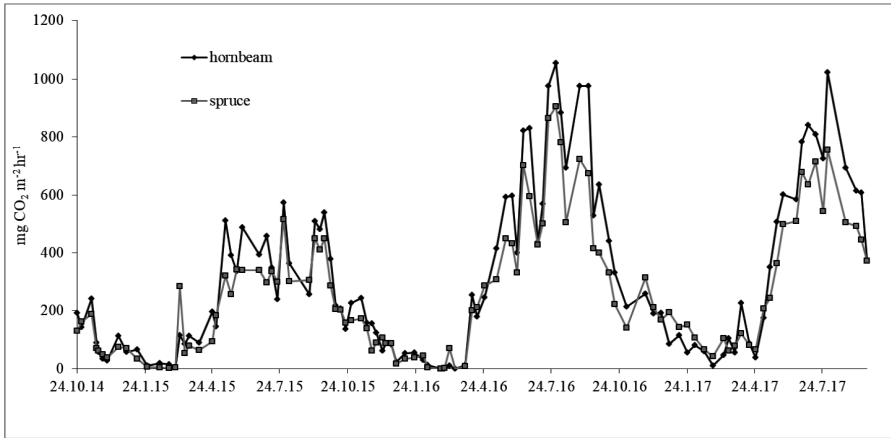
\* GW, gravimetric soil moisture

### 3.2 Seasonal Variation of Soil Respiration

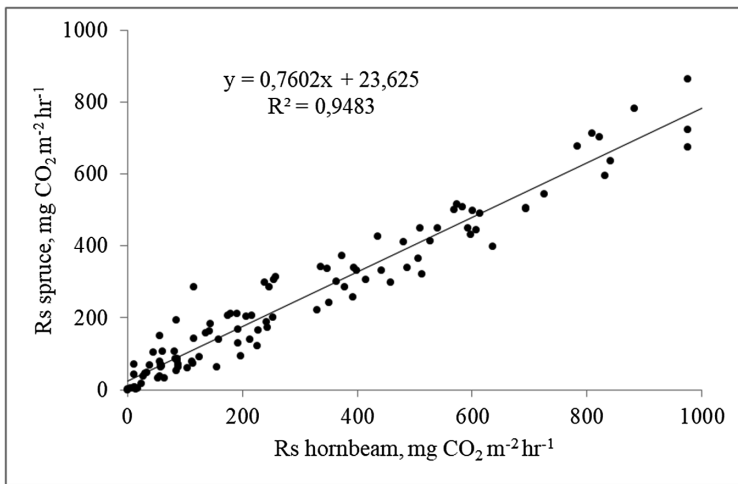
Soil Rs has a distinct seasonal variation. Soil Rs at both sites during the years ranged from 0 (February) to 1000 (July) mg CO<sub>2</sub> m<sup>-2</sup> h<sup>-1</sup> (Fig. 1). In winter, about zero soil CO<sub>2</sub> efflux values were observed only 5–6 weeks or was not observed at all (in winter 2016/2017). For both sites, soil Rs started increase in April and has reached its maximum in July–August. The soil Rs reduction observed since the end of September and was associated with a decrease of the air and soil temperature. The significant relationship in the annual cycle of soil Rs of studied sites was found ( $r = 0.97$ ;  $p < 0.05$ ) (Fig. 2). The soil Rs of the hornbeam plantation was higher than that of the spruce at Rs values amounted above 100 mg CO<sub>2</sub> m<sup>-2</sup> h<sup>-1</sup>. In summer period, this difference reached up to 25%. In the mid-seasons (spring and autumn) Rs was slightly higher in spruce forest. It is associated with different dates of snow falling and melting and with different rates of cooling-warming of upper soil horizons.

### 3.3 Environmental Regulation of Soil Respiration

Over the year, Rs correlated stronger with soil temperature at 10 cm depth (T<sub>10</sub>) ( $r = 0.9$ ;  $p < 0.05$ ) than with air temperature (Ta) ( $r = 0.7$ ;  $p < 0.05$ ). Soil moisture has no effect on Rs in the annual cycle ( $r = -0.04$ ;  $p > 0.05$ ). Rs measurement period (2016 yr, hornbeam plantation) was conditionally divided on “winter”, “spring”,



**Fig. 1.** Temporal dynamics of soil Rs for hornbeam and spruce plantations in the period from October 2014 to October 2017.

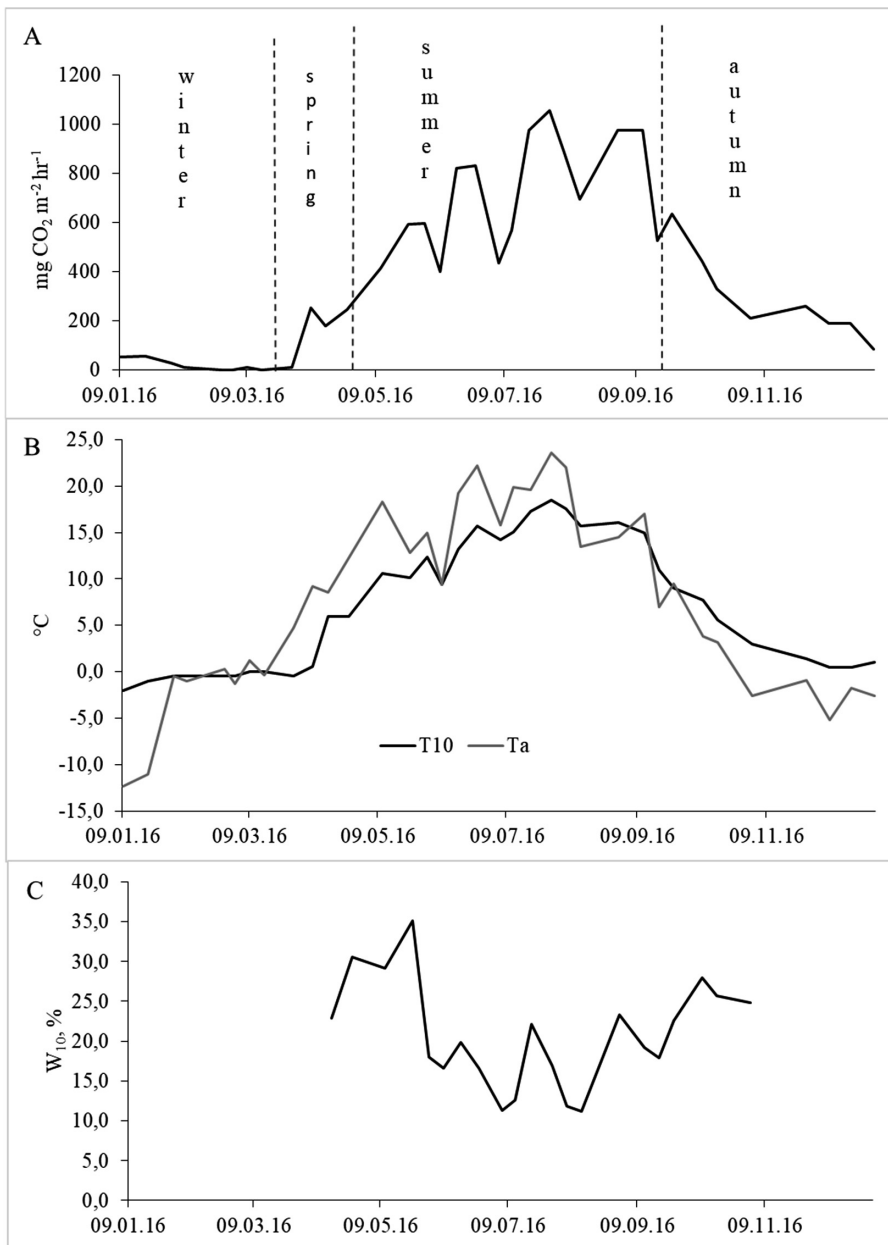


**Fig. 2.** Relationship between soil Rs of hornbeam and spruce plantations.

“summer” and “autumn” regarding to  $T_{10}$  (Fig. 3). The summer season was distinguished by soil temperature above 10 °C. The winter season was characterized by negative soil temperatures ( $T_{10} \leq 0$  °C). The summer season began from the end of May and ended in the middle of September. Period of the winter season varied greatly over the years. It started from the beginning of December to early January and ended by the end of March–early April.

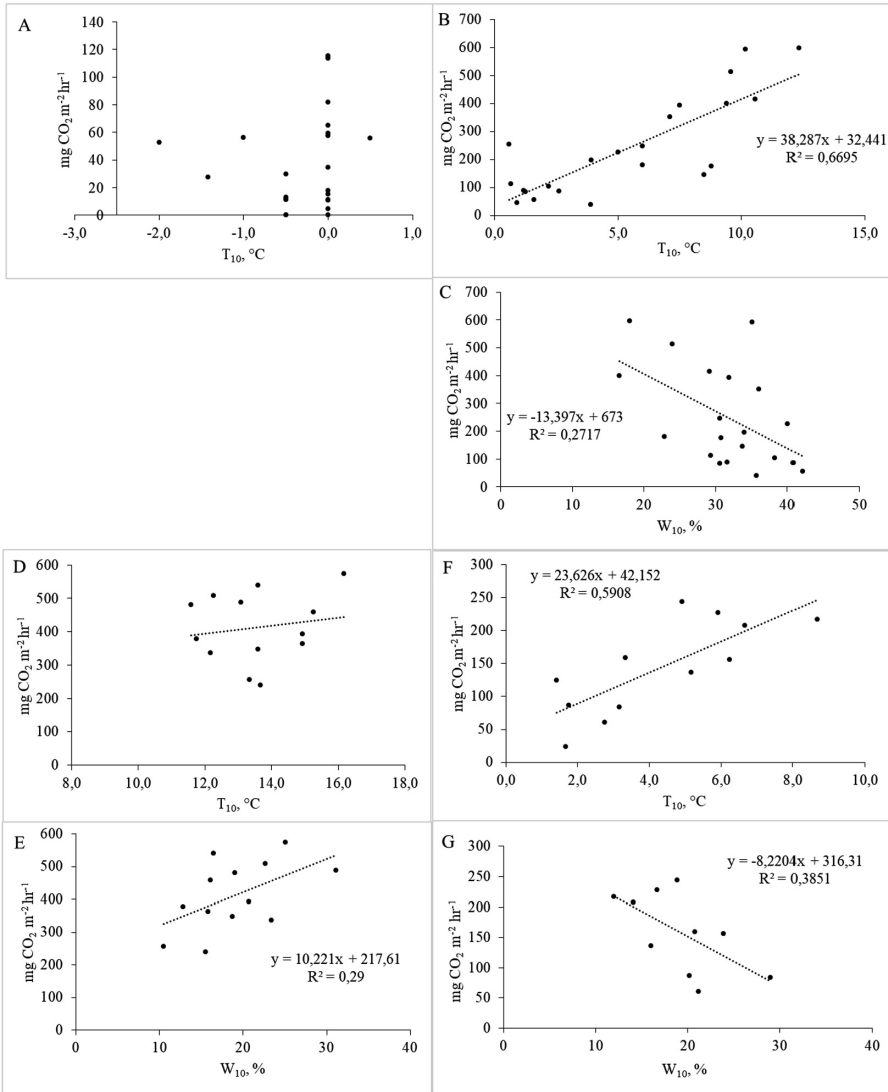
In winter, at negative soil temperatures, and in the early spring, the main factors driving Rs were the soil freezing-thawing processes, not air or soil temperature (Fig. 4A). The lowest soil Rs was observed not in the coldest period, but only at the





**Fig. 3.** Seasonal dynamics of soil Rs for hornbeam plantation in 2016 year (A), air (Ta) and topsoil (0–10 cm, T10) temperature (B); topsoil volumetric water content,  $W_{10}$  (C). Soil moisture was not measured when the soil was frozen and/or covered with snow.

end of winter, in February–March (Fig. 4A, B). We think this is due to the fixation of the gas during the formation of ice crust on the soil surface at the moment when short-term thaws with an insignificant snowmelt began. This is consistent with our data on the dynamics of soil CO<sub>2</sub> concentration [30]. This is indicated in a soil Rs overshoot after soil thawing in the end of March (Figs. 1 and 3A).



**Fig. 4.** Correlation between soil respiration and soil temperature (T<sub>10</sub>), moisture (W<sub>10</sub>) of hornbeam plantation site for different seasons (: A – winter; B, C – spring; D, E – summer, F, G – autumn. The regression equations are presented at the significant correlation (p < 0.05).

In spring, when the soil warmed up, an increase in Rs was observed. In this period, the strong correlation ( $r = 0.8, p < 0.05$ ) of Rs with soil temperature was noted in comparison with other seasons ( $r < 0.7$ ) (Fig. 4). A negative correlation of soil Rs with moisture was observed (Fig. 4B, C). High  $W_{10}$  (30–40%, the maximum for a year) could inhibit the activity of soil microorganisms [31]. In addition, in this period  $CO_2$  could dissolve in cold soil solutions [28].

In summer, when the  $T_{10}$  exceeded  $10\text{ }^\circ\text{C}$ , the maximum Rs values were observed associated with the microbial activity and root respiration during the maximum vegetation. In this period, the soil temperature effect on Rs decreased ( $r \approx 0.6$ ; in 2015 correlation was not significant), and the moisture effect, on the contrary, increased ( $r = 0.5\text{--}0.7, p < 0.05$ ) (Fig. 4D, E). Rainless period can reduce the soil Rs by two times. It was observed, for example, in August 2016.

In early autumn, there was an abrupt decrease in soil Rs, associated with a decrease in temperature and leaf abscission. During this period, a stable high correlation between Rs and soil temperature was observed ( $r \approx 0.7; p < 0.05$ ) (Fig. 4F). At the same time, there was inverse correlation with moisture in this period (Fig. 4G). Because soil moisture values were not too high (20–25%), biota inhibition could not be observed. We think that this correlation is nonsense (Rs decrease synchronous with an autumn increase in soil moisture). In late autumn and early winter, even at negative air temperatures, soil Rs are maintained by the diffusion of gas accumulated in the soil profile during the summer [30].

Thus, based on our data, in the seasonal aspect, the role of abiotic factors (soil temperature and moisture) in the dynamics of soil respiration is different. Soil temperature plays a key role in the dynamics of soil respiration during the mid-seasons (spring and autumn). When the soil temperature reaches  $10\text{ }^\circ\text{C}$ , its role decreases, the soil moisture becomes the determining (limiting) factor. In the winter, early spring and, possibly, late autumn periods, other factors and processes may be leading, such as soil freezing-thawing, pronounced gas diffusion and dissolution.

### 3.4 Annual Soil Respiration

We calculated the annual soil Rs for two years of research: 2015 and 2016 (Table 2). The contribution of each season to the total annual Rs is constant for two years of research. Summer soil Rs was more than half of the annual. In winter, only 2–3% of soil  $CO_2$  was released. Our estimations of annual carbon dioxide fluxes correspond to estimates of annual soil respiration obtained for forests in Moscow region [32].

**Table 2.** The annual soil respiration (ARs,  $g\text{ }CO_2\text{ m}^{-2}\text{ year}^{-1}$ ) at studied sites and portion of ARs for each season.

Sites	2015 yr					2016 yr				
	ARs	Winter	Spring	Summer	Autumn	ARs	Winter	Spring	Summer	Autumn
	Portion of ARs (%)					Portion of ARs (%)				
Hornbeam	2030	3	16	65	16	3180	2	18	56	24
Spruce	1750	3	13	63	21	2530	2	18	52	28

## 4 Conclusion

Despite the differences in the absolute values of  $R_s$  by soils of different plantations, it is observed to have the same seasonal dynamics, which are due to the seasonality of climatic parameters and functioning of vegetation, and not associated (or weakly associated) with the artificial origin of the soil profile. The seasonal dynamics and total value of carbon dioxide flux by the soils of the Botanical Garden are identical to those of temperate forest soils. From our point of view, this fact suggests the possibility of using artificial ecosystems such as the arboretum of the MSU Botanical Garden as objects for studies related to the turnover of carbon and other elements, making year-round manipulative experiments to assess the contribution of soil components (autotrophs and heterotrophs) to the total carbon dioxide production by soils.

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# Oil Destructive Activity of Fungi Isolated from the Soils of the Kola Peninsula

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**Abstract.** Oil-degrading microorganisms were isolated from the soil contaminated by oil products (diesel fuel, masut, gas condensate, used engine oil etc.). The effectiveness of bacterial, fungal and bacteria-fungi associations for soil cleaning from oil products in laboratory and field model experiments was estimated. The bacteria-fungi association (bacteria *Pseudomonas fluorescens*, *P. putida*, *P. baetica*, *Microbacterium paraoxydans* and fungi *Penicillium commune*, *P. canescens* st.1, *P. simplicissimum* st.1) is found to be the most effective in degrading oil products in laboratory conditions. The oil product degradation is found to be 38% of the initial amount (to 2.96 g/l) after 3 days, and 94% (to 0.21 g/l) after 10 days. The bacteria-fungi association has demonstrated the best result as compared to either bacterial or fungal associations in the field experiment as well: during 120 days oil products content was reduced by 82% (to 12.04 g oil/kg soil). Oil products decomposition rate after 30 and 120 days was maximum. Associations of oil-degrading native microorganisms in Al-Fe humus podzols of Kola Peninsula accelerate the oil product decomposition by 10–20% and are advised for environment post-cleaning from oil hydrocarbons. The soils of the Kola Peninsula are predominantly acid soils, therefore, the efficiency of fungi-containing biopreparations will likely be higher than that of bacterial preparation.

**Keywords:** Fungi · Bacteria · Oil products · Soil · Bioremediation  
Oil destruction · Kola Peninsula

## 1 Introduction

Currently, due to the ongoing accidental situations, particularly in the oil production and transportation regions, the problem of removing oil contamination is considered to have important ecological and economic value [1–3]. When discharged to environment, oil hydrocarbons have suppressive effect on the living organisms and significantly change their habitat. Purification of oil contaminated natural objects is a part of the challenging problem in the environmental remediation. The technique development oriented to negative impact reduction of oil hydrocarbons on the natural ecosystems is sure to be the vital task up to date.

Fungi are important components of the soil microbial community. It is known that bacterial microbiota [4, 5] is essential for decomposition of oil hydrocarbons, however,

the fungi greatly contribute to soil self-cleaning against hydrocarbon contaminants [1, 4, 6–10], especially in acid soil with unfavorable conditions for bacterial growth. The fungi have the exceptional property of adaptation to the adverse environment with the benefit of mighty enzyme system and significant sporogenesis [8, 11]. They are capable of destructing not only oil but certain oil products (OP), such as aromatic petrochemicals, using them in the capacity of carbon and energy source [12–16].

According to the data from the national and foreign authors, studying different fungi taxonomic groups, it was estimated that the most active in the oil products decomposition are considered to be the fungi which belong to the genus *Aspergillus*, *Cladosporium*, *Penicillium*, *Fusarium*, *Trichoderma* [4, 6, 8, 17–21].

Process of degradation of oil hydrocarbons in soil aided by fungi in climatic conditions of Murmansk region is still unexplored. Low potential of self-cleaning of arctic ecosystems characterized with short vegetation period and low temperatures calls for the need to find a technology of environment clean-up from oil contamination to practicable level of recovery of disturbed northern ecosystems. While the southern regions nature quickly heals damage caused by anthropogenic activity, the nature of the Kola North is easily destroyed in the process of its developing [22]. The biological method for soil post-cleaning from oil contamination is used after mechanical, physical and chemical recultivation of polluted soils. The method consists in introducing into the soil oil-oxidizing microorganisms which were obtained either out of the contaminated soils or genetically modified before.

The biological method also involves native oil oxidizing microbiota stimulation with agrotechnical methods (soil vaccination, cultivation, watering) [8, 23–26]. Environment cleaning efficiency depends on factors including the appropriate choice of a microbial decomposer. To respond to regional oil contamination, it is preferable to use the microorganisms – decomposers adapted to specific conditions [27]. The focus is on creation of microbial communities which oxidize oil products more efficiently as compared to other individual species [28].

Our conducted research is ahead of time, as there are no large scale oil products spills on the Kola Peninsula terrestrial ecosystems, fortunately. The Barents Sea shelf development, oil products transportation may cause contamination. And this is proved by the national and world practice in the utilized oil and gas regions.

The goal of this research is search of active strains of hydrocarbon oxidizing fungi isolated from the Kola Peninsula soils and investigation of hydrocarbon destruction in soil by microbial associations in the field model experiment.

## 2 Materials and Methods

Destruction activity of eighty-one fungi strains isolated from the oil contaminated soils has been studied. To isolate the fungi, we carried out the field model experiment on the territory of the Branch of the All-Russian Crop Research Institute, The Polar Experimental Station, which is situated 1.5 km from the town Apatity, Murmansk region (67° 34'N, 33°22'E). The soil was represented by arable Al-Fe humus podzol. Plots of 1 m<sup>2</sup> were artificially contaminated with light and heavy oil products in various concentrations, in different research years (diesel fuel (DF); DF+gasoline 76 octane+masut;



masut; stable gas condensate; DF+masut) [17, 29]. The mountain Kaskama soils (69° 16'N, 29°28'E, 320 m below sea level) contaminated with oil products due to the military unit activity were also used for fungi isolation.

The soil samples for mycological analysis were picked up from the upper layer 0–10 cm in three replicates. In the whole, 287 samples were analyzed. Fungi identification was carried out on the basis of culture-morphological characteristics using identification keys [30–34]. The species names were specified in accordance with the replenished species lists in the data base Species fungorum ([www.speciesfungorum.org](http://www.speciesfungorum.org)).

The oil oxidizing capacity of the fungi isolated from the contaminated soils was studied in the laboratory experiment. The fungi cultivation was achieved in Erlenmair's flasks with 50 ml of Chapek's fluid medium in the following composition (g/l):  $\text{NaNO}_3$ –3.0;  $\text{KH}_2\text{PO}_4$ –1.0;  $\text{MgSO}_4$ –0.5;  $\text{KCl}$ –0.5;  $\text{FeSO}_4$ –0.01. Fifty ml of medium were inoculated by five ml of fungi suspension with  $10^5$ – $10^6$  CFU per 1 ml density. In the capacity of carbon source, oil was applied with 1% concentration by volume in the medium. The experiment replication was triple. Sterile medium with oil and without fungi served as a control. The incubation took place in the thermostat at 27 °C, during 14 days. The remaining content of oil products in the medium was measured with infrared spectrometry method using analyzer AN-2. Fungi biomass was defined as well, being dried out at +105 °C to the point of complete dry matter. The most active strains were determined by the ratio of the oil products mass loss to the fungi biomass increase. After this the oil destruction over time (in 1, 3, 7 and 10 days) by the most active fungi strains, taking into account the previous experiment results was studied.

Then the destruction activity of fungal and bacterial associations in relation to oil products in the time period in 3, 7 and 10 days was studied. The most active fungi strains (*Penicillium canescens* st.1, *P. commune*, *P. simplicissimum* st.1) were chosen for the experiment, as well as the active hydrocarbon oxidizing bacteria which had been isolated from the Kola Peninsula soils before (*Pseudomonas fluorescens*, *P. putida*, *P. baetica*, *Microbacterium paraoxydans*) [35]. Bacterial biomass was grown in meat-peptone broth in the laboratory fermenter Sartorius Biostat A-plus. The fungal biomass was grown in Erlenmeyer flasks with the liquid medium of Chapek's. The density of the bacterial suspension is  $10^8$ – $10^9$  cells per ml, the fungal suspension is  $10^5$ – $10^6$  CFU in 1 ml. Experiment variants: control (C), bacterial association (B); fungal association (F); bacteria and fungi association (B+F).

Finally, the active microorganisms associations according to the results of the previous experiment were tested in the field experiment. Experimental plots per 1 m<sup>2</sup> were formed based on arable Al-Fe humus podzol of the Polar Experimental Station. Diesel fuel in the amount of 10 l/m<sup>2</sup> was inserted as contaminator. Variants of the experiment: control – soil without OP; OP; OP+bacteria (OP+B); OP+fungi (OP+F); OP+bacteria and fungi (OP+B+F). At 1 and 30 days biological inoculums were injected into the soil in an amount of 1.2 l/m<sup>2</sup> (for 3 plots) and a complex mineral fertilizer of azofoska (NPK) in an amount of 60 g/m<sup>2</sup>. The top layer of the soil in all variants was loosened to a depth of 5 cm.

### 3 Results and Discussions

#### 3.1 The Search of Active Oil Products Destructors Among Fungi Isolated from the Oil Contaminated Soil

The ability to appropriate the oil hydrocarbons has never been considered as peculiarity of certain filamentous fungi genera and species. It is a characteristic feature for them, as well as assimilation of the other carbon sources. This is one of the most important physiological functions concerning not only filamentous fungi, but other microorganisms as well [8].

Most of the fungi species used in the laboratory experiment referred to *Penicillium* genus – 31. The genus *Trichoderma* was represented by 4 species, *Fusarium* and *Phoma* were represented by 3 species. The genus fungi *Acremonium*, *Alternaria*, *Aspergillus*, *Aureobasidium*, *Botrytis*, *Cephalosporium*, *Cephalotrichum*, *Chaetomium*, *Cladosporium*, *Clonostachys*, *Fusicolla*, *Gibberella*, *Gibellulopsis*, *Gongronella*, *Humicola*, *Lecanicillium*, *Mucor*, *Pseudogymnoascus*, *Rhizopus*, *Rhodotorula*, *Scopulariopsis*, *Stachybotrys*, *Streptothrix*, *Talaromyces*, *Torula*, *Ulocladium*, *Umbelopsis*, *Wallrothiella* were presented by 1–2 species.

The oil toxicity is known to be defined mostly by the existence in it volatile aromatic hydrocarbons (toluene, benzol, xylene), naphthalene and some other compounds [36]. These compounds comparatively easy and fast disappear and disintegrate. The laboratory research revealed that most of the oil compounds in the solution, which comprise light fractions (27%), decreased due to evaporation. According to data provided by McGill [37], from 20 to 40% of oil hydrocarbon light fractions remove through evaporation from the oil.

The received experimental data testify to the fact that hydrocarbons oil destruction processes in all the variants during the experiment demonstrated different intensity (Table 1). The destruction activity scale of fungi respect to oil hydrocarbons during 14 days was elaborated according to the laboratory experiment report. All the cultures under investigation were divided into 3 groups:

- the species with high activity, decreasing oil content in the medium to 80–98%;
- the species with mean activity, decreasing oil content in the medium to 50–79%;
- the species with low activity, decreasing oil content in the medium to 49% and less.

The species group with low destruction activity which is represented by 43 species, is the most multifarious in species composition. These fungi have poor growth ability on the hydrocarbons and they are without interest for further study. The species group with mean activity is represented by twenty fungi species. Eighteen fungi strains belong to the active destruction group (see Table 1). The genus *Penicillium* prevailed by species diversity. Its representatives are well balance to other contaminations as well [38, 39].

The oil hydrocarbons decomposition process was the most intensive among five fungi species: *Penicillium canescens* st.1, *P. simplicissimum* st.1, *P. commune*, *P. ochrochloron*, *P. restrictum*. We tested the active cultures ability to oil hydrocarbon destruction over time.

**Table 1.** Hydrocarbon oxidizing activity of fungi species during 14 days (the initial concentration of OP is 1% by volume in the medium).

Species of fungi	Oil destruction, % of the initial amount	Destruction activity, g oil/g fungi	Dry biomass, g
<i>I group – high activity</i>			
<i>Penicillium commune</i> Thom	98	0.414	0.596
<i>P. canescens</i> (st.1) Sopp	98	0.372	0.867
<i>P. simplicissimum</i> (st.1) (Oudem.) Thom	96	0.353	0.687
<i>P. canescens</i> (st.2) Sopp	95	0.335	0.758
<i>P. restrictum</i> J.C. Gilman & E.V. Abbott	95	0.330	0.738
<i>P. ochrochloron</i> Biourge	94	0.337	0.615
<i>P. velutinum</i> J.F.H. Beyma	93	0.253	0.335
<i>Ulocladium consortiale</i> (Thum.) E.G. Simmons	92	0.343	0.518
<i>P. implicatum</i> Biourge	92	0.327	0.530
<i>P. decumbens</i> Thom	92	0.266	0.810
<i>P. canescens</i> (st.3) Sopp	88	0.229	0.651
<i>P. simplicissimum</i> (st.2) (Oudem.) Thom	87	0.311	0.519
<i>P. miczynskii</i> (st.1) K.M. Zaleski	85	0.294	0.573
<i>P. nigricans</i> K.M. Zaleski	84	0.245	0.847
<i>P. jensenii</i> (st.1) K.M. Zaleski	84	0.312	0.667
<i>Fusarium solani</i> (Mart.) Sacc.	84	0.310	0.251
<i>Alternaria alternata</i> (Fr.) Keissl.	83	0.304	0.515
<i>F. oxysporum</i> (st.1) Schldtl.	80	0.311	0.268
<i>II group – medium activity</i>			
<i>P. aurantiogriseum</i> (st.1) Dierckx	79	0.269	0.620
<i>Rhizopus stolonifer</i> (Ehrenb.) Vuill.	76	0.285	0.485
<i>P. adametzii</i> K.M. Zaleski	75	0.267	0.716
<i>P. glabrum</i> (Wehmer) Westling	74	0.248	0.406
<i>P. spinulosum</i> (st.2) Thom	74	0.281	0.463
<i>P. miczynskii</i> (st.2) K.M. Zaleski	73	0.265	0.525
<i>Lecanicillium lecanii</i> (Zimm.) Zare and W. Gams	72	0.298	0.352
<i>Stachybotrys echinata</i> (Rivolta) G. Sm.	70	0.239	0.406
<i>P. canescens</i> (st.4) Sopp.	70	0.295	0.466
<i>Trichoderma viride</i> Pers.	67	0.233	0.283
<i>P. aurantiogriseum</i> (st.2) Dierckx	67	0.247	0.418
<i>P. nalgiovense</i> Laxa	66	0.266	0.628

(continued)

**Table 1.** (continued)

Species of fungi	Oil destruction, % of the initial amount	Destruction activity, g oil/g fungi	Dry biomass, g
<i>Umbelopsis isabellina</i> (Oudem.) W. Gams	63	0.294	0.415
<i>Cephalotrichum stemonitis</i> (Pers.) Nees	62	0.257	0.563
<i>Talaromyces stipitatus</i> C.R. Benj.	62	0.270	0.361
<i>Chaetomium bostrychodes</i> Zopf	60	0.294	0.365
<i>Acremonium egyptiacum</i> (J.F.H. Beyma) W. Gams	57	0.215	0.391
<i>Fusicolla merismoides</i> (Corda) Gräfenhan, Seifert and Schroers	57	0.218	0.224
<i>Wallrothiella subiculosa</i> Höhn.	55	0.241	0.300
<i>P. multicolor</i> Grig.-Man. and Porad.	50	0.231	0.407

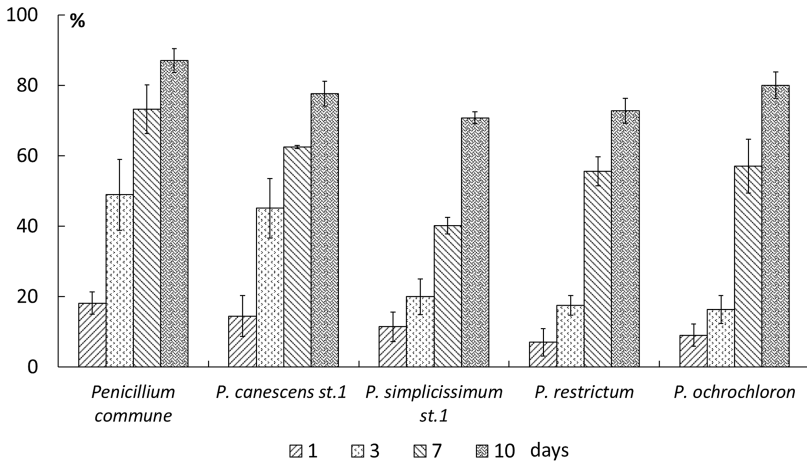
### 3.2 Fungi Oil Destruction Activity over Time

The natural recovery process of the oil contaminated soils is time-consuming, therefore it is essential that modern technologies for the rehabilitation of the disturbed soils should be established and implemented. The oil components decomposition rate is thought to be the key factor of such technologies. The intensity of microorganisms to absorb oil hydrocarbons within the shortest possible period of time is the most significant factor. The analyses to determine the content of oil products residues, revealing destruction degree dynamics under fungi impact were performed in a given time. The studied in the experiment fungi had different activity of oil components intake (Fig. 1).

As late as the first day, the fungi decomposed from 6 to 18% of oil products; on the third day the amount was from 16 to 49%; on the seventh day the number was from 40 to 73%; on the tenth day it was from 71 to 87% out of the original amount.

The fungus *Penicillium commune* revealed the greatest destructive activity throughout the experiment; whereas in contrast, the fungus *Penicillium canescens* st.1 exhibited the least activity. The oil products rate destruction among the studied fungi species varied during the experiment (Table 2).

For example, the most active destructor *P. commune* had a high rate already the third experiment day, with slightly increase up to the seventh and the tenth days. All the rest species had 1.5–3 times less destruction speed than *P. commune* during the first experiment days. Up to the seventh day, the destruction rate considerably grew up among three more species: *Penicillium canescens* st.1, *P. restrictum*, *P. ochrochloron*. By the tenth day, all the investigated species had a high oil products rate destruction: 0.123–0.152 grams per day.



**Fig. 1.** Degree of oil destruction by fungi over time (% of the initial).

**Table 2.** The rate of oil loss from the liquid medium (g/d) over time (the initial concentration of OP is 1% by volume).

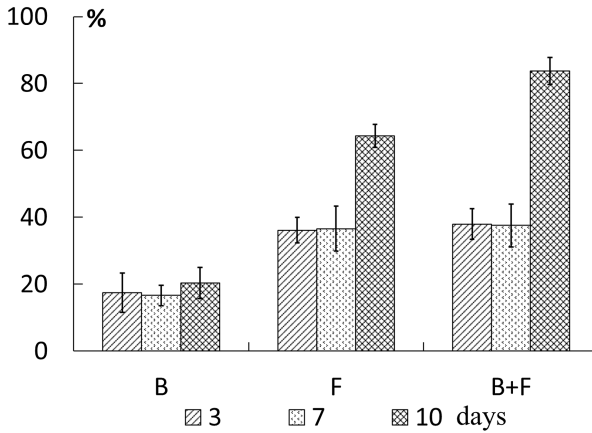
Fungi species	Day			
	1	3	7	10
<i>Penicillium commune</i>	0.049	0.138	0.163	0.157
<i>P. canescens st.1</i>	0.040	0.103	0.128	0.138
<i>P. simplicissimum st.1</i>	0.031	0.046	0.058	0.126
<i>P. restrictum</i>	0.013	0.039	0.107	0.129
<i>P. ochrochloron</i>	0.024	0.062	0.127	0.145

### 3.3 Microorganisms Associations Oil Destruction Activity over Time

The necessity of applying associations, including two or more microorganisms – destructors species, is caused by the oil complex chemical composition. In the experiment with microorganisms associations, the decrease of oil products in the medium from 11 to 38% took place by the third day; it was from 17 to 83% by the seventh day; it was up to 94% by the tenth day (Fig. 2).

In laboratory experiment the most effective associations proved to be the fungi and bacteria-fungi associations. In these variants the active oil products decomposition (36% and 38% from the initial, correspondingly) took place during the first three days; and in the period from seven to ten days (64% and 84% from the initial, correspondingly). It should be noted, that bacteria association appeared to be more passive relative to oil hydrocarbon destruction. Its destruction amounted to 20% in 10 days.

The oil products decomposition rate varied from 0.040 to 0.071 grams per day in different experiment variants during three days (Table 3). The largest rate was registered with the association B+F for the given period. It remained the same up to seven days. It is likely to be connected with the competitive interaction of two microorganisms groups



**Fig. 2.** Oil hydrocarbon destruction (% of the initial) by microorganisms associations: B – bacterial association, F – fungal association; B+F – bacteria-fungi association.

which are included into the association. The oil products decomposition rate with variant B+F was the highest in comparison with others by the tenth day. The rate of the associations B and F gradually increased with the experiment time, approaching the upper bound up to the tenth day.

**Table 3.** The rate of oil hydrocarbons content decrease (g/d) in liquid medium over time (the initial concentration of OP is 1% by volume in the medium).

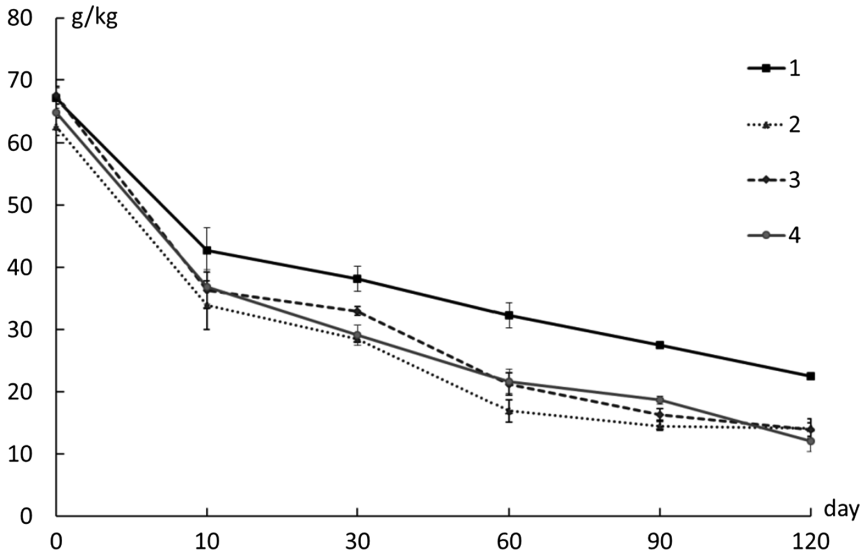
Variant	Day		
	3	7	10
OP+B (bacteria)	0.049	0.097	0.099
OP+F (fungi)	0.040	0.068	0.090
OP+B+F (bacteria and fungi)	0.071	0.069	0.114

### 3.4 Microorganisms Associations Oil Destruction Activity in Model Field Experiment

In the field experiment, three microbial associations showed approximately the same behavior (Fig. 3).

In case of association based on bacteria and fungi, after 30 days oil product content reduced to 29 g/kg (oil product removal was 57% vs. initial level), after 120 days – 12 g/kg (oil product removal was 82% vs. initial level). In cases of bacteria-fungi association, after 30 days oil product content reduced by 55% and 51% respectively, after 120 days – by 77% and 79% vs. initial level, respectively (Table 4).

During initial 30 days of experiment, oil product content reduces most intensively due to evaporation [5]. Introduction of microbial associations accelerates the oil product decomposition process by 10–20%.



**Fig. 3.** Dynamics of oil products content in the soil of model experiment: 1 – OP; 2 – OP+bacteria; 3 – OP+fungi; 4 – OP+bacteria and fungi.

**Table 4.** The loss of the oil products content (% of the initial) in a certain time period (the initial concentration of OP is 64.97 g oil/kg soil).

Variant	Day				
	10	30	60	90	120
OP	36	43	52	59	67
OP+B	46	55	73	77	77
OP+F	46	51	69	76	79
OP+B+F	46	57	68	73	82

The rate of oil product reduction in soil changes with time of experiment (Table 5). During initial 10 days the rate was maximum due to the most intensive evaporation. Thereafter, the rate of oil product decomposition decreased. In case of OP+B+F, the most significant decomposition rate was observed during 10–30 days of the experiment, in cases of OP+B and OP+F – during 30–60 days.

After assessment of performance of microbial associations in studied soil during different periods, it can be stated that their best effect was observed during 30–60 days of the experiment, however, the case of bacteria-fungi community maintained its efficiency even during 120 days.

Thus, use of microbial associations based on native microbes in Al-Fe humus podzol of Kola Peninsula accelerates the oil product decomposition in soil and can be advised for environment post-cleaning from oil hydrocarbons. In the field experiment conditions, the microbial associations based on bacteria and fungi demonstrated the best effect: during 120 days oil products content reduced by 82%, oil products

**Table 5.** The average rate of oil products (OP) loss from the soil (g oil/kg soil) for 1 day in a certain time period.

Variant	Time period				
	1–10	10–30	30–60	60–90	90–120
OP	2.43	0.23	0.20	0.02	0.02
OP+B	2.87	0.27	0.39	0.08	0.01
OP+F	3.12	0.16	0.39	0.16	0.08
OP+B+F	2.81	0.39	0.25	0.10	0.20

decomposition rate after 30 and 120 days was maximum as compared to other experiment scenarios. It is noteworthy that Kola Peninsula soil is acid soil and, therefore, the efficiency of using the associations based on fungi will likely be higher than that of bacterial association.

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# Biodiversity of Algae and Cyanobacteria in Soils of Moscow

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**Abstract.** Biodiversity and structure of algal–cyanobacterial communities were studied in soils of background plots in the undisturbed morainic landscape of Moscow region and in urban soils of different land-use zones in two administrative districts of Moscow. Their specific features were identified, and their relationships with the major directions of transformation of the properties of urban soils were shown.

**Keywords:** Algae · Cyanobacteria · Biodiversity · Soils · Pollution  
Heavy Metals (HMs) · Deicing reagents

## 1 Introduction

Microscopic algae and cyanobacteria are soil indispensable inhabitants which form algal-cyanobacterial communities representing an obligatory part of any phytocenosis. Soil algae and cyanobacteria are very sensitive to soil properties transformation and react on it by biodiversity, composition and structure transformations [1]. The strength of these transformations indicates the degree of integral anthropogenic impact on soils, this opportunity is applied in urban landscapes bioindicational researches [2–5].

The aim of this research was to determine the major factors that control algal-cyanobacterial communities in urban soils. The city of Moscow was chosen and urban soils were compared to soils in background landscapes.

It includes the following tasks:

- (1) to obtain data on the physicochemical properties of undisturbed soils in background morainic landscapes of Moscow region and to characterize the main directions of their anthropogenic transformation in the urban environment;
- (2) to characterize algal–cyanobacterial communities of background and urban soils; and
- (3) to identify factors affecting algal–cyanobacterial communities biodiversity, composition, and structure.

## 2 Study Area and Methods

### 2.1 Study Area

The study area is found in the taiga zone on the Smolensk–Moscow Upland in the central part of the East European Plain [4]. It is characterized by the moderately continental climate, the mean annual temperature is +5.4 °C and the mean annual precipitation is 700 mm. The summer is moderately warm, the winter is moderately cold; the frosty period (with the mean daily temperature below –5 °C) lasts about 100 days; the average snow thickness is 40–45 cm [4, 6].

The background site was located 40 km to the west of Moscow on the morainic plain with native soddy-podzolic soils (Glossic Retisols) under spruce or mixed forests with herbs and mosses in the ground cover and with cultivated soddy-podzolic soils (Glossic Retisols (Aric)) under sown grass meadows.

In Moscow the research was carried out on the territory of two administrative districts – North-Western and Western – in different land-use zones (recreational, traffic and residential). Land-use zones differ according to the level of anthropogenic impact [7]. The recreational zone is a city park with slightly disturbed soddy-podzolic soils (Glossic Retisols) under forest phytocenoses (herbaceous pine forest, yellow archangel-herbaceous birch–linden forest, yellow archangel maple forest with pine) [4]. The traffic zone is roads and adjoining areas, the residential zone - apartment buildings. Among the studied urban soils, urbanozems (Urbic Technosols) predominate [8].

### 2.2 Methods

**Field Research.** Samples for algological examination were taken from the upper soil layer (0–5 cm) in spring, soon after the snowmelt season (April–the beginning of May) both in the background site and in different land-use zones of the city. In the recreational zone samples were taken at a distance 1–3 m from walking roads, in the traffic zone – 1–3 m from the highways. In the residential zone, samples were taken from the lawns near sidewalks, near garbage containers, and near parking lots.

**Studying Algae and Cyanobacteria.** Species biodiversity of soil algae and cyanobacteria was studied by standard methods of soil algology – in soil cultures with fouling glasses and in liquid cultures on the Bold medium [9, 10]. The cultures were grown under daylight at 20 °C for 2 months. The species composition of diatoms was determined in constant preparations on the Elyashev's medium using fouling glasses calcinated on a copper plate for 1.5 h.

The ecological characteristics of indicator species were taken from [11], and life forms (ecobiomorphs) of soil cyanobacteria and algae were described according to the monograph by Shtina and Gollerbakh [12]. The life forms of microphototrophs are the ecological groups with similar adaptations to life in soil. The main characteristics of them are described below.

C, H, X-life forms are shade-tolerant and hygrophilous, but differ in their adaptations to the soil desiccation. C-form is represented by algae and cyanobacteria that react to the decrease in soil moisture content by the formation of abundant mucus, having a

high water retention capacity. X-form is represented by unicellular algae that avoid low soil moisture by living inside soil and capable of both photosynthesis and the use of organic carbon. H-form is filamentous algae, scattered among soil particles or forming deposits on the soil surface under the protection of higher plants. M- and P-forms include filamentous cyanobacteria-xerophytes, which possess a cell protoplast resistant to low soil moisture, the M-form also has hydrophilic coatings. B-form is represented by diatoms: cold-resistant, light-loving, many of them are halophilic. Ch-form is unicellular and colonial green and partly ochrophyte algae with exceptionally high resistance to a variety of extreme environmental conditions due to the features of the protoplast and the ability to heterotrophic nutrition.

The composition of the life forms of microphototrophs allows us to identify such directions of anthropogenic soil transformation as xerophytization and surface insolation.

The following biological parameters were analyzed: the algae and cyanobacteria species composition and life forms; ecological groups of diatoms-indicators of alkaline-acidic conditions and salts content ratio; dominant species number, species in one sample average number.

**Chemical Analysis of Soils.** The soils on the same sites were investigated at the Ecological-Geochemical Center of the Faculty of Geography, Moscow State University. In the soil samples, the following physicochemical parameters were measured [4]:  $\text{pH}_{\text{water}}$  and TDS in the water extract (soil:solution ratio 1:5) by potentiometry on a HANNA 2/3 instrument (the Netherlands); the anionic and cationic composition of water extract on a Staier ion chromatograph (Russia). The content of HMs mobile forms extracted with 1 N ammonium acetate buffer solution with EDTA (pH 4.8; soil:solution ratio 1:10) was measured by atomic absorption spectroscopy on a novAA-400 spectrometer (Analytik-Jena AG, Germany) with flame ionization and an AA-240Z atomic absorption spectrometer (Varian, USA) with electrothermal atomization. Detailed analysis of the soil properties was published earlier [4, 13].

**Data Analysis.** To assess the intensity of accumulation of mobile forms of HMs in the urban soils, the concentration coefficient  $K_c$  [14] was calculated according to Eq. (1):

$$K_c = C/C_b, \quad (1)$$

where  $C$  is the average concentration of the mobile forms of the element in the studied soils, and  $C_b$  is the average concentration of the mobile forms of the element in the soddy-podzolic soils of the background site under natural forest vegetation.

To evaluate the ecological risk of soil pollution with mobile forms of HMs, the environmental hazard coefficient  $K_o$  was counted up according to Eq. (2):

$$K_o = C/MPC, \quad (2)$$

where  $C$  is the average concentration of the mobile forms of the element in the studied soils, and  $MPC$  is the maximum permissible concentration for the mobile forms of the element in soils. In Russia MPCs of HMs mobile forms in the soil are (mg/kg): Cu, 3.0;

Zn, 23.0; Pb, 6.0 [15]. For the mobile forms of cadmium in soils MPC has not been established.

Quantitative data were processed using software Statistics 8.

### 3 Results and Discussion

#### 3.1 Physicochemical Properties of Soils

**Soils of the Background Site.** Background soddy-podzolic soils under forest communities have a slightly acid reaction, and those under sown meadow have a neutral reaction due to the liming. They are not saline;  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  predominate among ions in the water extracts (Table 1). Liming and fertilizer application does not cause the contamination of cultivated soddy-podzolic soils. Most of the determined heavy metals are in lower concentrations as compared with their average abundances in the lithosphere [13]. The Cu and Zn mobile forms content in background soils is significantly below the MPC, at the same time the Pb level exceeds MPC twice. This excess can be apparently explained by the aerial lead addition from roads and by its mobile forms formation in acidic forest soddy-podzolic soils.

**Table 1.** Physicochemical soils properties in the background site and in different Moscow land-use zones (from [4, 13])<sup>a</sup>

Parameters	Background site		Recreational zone (park, n = 3)	Residential zone (n = 10)	Traffic zone (n = 15)
	Forest (n = 5)	Meadow (n = 3)			
pH <sub>H2O</sub>	<u>6.2</u> 6.0–6.5	<u>6.7</u> 6.5–6.9	<u>6.4</u> 6.4–6.5	<u>6.9</u> 6.6–7.5	<u>7.0</u> 6.3–7.7
Salts, %	<u>0.05</u> 0.04–0.07	<u>0.06</u> 0.05–0.08	<u>0.05</u> 0.04–0.07	<u>0.10</u> 0.04–0.20	<u>0.11</u> 0.03–0.23
Ionic composition of water extracts	$\text{HCO}_3\text{-Ca}$	$\text{NO}_3\text{-HCO}_3\text{-Ca}$	$\text{HCO}_3\text{-Na-Ca, Cl-HCO}_3\text{-Ca-Na}$	$\text{HCO}_3\text{-Na-Ca, Cl-HCO}_3\text{-Ca-Na, NO}_3\text{-HCO}_3\text{-Na-Ca}$	$\text{Cl-HCO}_3\text{-Ca-Na, Cl-NO}_3\text{-HCO}_3\text{-Na-Ca, Cl-HCO}_3\text{-NO}_3\text{-Ca-Na}$
<i>K<sub>c</sub></i> for mobile forms:					
Cu	1.0	0.8	5.4	8.8	4.6
Zn	1.0	0.3	1.7	3.0	4.7
Cd	1.0	1.1	1.9	5.1	1.7
Pb	1.0	0.4	0.9	0.7	1.2

<sup>a</sup>Numerator—average; denominator—maximum and minimum values.

**Urban Soils.** Anthropogenic impact on soils includes mechanical changes (mechanical impact) and chemicals additional supply (geochemical impact). In addition, in the city the spot illumination and the soil moisture content may influence the development of soil microorganisms. The background cultivated soddy-podzolic soils and the urban soils differ by the type and the intensity of anthropogenic impact. According to these criteria, different city land-use zones are identified (Table 2). Geochemical impact on urban soils leads to their alkalinization, additional input of sodium and calcium chloride and nitrate with deicing reagents (DRs), and to contamination with HMs (where Zn, Cu, Cd, Pb predominate) – Table 1.

**Table 2.** Main types of anthropogenic impact on cultivated background soils and on different Moscow land-use zones soils

Impact type	Background site, meadow (n = 3)	Moscow land-use zones		
		Recreational (park, n = 3)	Residential (n = 10)	Traffic (n = 15)
Mechanical	Plowing	Compaction as a result of soil trampling		
			Fertile ground periodic addition	
Geochemical	Lime and fertilizers addition	Pollutants, marble debris, deicing reagents addition		
Change in surface insolation	Insolation increasing as a result of plowing and grass mowing in the fall	Insolation increasing as a result of lawns mowing and projective cover decreasing due to soil trampling		
			Buildings shading	

Urban soils are characterized by high spatial heterogeneity of all physical and chemical parameters. Specifically, in the recreational zone (in the park), the soils have a slightly acid reaction, in the residential and traffic zones, neutral soils predominate, and in some parts of the lawns near the roads soils with slightly alkaline reaction are found.

According to the salt content in the upper horizon (estimated on the basis of the insoluble residue), urban soils are classified as non-saline (<0.1% salts), slightly saline (0.1–0.2% salts) and in some cases as moderately saline (0.2–0.4%) [16].

In urban soils, the levels of HMs accumulation are also different (Table 1). At the same time, in all land-use zones the contents of all studied HMs mobile forms reach levels, dangerous for urban ecosystems. Ranked according to the environmental hazard coefficient *K<sub>o</sub>*, the elements are presented in the following order: Cu<sub>2,2</sub>Pb<sub>1,8</sub> in the recreation zone, Cu<sub>3,5</sub>Pb<sub>1,5</sub> in the residential zone and Pb<sub>2,5</sub>Zn<sub>2,1</sub>Cu<sub>1,8</sub> in the traffic zone.

The spatial heterogeneity of the studied urban soils parameters is partly caused by the upper soil horizons replacement with unpolluted fertile ground. In the same administrative district this replacement is occurring with different frequency.

### 3.2 Algal-Cyanobacterial Communities

**Algal-Cyanobacterial Communities of the Background Site.** In the background soils the vegetation type determines the algae and cyanobacteria composition. In the background forest soddy-podzolic soils the algal-cyanobacterial communities typical for taiga zone forest soils are developing. Green and streptophyte algae definitely predominate; the ochrophyte algae are quite diverse, while the diatom algae and cyanobacteria are represented by small number of species (Table 3). Organic matter and heterotrophic microorganisms abundance in the forest litter horizon suppress diatom algae and cyanobacteria growth. As a result, there is a low number of species in one sample. The algae species, shade-tolerant but non-resistant to soil desiccation (the C-, X- and H- life forms), predominate (Table 4).

**Table 3.** The algal-cyanobacterial communities composition in the background site soils and in different Moscow land-use zones soils<sup>a</sup>

Parameters	Background site		Recreational zone (n = 3)	Residential zone (n = 10)	Traffic zone (n = 15)
	Forest (n = 5)	Meadow (n = 3)			
Cyanobacteria	$\frac{3}{8.1}$	$\frac{16}{32.7}$	$\frac{1}{3.3}$	$\frac{9}{12.3}$	$\frac{22}{21.8}$
Algae:					
Chlorophyta + Streptophyta	$\frac{22}{59.5}$	$\frac{20}{40.8}$	$\frac{12}{40.0}$	$\frac{28}{38.4}$	$\frac{40}{39.6}$
Ochrophyta	$\frac{10}{27.0}$	$\frac{5}{10.2}$	$\frac{9}{30.0}$	$\frac{13}{17.8}$	$\frac{12}{11.9}$
Bacillariophyta	$\frac{2}{5.4}$	$\frac{8}{16.3}$	$\frac{8}{26.7}$	$\frac{23}{31.5}$	$\frac{27}{26.7}$
Total number species	$\frac{37}{100.0}$	$\frac{49}{100.0}$	$\frac{30}{100.0}$	$\frac{73}{100.0}$	$\frac{101}{100.0}$
Species number in one sample	7	16	10	7	7
Dominant species number	11	10	8	4	2–9

<sup>a</sup>Numerator—number of species; denominator—their percentage of the algae and cyanobacteria species total number.

In cultivated soddy-podzolic soils, annually plowed and periodically limed, under sown meadows the typical for arable soils algal-cyanobacterial communities are formed. The leading groups are cyanobacteria, green and streptophyte algae, besides, the role of diatom algae is considerable (Table 3). The number of species in one sample increases in comparison with the one in forest soddy-podzolic soils. The most diverse species of cyanobacteria are the ones that prefer no grass cover sites (the P- life form). As for the diatoms, the alkaliphilic species number reaches 40% due to periodic lime addition to soil; halophilic species are absent.



The algal-cyanobacterial communities of background site uncontaminated soils are characterized by the multispecies complex of dominant species (Table 3).

In the soils of the traffic zone the increase of the amphibial and hydrophilic algal species diversity is observed. This fact is explained by their additions into soils during daily roadway watering in the summer-autumn period.

**Table 4.** Algae and cyanobacteria life forms in the background site soils and in different Moscow land-use zones soils<sup>a</sup>

Habitats	Life forms
Background site, forest	H <sub>27.7</sub> X <sub>22.2</sub> Ch <sub>22.2</sub> C <sub>16.7</sub> P <sub>2.8</sub> B <sub>2.8</sub> Amph. + Hydr. <sub>5.6</sub>
Background site, meadow	P <sub>21.6</sub> Ch <sub>17.6</sub> H <sub>15.7</sub> X <sub>13.7</sub> C <sub>13.7</sub> B <sub>11.8</sub> M <sub>2.0</sub> Amph. + Hydr. <sub>3.9</sub>
Moscow recreational zone, park	Ch <sub>29.2</sub> X <sub>25.0</sub> H <sub>20.8</sub> B <sub>20.8</sub> M <sub>4.2</sub>
Moscow residential zone, lawn	Ch <sub>20.3</sub> H <sub>20.3</sub> B <sub>18.8</sub> X <sub>17.2</sub> P <sub>10.9</sub> C <sub>7.8</sub> M <sub>1.6</sub> Amph. + Hydr. <sub>3.1</sub>
Moscow traffic zone, lawn	Ch <sub>20.7</sub> H <sub>14.9</sub> X <sub>12.6</sub> B <sub>12.6</sub> C <sub>11.6</sub> P <sub>11.5</sub> M <sub>5.8</sub> Amph. + Hydr. <sub>10.3</sub>

<sup>a</sup>Numbers indicate % of the life forms of the algae and cyanobacteria species total number.

**Algal-Cyanobacterial Communities of Urban Soils.** *In the recreational zone* (in the park) the algal-cyanobacterial communities of “forest” type are formed. They possess a multicomponent complex of dominant species similar to the background forest soils (Table 3). This fact means the low degree of soddy-podzolic soils anthropogenic transformation. However, due to park territory maintenance, the soil surface sun exposure is increasing, the soils alkalization and seasonal salinization because of deicing reagents application is observed. As a consequence, considerable amount of shade-tolerant and salt-nonresistant green and streptophyte algae species (the C- and H- life forms) disappears. At the same time, the photophilous diatom algae (the B- life form) appear in algal-cyanobacterial communities. Among the diatom algae the species indifferent to high salt concentration and preferring neutral pH conditions prevail. Alkaliphilic species number reaches 25% of the total diatoms number, halophilic species constitute 20% of the diatoms number. There are also unicellular green and eustigmatophyte algae that belong to the particularly resistant in extreme conditions Ch- life form. As a result, the algal-cyanobacterial communities biodiversity is increasing (the number of species in one sample - see in the Table 3).

In the urbanozems of *residential and traffic zones* algal-cyanobacterial communities are of “meadow” type, the leading groups in them being cyanobacteria, green and streptophyte algae. Soil pollution, seasonal salinization, changes in exposure to sun and trampling are stronger than in the recreational zone and lead to the decrease of photosynthetic microorganisms biodiversity (average number of species per sample). In comparison with the algal-cyanobacterial communities of the cultivated soddy-podzolic soils of the background site with meadow grass cover, the ratios between cyanobacteria and algae in algal-cyanobacterial communities is changing (Table 3). The cyanobacteria share is decreasing, while the algae component share is increasing due to the diatom species diversity growth (the B- life form). Similar to the recreational zone, the halophilic and indifferent to high salt concentrations diatom species, which prefer neutral or alkaline conditions, prevail. Many of them are resistant to trampling. The

diatoms halophilic and alkaliphilic species number is slightly higher in the soils of the traffic zone (24% and 44% respectively, compared to 20% and 36% in the residential zone) that reflects slightly high soil alkalization and salinity degree. This fact is supported by soil chemical analysis.

The cyanobacteria species, typical for arable soils, disappear and are replaced by filamentous cyanobacteria which are extremely resistant to soil desiccation and high temperatures (the M- life form). This replacement is more frequently observed in the traffic zone soils and indicates soils strong drying. As for green and eustigmatophyte algae species, the most diverse species belong to the Ch- life form (including the halophilic ones). At the same time, many of shade-tolerant and moisture-demanding species (the C- and some H- life forms) disappear.

Investigations in the Western Administrative District (WAD) have demonstrated that, even with the same land use, the algal-cyanobacterial communities structure and basic parameters vary in space, reflecting the spatial heterogeneity of the properties of urban soils. Specifically, in the WAD transport zone, the structural changes in the microphototrophs communities are the most expressed in the soils adjacent to the Moscow ring road. The diatom algae share in these soils reaches 21.1% of the total species number, and the cyanobacteria share decreases to 15.8%. Halophilic diatom species (33.3% of their number) and the Ch-form representatives (28.5%) possess the most considerable diversity. Moreover, the minimal number of dominant species is revealed.

At the same time, the diatoms (16.0%) and cyanobacteria (28.0%) ratio in the soils adjacent to the major highways is closest to the algal-cyanobacterial communities of the uncontaminated cultivated soddy-podzolic soils; the halophilic diatom species (16.7%) and Ch-form representatives (19.1%) share is also close to the background site cultivated soils; the dominant species number is significantly high. The main reason of all these transformations is the upper soil horizon replacement with an unpolluted ground that occurs annually near the highways in WAD.

In contrast, near the Moscow Ring Road and in the WAD residential zone this replacement is more rarely observed (less often one time in five years). The algal-cyanobacterial communities composition in these soils is similar and, as a result, it is possible to make a conclusion about a similar chronic anthropogenic impact on the soils.

The influence of phytocenosis type, salts and HMs mobile forms in soils on algae and cyanobacteria species diversity was confirmed by regression analysis [17, in press].

## 4 Conclusion

Xerophytization, compaction, alkalization, seasonal salinization and pollution are the main trends in anthropogenic transformations in the observed urban soils. In accordance with these transformations, the algal-cyanobacterial communities composition is also modified. Resistant species replace sensitive to anthropogenic impact, i.e. – photophilic, soil compaction and desiccation-resistant, alkaliphilic, halophilic and tolerant to high HMs level. This replacement is occurring in all land-use zones and indicates that all observed urban soils belong to the resistance zone, which is characterized by a high anthropogenic impact [18]. The observed algal-cyanobacterial

communities composition indicates that the main factors affecting the algal-cyanobacterial communities parameters are vegetation type, soil pH, water-soluble salts and HMs mobile forms contents, soil surface sun exposure and soil moisture. Two trends are observed in the transformation of microphototrophs' diversity. The first one is recorded in the recreational zone forest soils (in the park) that are under a relatively low mechanical and geochemical impact. As a result, the algae and cyanobacteria diversity increases in comparison with background forest site soils. The second trend is observed in the residential and traffic land-use zones soils covered with a lawn: the algae and cyanobacteria biodiversity decreases and the species number in one sample decreases more than two times in comparison with background soils biodiversity. This fact means a considerable increase of the soils anthropogenic impact level.

Algal-cyanobacterial communities are perspective for research as their parameters provide an additional data about current urban soils transformations. The important informative parameter is the ratio of indicator species with different requirements to soil moisture, spot illumination, acid-base conditions and salt content. This ratio helps to identify different technogenic processes in urban soils: waterlogging-desiccation, acidification-alkalization and salinization.

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# Application of Silicon-Contained Mining Wastes in Urban Greening

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**Abstract.** The problem of urban landscaping in the Arctic region is related to unfavorable climatic conditions for human and plants and to a shortage of natural organic soils. The ecological and aesthetic functions and services provided by the urban green infrastructure are crucial in regions with a high level of urbanization located beyond the Arctic Circle. Murmansk region is situated on the north-west of Russia, where 93% population lives in cities. It has deposits of more than 700 minerals and a high level of development of mining complex. Therefore, various mining wastes have a potential to be used as a component for green infrastructures in urban and industrial environments. This study examined the effect of serpentine and phlogopite wastes' additions to natural podzolic soils on the productivity and chemical composition of 6 species of grasses. The addition of mining wastes increased biomass up to 25–95% and height of grasses up to 20–50% comparing to the control. Highest values of biomass and height are corresponded to grass on the soil with the addition of 7 mg kg<sup>-1</sup> of serpentine wastes. Serpentine wastes with 400 mg kg<sup>-1</sup> of phytoavailable silicon created plant resistance to negative environmental factors. Serpentine wastes are a potential material for application in the construction of urban soil in the Arctic region.

**Keywords:** Urban soil · Mining waste · Grass · Serpentine · Phlogopite  
Silicon · Arctic

## 1 Introduction

Urban lawns with high values of ecological and aesthetic functions and services are of great importance in regions with a high level of urbanization located beyond the Arctic Circle. Creation of quality lawns in harsh climatic conditions of the Russian Arctic zone is associated with such problems as a short growing season with low autumn and spring temperatures, frequent and heavy rainfall, strong winds, scarcity and depletion of soil resources, lack of peat as a source of bulk ground, and the need for action for increasing urban soils fertility [1, 2]. One of the main goals in the formation of soil

structures in cities is to create favorable conditions for plants' development, as well as to ensure optimal conditions for water infiltration [8]. In addition to agricultural soils, various waste and other secondary materials with suitable functions can be used as part of such structures [3, 4].

The mining industry is well developed on the mineral-rich Kola Peninsula, therefore the by-products of enterprises have a potential for land reclamation in order to improve the physical and mechanical properties and nutritional status of the soil [5]. Two types of wastes of the phlogopite enterprise, located near Kovdor city (Murmansk region, Russia), were selected for the study.

Phlogopite is magnesian mica  $\text{KMg}_3[\text{AlSi}_3\text{O}_{10}](\text{OH},\text{F})_2$ . One of the largest phlogopite deposits in the World is located on the Kola Peninsula. Phlogopite waste (PW) is formed during the processing of phlogopite and consists mainly of substandard phlogopite and waste rock. The serpentine minerals  $\text{Mg}_6[\text{Si}_4\text{O}_{10}](\text{OH})_8$  are a widespread raw material; large reserves of serpentinites are concentrated, in particular, on Russian Kola Peninsula, as part of overburden rocks of the phlogopite deposit. Serpentine waste (SW) at the place of phlogopite production occupy an area of more than 10 ha and contain hundreds of thousands of tons of serpentine and vermiculite [6].

Air purification, regulation of the environment, biomass production and remediation of pollutants are important ecological functions of urban soil constructions [3, 7]. Most of cities in the Arctic circle have been affected by the negative influence of mining waste and extractive industries, therefore sustainable functioning of soil construction is essential for the urban environment. Population of the cities at high latitudes is affected by severe climatic–geographical conditions resulting in the emergence of the “polar stress syndrome”, which have such manifestations as psycho-emotional lability and depression [8]. Therefore, ornamental function of the sustainable urban lawn contributes to the improvement of the socio-psychological environment of cities [9, 10]. Thus, both the aesthetic and ecological functions of urban lawns are extremely important in the Arctic region.

The aim of the study was to investigate the possibility of using two kinds of mining waste as a component for urban soil constructions.

## 2 Materials and Methods

The experimental site is located near the city of Apatity, Murmansk region, Russia ( $67^\circ 34'\text{N}$ ,  $33^\circ 22'\text{E}$ ). The city is located beyond the Arctic Circle, in the center of the Kola Peninsula. The territory is a part of the Arctic zone of the Russian Federation.

Chemical analyses of the soil, mining wastes and plant samples were performed in specialized accredited laboratories of the I.V. Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials of the Kola Science Centre of the Russian Academy of Sciences (Apatity, Murmansk region, Russia) and the Institute of Forest of the Karelian Research Center of the Russian Academy of Sciences (Petrozavodsk, Russia).

Elemental analysis of soil and plants after the samples were transferred to solution was performed on a quadrupole mass spectrometer with inductively coupled plasma ELAN-9000 DRC-e (PerkinElmer) and atomic absorption spectrometers “Kvant-2A”

("Cortec") and AAnalyst 400 (PerkinElmer). The total amount of elements in the soil was determined after an autoclave microwave digestion in a SW4 system with DAK 100 autoclaves (Berghof) using a concentrated acid mix (47% fluoric acid and 65% nitric acid). The concentrations of phytoavailable forms of elements in the soil and in the mining wastes were determined using a standard procedure involving an acetate-ammonium buffer solution (pH 4.65). Nitrogen was determined by the Kjeldahl method with a titrimetric termination.

The soil of the site is a cultivated illuvial-humus podzol ( $\text{pH}_{\text{H}_2\text{O}}$  6.6,  $\text{pH}_{\text{KCl}}$  5.9,  $\text{Ca} = 2.26 \text{ mEq } 100 \text{ g}^{-1}$ ,  $\text{Mg} = 0.41 \text{ mEq } 100 \text{ g}^{-1}$ ,  $\text{C} = 3.38\%$ ,  $\text{N} = 0.3\%$ ). The material for the experiment was obtained by screening out a fine fraction with a particle size of less than 20 mm for SW and 10 mm for PW. The main components of mineral substrates are (mass %):  $\text{SiO}_2$  – 30–35,  $\text{MgO}$  – 25–30,  $\text{CaO}$  – 5–10,  $\text{Fe}_2\text{O}_3$  – 2–7,  $\text{FeO}$  – 2–5,  $\text{Al}_2\text{O}_3$  – 2–6,  $\text{K}_2\text{O}$  – 0.5–4. The content of nitrogen was found to be 51 and 84  $\text{mg kg}^{-2}$  for SW and PW, respectively. The phytoavailable concentrations for SW and PW ( $\text{mg kg}^{-1}$ ) were as follows: Si - 400 and 100, Mg - 2500 and 650, Ca - 3500 and 4000, K - 60 and 6, P - 60 for both substrates.

The experiment involved four variants of soil mixtures, in three replicates for each variant. The variants included soils with the application of serpentinite and phlogopite in doses 0 (control), 3, 5 and 7  $\text{kg m}^{-2}$ . Such grass species as *Phleum pratense* L., *Festuca pratensis* L., *Galega officinalis* L., *Hordeum vulgare* L., *Avena sativa* L., *Secale cereale* L. were seeded in each variant of soil mixtures.

Although some of these cereals are not typical for urban landscaping, they can be used for various purposes in the greening of territories in the Arctic zone. They can quickly accumulate large biomass, which is an important factor for a short growing season. In addition, these types of grasses are used as fodder plants in this region; it is crucial to study the ways to increase their yield.

### 3 Results and Discussion

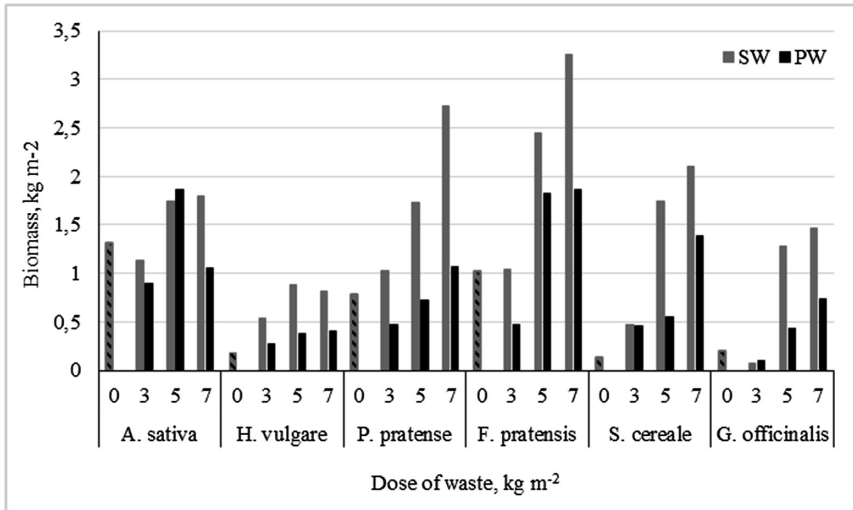
#### 3.1 Biomass and Height of Grasses

The biomass in the variants with the addition of mineral substrates in the doses of 5 and 7  $\text{kg m}^{-2}$  was 25–95% higher than the biomass in the control. At the same time, the majority of the grass species' biomass in the plots treated with SW was 20–50, 60–70 and 30–50% higher than in the variant with the PW addition at doses of 3, 5 and 7  $\text{kg m}^{-2}$ , respectively (Fig. 1).

The height of the plants increased as the concentration of mining waste in the soil increased. At the dose of 7  $\text{kg m}^{-2}$ , it was 20–50% higher than in the control, reaching 40–160 cm (depending on the plant species).

#### 3.2 Content of Major Elements in Vegetative Parts of Grasses

The content of such macronutrients as Ca, Mg, N, K, and P in the aboveground parts of plants differed insignificantly between the variants of the soil mixture and depended more on the plant species than on the dose of mining waste (Fig. 2). At the same time,



**Fig. 1.** Biomass of grasses at different doses of waste introduction (0–7 kg m<sup>-2</sup>)

the Si content in all plant species in the experiment with SW is significantly higher than in the experiment with PW.

### 3.3 Silicon in the Upper Parts of Grasses

The accumulation of Si in the experiments with SW was 2–3 times higher in comparison with PW (Figs. 2 and 3). Figure 3 shows that the introduction of SW even in a minimum dose of 3 kg m<sup>-2</sup> led to an increase of Si content in the aboveground organs by 2–7 times, compared with a similar dose of PW. The one-way ANOVA-test demonstrates that content of Si in the grass growing on SW and PW are statistical significant (\*p < 0.05, \*\*p < 0.01) (Fig. 3).

Plants absorb Si from the soil mainly in the form of monosilicic acid (H<sub>4</sub>SiO<sub>4</sub>), located in the liquid phase of the soil [11]. The phytoavailable concentration of Si in the serpentine wastes was 4 times greater than in the phlogopite waste. The silicon content in the aboveground parts of plants in the variant with SW was on average 3.3 times higher, and the biomass was on average 2 times greater than in the variant with PW.

There are two ways of absorbing silicon from soils. Some cereals (ryegrass, rice) absorb Si actively [12, 13], where other cereals (e.g. oat) absorb it passively [13]. Currently, two classifications of plants have been developed for the content of Si in the plants. The first classification is based on SiO<sub>2</sub> content, where plants are divided into active accumulators (>1% of dry weight), passive accumulators (0.5–1%), and excluders (<0.5%). The second classification is based on the Si:Ca ratio, i.e. for active accumulators, this ratio is >1, for passive accumulators - 0.5–1, for excluders - 0.5 [4].

The content of SiO<sub>2</sub> in leaves and stems with a low content of Si in the soil (variant with PW) was 0.2–1% with the Si:Ca ratio of 0.3–1. The SiO<sub>2</sub> content in aboveground plant organs increased to 1.4–2.1% with the Si:Ca ratio of 1.6–4.9 on soil mixtures



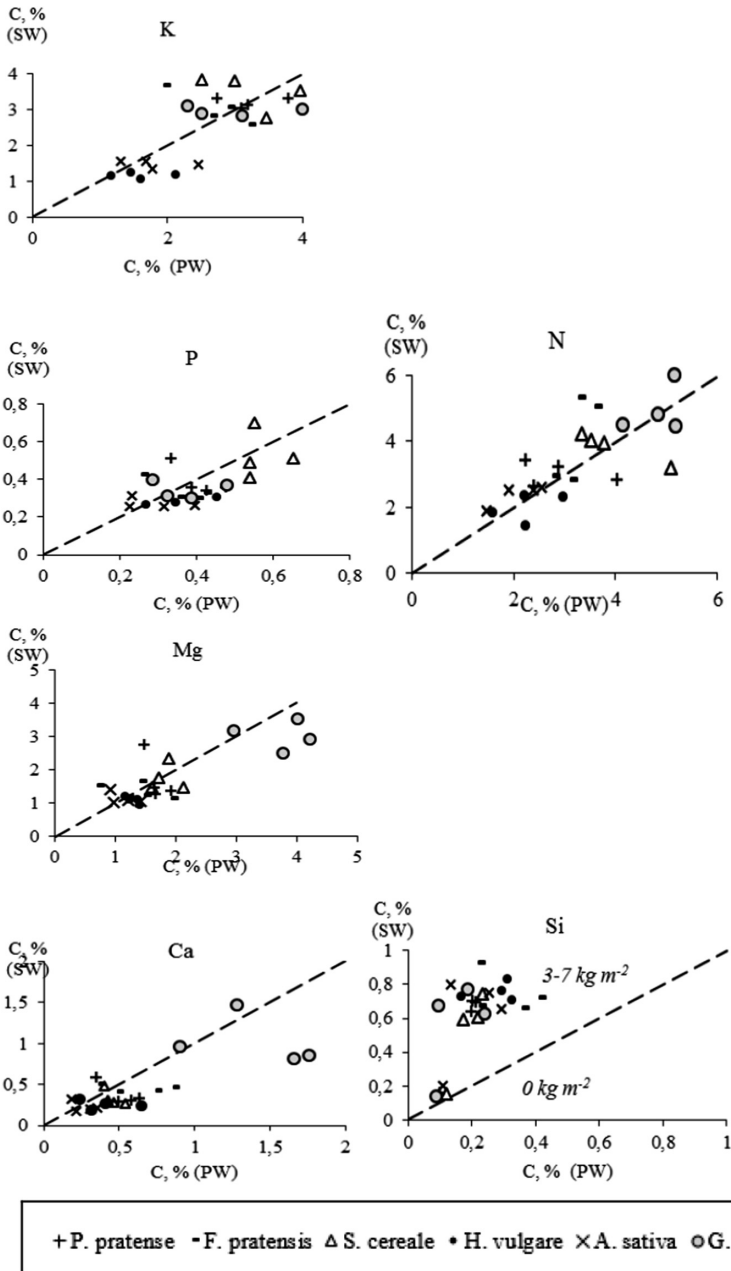
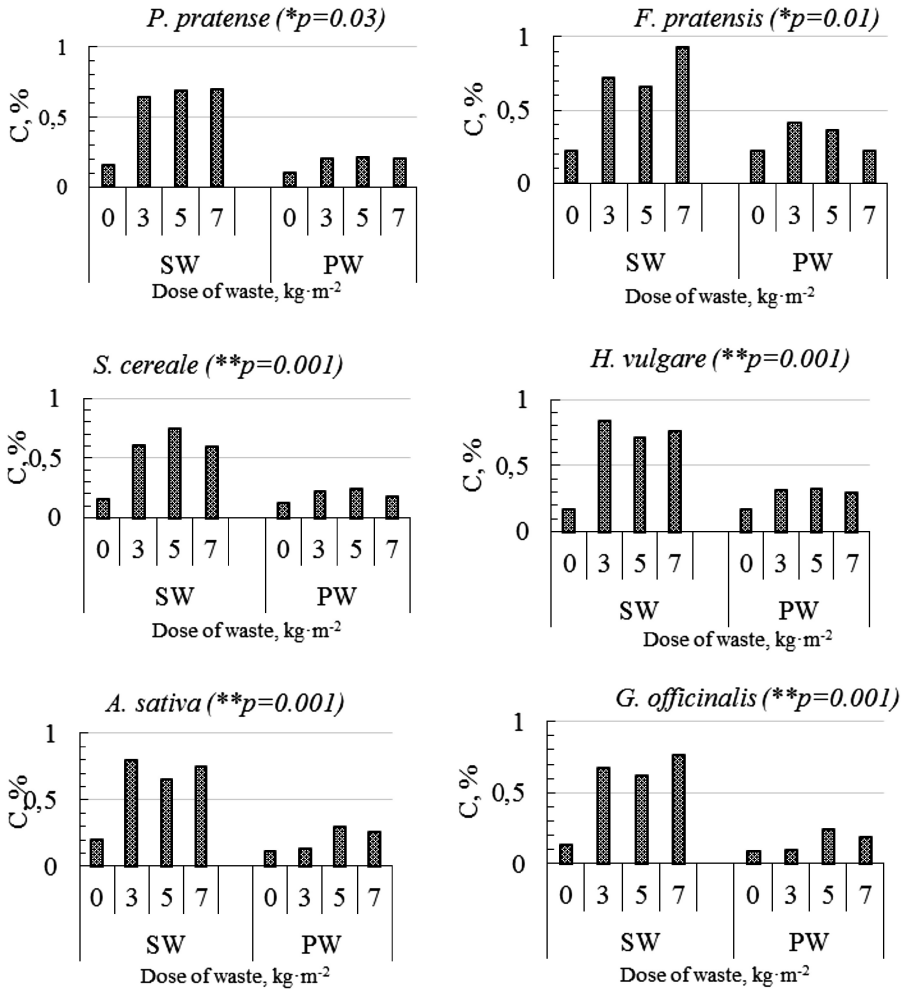


Fig. 2. The content of major elements in the vegetative organs of plants



**Fig. 3.** Silicon content (%) in the vegetative parts of the above-ground parts of grasses

containing higher concentrations of bioavailable Si (SW). The exception was *G. officinalis*, because Si:Ca ratio in this species on the PW-contained soils was 0.1, and in the variant with SW this ratio increased, but remained less than 1 (0.7–0.9).

Thus, the studied cereal species, such as *Phleum pratense*, *Festuca pratensis*, *Hordeum vulgare*, *Avena sativa*, *Secale cereale* can be classified as active Si accumulators.

According to research results [11, 12], Si improves resistance to biotic and abiotic stress factors, including increase of the photosynthetic activity and resistance of plants to low temperatures, strong wind and rain. These properties of Si are extremely important for the creation of a qualitative vegetation cover in the conditions of the Arctic zone. Furthermore, many studies show that the addition of Si increases the

resistance of plants to the toxic effects of heavy metals and salinity [11, 14], this is extremely important in urban and industrial soils.

## 4 Conclusion

Mineral industrial wastes containing serpentine and phlogopite in the application amount of 5–7 kg m<sup>-2</sup> can be used as a component of urban soil structures, to increase the productivity of grasses.

Currently, there is a high demand for search and study of siliceous materials, a source of soluble Si, because they are suitable for use as biostimulants in growing [4]. They must have appropriate physical and mechanical properties, as well as low content of heavy metals and low cost. Selection of such materials is a quite complex and important task for modern greening and crop production.

Two types of mining waste were studied, both of which contain Si in their composition. Serpentine waste meets the requirements, thus, can be used as a source of Si in plant growing in urban conditions.

The presence of sufficiently large concentrations of phytoavailable Si in the composition of serpentine waste allows them to be used for remediation of industrial barrens and other soils with a high content of heavy metals.

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# Evaluation of Peat Stability Under Various Temperature and Moisture Conditions

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**Abstract.** The study explores relationships between the peat decomposition rate and moisture-temperature conditions. Decomposition was evaluated through studying microbial production of CO<sub>2</sub> and CH<sub>4</sub>. Decomposition of the original peat substrate (peat) was compared to one of the peat-sand mixture from 5 year old urban lawn (mixture). In the research the CO<sub>2</sub> and CH<sub>4</sub> emissions were studied under following temperatures and moisture conditions: temperature – 5 °C, 10 °C, 15 °C и 40 °C and moisture – 30%, 60%, 120%, 300%. The obtained results showed significant correlations between moisture and temperature conditions and CO<sub>2</sub> and CH<sub>4</sub> emissions. Differences of moisture and temperature impacts on the soil organic carbon (SOC) decomposition in the peat and peat-sand mixtures were observed as well. The CO<sub>2</sub> emissions from the peat-sand mixture were higher compared to the peat, whereas SOC content in both substrates was similar.

**Keywords:** Urban green infrastructure · Peat · Soil construction  
Microbial respiration

## 1 Introduction

High anthropogenic impact and the rate of urbanization result in a decrease of urban soils capacity to perform important ecosystem services [1–4]. The urban green infrastructure development allows regulating urban soil properties and therefore improving the quality of life in the cities. Constructing artificial soils is one of the approaches contributing to the sustainability and management of green areas [5]. Properties and functions of urban soil constructing primarily depend on the substrate material, depth and sequences of the layers.

Currently the peat is the most common substrate material applied in urban soil constructions. The fact is related to a high organic carbon content in peats and low decomposition rate of peat lands [6]. However, peat lands are characterized with a low decomposition rate only in natural conditions due to the limited oxygen availability and low temperatures. In peat soils, where environmental conditions are primarily

submerged, reduction in moisture content through the drainage, followed by increased oxygen diffusion, enhances microbial activity and decomposition rate. The aim of the research is to estimate the stability of peat material in case of the different temperature and moisture humidity conditions including stress degrees of heat and moisture for modeling the peat stability in different weather conditions.

## 2 Materials and Methods

Peat material commonly used as a substrate in soil constructions of lawn ecosystems in North Administrative District of Moscow have been studied. Peat decomposition rates were determined before applying in urban soil construction (peat) and after the 5 year remaining in the urban lawn (mix - peat-sand composition, ratio 2:1).

Peat stability was estimated by the rate of organic matter decomposition as a result of microbiological activity – basal respiration (BR) [3, 7]. SIR and BR were determined by measuring of CO<sub>2</sub> emissions produced by soil microbiota during the 7 days pre-incubation and 24 h incubation pre-incubation under standardized moisture and temperature conditions [8–10]. CH<sub>4</sub> emission was also measured during the experiment. Microbial production of CO<sub>2</sub> and CH<sub>4</sub> were analyzed by the gas chromatograph «Kristal-5000».

In the research temperature and moisture conditions were controlled during BR pre-incubation as well to determine the effect of these factors on the decomposition rate.

Studied temperature conditions were 5, 10, 15 and 40 °C, and moisture – 30, 60, 120 and 300%. Temperature conditions were regulated in the thermostat; moisture content – according the water capacity and initial peat moisture content.

Determination of CO<sub>2</sub> and CH<sub>4</sub> specific gravity at different temperature was carried out according to the following equation:

$$\rho_{CO_2} = 273.2 \times 44(273.2 + t) \times 22.4$$

$$\rho_{CH_4} = 273.2 \times 16(273.2 + t) \times 22.4$$

Organic carbon content was determined on the CN analyzer. Carbon and nitrogen content in the peat were  $16,36 \pm 0,37$  and  $0,64 \pm 0,03\%$  accordingly and for mix after 5 years of remaining in the field –  $18,22 \pm 1.52$  and  $0,70 \pm 0,13\%$ .

Statistical analysis was performed by STATISTICA 10.0 software.

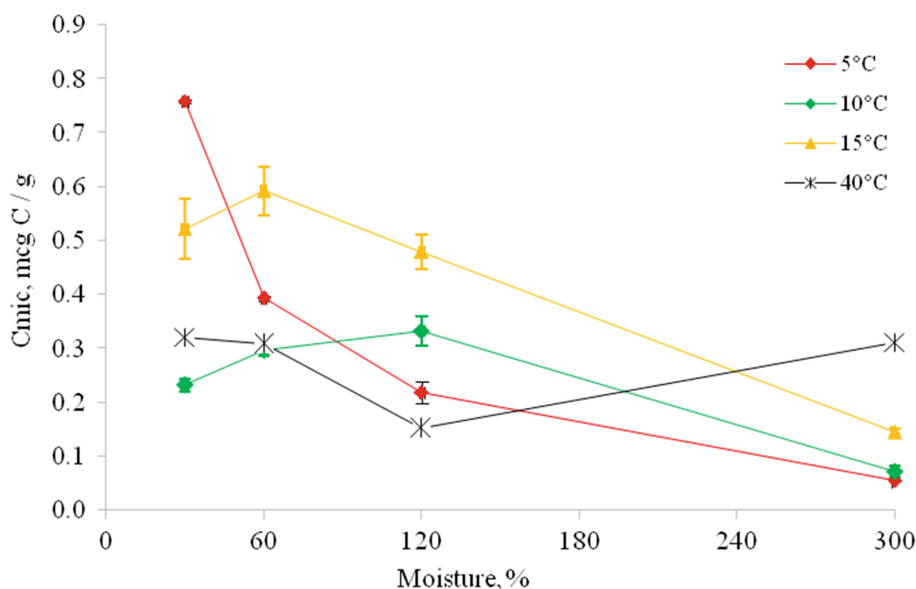
## 3 Results

### 3.1 Carbon Dioxide Emission

As a result of statistical analysis the different influences of temperature-moisture conditions on the CO<sub>2</sub> emission and hence on the decomposition rate in the peat and mix variants were observed. The significant correlation between CO<sub>2</sub> emission and temperature conditions ( $R = -0,62$ , for 64 cases) was revealed only in the mix variant, whereas temperature conditions did not affect the CO<sub>2</sub> emission from the peat variant

significantly. Likely, the revealed results are explained by higher content of microbial biomass in the mix variant due to exposition in the field [11].

As for the moisture conditions, their influence on the CO<sub>2</sub> emission was similarly negative for both substrates. However, for the mix variant correlation coefficient was higher ( $R = -0,62$ ) in comparison with the peat variant ( $R = -0,56$ ). Analysis of variances confirmed a significant retarding effect of moisture conditions on the microbial respiration from both substrates. In case of peat the variant with moisture 30% and temperature 5 °C had the maximum CO<sub>2</sub> emission. For the other temperature conditions, start of emission decreasing was observed from 60% of moisture for 15 and 40 °C and from 120% for 10 °C. LSD-test showed significant differences for all moisture variables (Fig. 1).



**Fig. 1.** Carbon dioxide emission from the peat

The maximal emission of carbon dioxide from the mix was observed for 30% moisture and all temperatures except 5 °C (Fig. 2). LSD-test showed the statistical differences for emissions under the temperatures 5–10 °C, 10–15 °C and for 15–40 °C. In general, for both substrates increasing temperature facilitated an increase in respiration whereas high soil moisture content inhibited it.

Considering that peat was the major source of CO<sub>2</sub> emission in both substrates and in order to eliminate the difference between the substrates, we modelled CO<sub>2</sub> emission from the peat-sand ratio (2:1) based on the results obtained for the peat substrate (blue line on Fig. 2). Despite the fact of initial lower content of SOC (peat-sand mixture), the total emission of CO<sub>2</sub> in the mix variant was higher than in peat one.

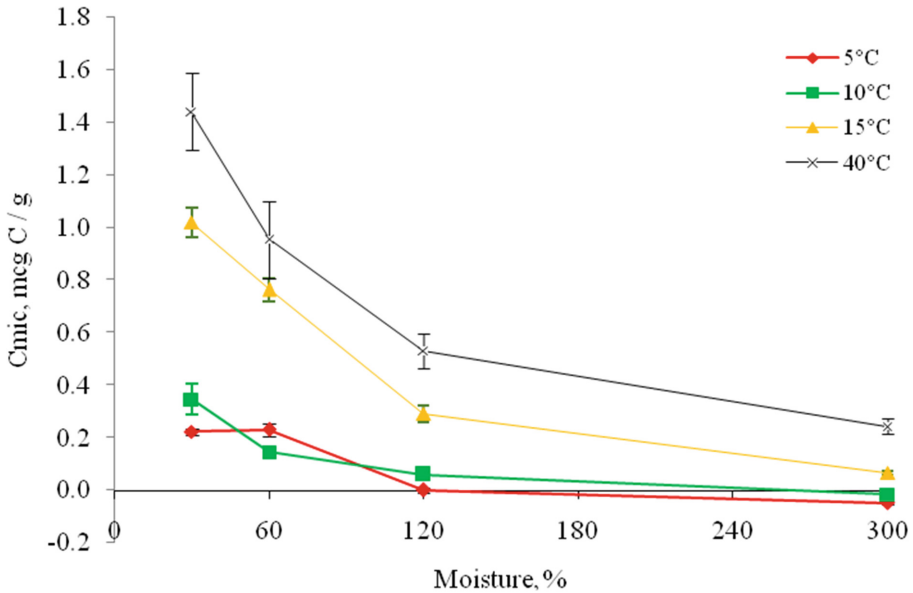


Fig. 2. Carbon dioxide emission from the mixture

### 3.2 Methane Emission

Correlation analysis of methane emission and absorption in the peat and mix variants revealed the relationships between the parameter and soil conditions. In the peat variant, methane absorption was significantly affected by temperature ( $R = -0,7$ ), whereas the moisture content did not have an influence on the methane absorption. In case of the mixture variant the similar non-statistically significant affect of moisture on the methane parameters were founded ( $R = -0,05$ ). Analysis of variances also revealed the lack of significant influence of moisture on  $\text{CH}_4$  absorption in both variants ( $p > 0,11$ ). A substantial increase of the methane absorption in the peat was observed at temperatures above 15 °C (Fig. 3).

An opposite pattern was obtained incase of the mix variant – a  $\text{CH}_4$  emission was found at the soil temperatures above 10 °C. However, the differences between methane emission and absorption in the cases of 10–40 °C were not significant (Fig. 4).

Thus, the obtained results confirmed a substantial effect of the temperature factor on the methane emission and absorption in the peat. Besides, the results indicate the lower stability and hence the higher decomposition rate of the peat from the soil-peat mixture at the 5 year old urban green lawn compared to the original peat substrate.



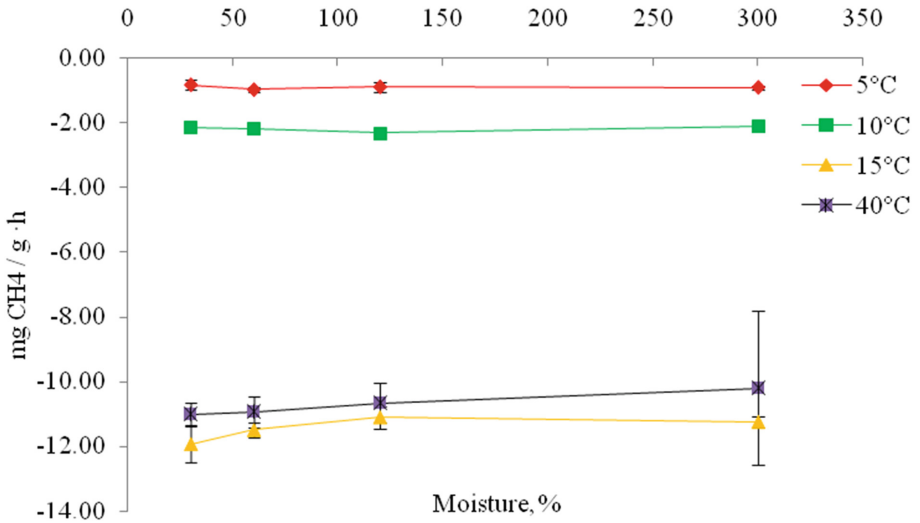


Fig. 3. Methane absorption in the peat variant

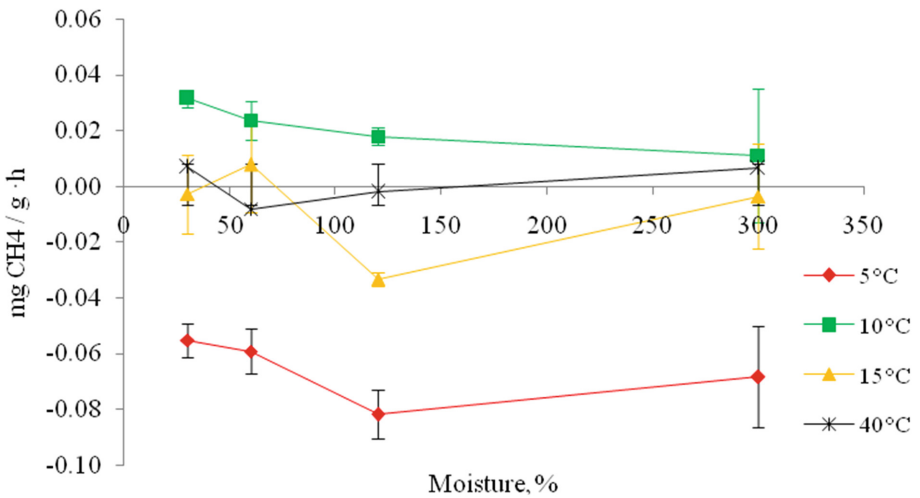


Fig. 4. Methane absorption and emission in the mix variant

### 4 Conclusion

In the research, the differences of stability of the original peat and peat-sand mixture from urban soil construction were studied. The comparison of the variants was based on the modeling of the mix variant due to the known peat-sand ratio and results obtained for the original peat. Thus, the modeled variant was compared with the mixture variant exposed in the field and the features of the peat and 5 year old

peat-sand mixture were studied. Lower stability of the peat was shown for the peat-sand mixture, based on the higher CO<sub>2</sub> emissions and lower initial content of the SOC. Also the mix variant was characterized with the lower capacity for the CH<sub>4</sub> absorption. Likely, the outcomes have to do with the SOC composition content – the mix variant may contain more low-organic materials (characterized with higher decomposition rate) due to the exposition in the field and more favorable conditions for microbiota. Detailed investigations of the SOC composition content would be important for better interpretation of the results.

The obtained results allow predicting peat decomposition in different climatic and hydrologic conditions, which is relevant for environmental monitoring and management of urban soils, where peat component is a potential source of green house gases' emission [12].

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# Bitsevsky Forest Natural and Historical Park of Moscow: Rare and Protected Plant Species Population Structure Under Recreational Load

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**Abstract.** The paper presents research findings on the populations structure of rare and protected species included in the Red Data Book of Moscow and the Moscow region due to the increased recreational load in the forest belt of Moscow city. For the first time, the ontogenic structure of coenopopulations has been described and analyzed on the basis of the characteristics of ontomorphogenesis in the Bitsevsky Forest Park for such species as May lily (*Convallaria majalis* L.), Eurasian Solomon's seal (*Polygonatum multiflorum* L., All.), European sanicle (*Sanicula europaea* L.). These results provide some evidence that the spectrum of coenopopulations for listed species has been modified; the systematic organization of coenopopulations has been broken under the influence of recreational load. Comparing the protected species coenopopulations structure, the authors showed its different types depending on the recreational load.

**Keywords:** Recreational load · *Convallaria majalis* L.  
*Polygonatum multiflorum* L., All. · *Sanicula europaea* L. · Rare species  
Ontomorphogenesis · Coenopopulation  
Ontogenic structure of coenopopulation · Ontogenic spectrum

## 1 Introduction

Moscow, being the largest metropolis, has one feature that distinguishes it from others major cities: the presence of a relatively well-preserved natural forest arrays in a green part of the city. Many plant species, including rare and endangered species, grow in these urban woodlands. In the setting of a big city, environmental factors as light, humidity, soil composition and drainage are obviously far from ideal for plants grows. As a result, the tree growth rate is declining; herbaceous plants are changing their magnitude and population structure.

Recreational load is one of the main negative anthropogenic factors affecting urban and suburban ecosystems. The powerful impact on the state of forest parks is caused by off-road recreation with the free movement of tourists within the area. Recreation in park has a direct impact on all components of the forest, but especially strong on the vegetation. Herbaceous plants in the deciduous forest "Bitsevsky Forest Park" are decreasing in their number due to the recreational load. Based on reduction in the

number of plant species and the recreational load degree on the woodland park environment, we can set up protection requirements for these species and community as a whole in the forest belt of Moscow city [1].

This study analysed the structure of rare and protected plant species included in the Red Data Book of Moscow and the Moscow region. Though all the representatives of flora in the deciduous forest “Bitsevsky Forest Park” are put on the growing anthropogenic load, a considerable interest presents the study of ornamental species with large inflorescences and attractive flowers, such as the May lily (*Convallaria majalis*) and Eurasian Solomon’s seal (*Polygonatum multiflorum*) and their coenopopulation structure for these rare and protected species. The aim of this work is to study the characteristics of coenopopulation ontogenic structure for some rare and protected species of natural and historical Park “Bitsevsky Forest Park” in relation to the recreational impact.

## 2 Material and Methods

The research was conducted from May 2011 to August 2017 in the natural-historical park “Bitsevsky Forest” which has become a protected natural reserve and a natural, historical and cultural heritage site of Moscow since 1992. This natural park maintained, represented species in a near-natural condition, and serves for biodiversity conservation and biogeocenosis restoration, which were disturbed as a result of the anthropogenic load caused by the close proximity to residential areas, road transport, heat-and-power plants emissions or other enterprises, etc. [2].

Due to the fact, that the territory is surrounded by large bedroom districts such as Chertanovo, Zyuzino, Severnoye Butovo, Yasenevo, Teplyy Stan and Konkovo where more than 1 million people live, the frequent park attendance by surrounding residents has increased the recreational load and has lead inevitably to the change of the coenopopulation structure as a whole, and populations of individual species.

Bitsevsky forest park represents a broad-leaved, Oak-Linden wood on soddy podzolic medium loamy soils. May lily (*Convallaria majalis*) is a ubiquitous native forest species (in the past and present) on the territory of rich floral woodland “Bitsevsky Forest Park”. More rarely in this same area occur Eurasian Solomon’s seal (*Polygonatum multiflorum*) and European sanicle (*Sanicula europaea*) - perennial herbaceous species typical for nemoral forests and broad-leaved plant communities growing in the park in small coenopopulation loci. All the model species are part of the group of vulnerable species (category 3), i.e., species which number in Moscow is under the influence of specific factors of the city surroundings and may be substantially reduced for a short period of time [3, 4].

The developments regarding the recreational load in Bitsevsky Park was first measured by researchers from Moscow University in accordance with the industry standard: “Methods and Measurement of Recreational Loads on Forest Complexes” [5]. The estimation of recreational load was carried out depending on the proportion of study plot in the total area, trampled down to the mineral horizon. In accordance with this indicator and subject to OST 56-100-95, five levels of recreational load are identified, so

as the stages of digression for each one, characterizing the phase of biogeocoenose variability. This approach has become widespread in recreational silviculture.

As the research objectives include a description of the population ontogenic structures for mentioned species and their characteristics in comparative analysis, we relied on the conception of the plant discrete ontogenesis, which was firstly developed by Rabotnov [6]. In order to identify and describe certain stages of ontogenesis for species under discussion there were used ontogenic condition criteria for herbaceous plants, described in details in many sources. Detailed ontogenetic researches of plants have already begun since the 70<sup>th</sup> [6–9].

Considering that the ontogenetic spectrum is an important characteristic of plant populations, as it is related to the biological characteristics of the species, we built the ontogenetic spectra of model species relying on the representations of base types of Spectra by Zaugolnova [9].

Widely used criteria for studying the ontogenesis of plants were applied in this work, and also the method of discount areas for the investigation of coenopopulation ontogenic structures [10].

Within Bitsevsky Forest Park 30 test plots of 10 × 10 m were located: in the heart of the oak-linden forest, in the piece of woodland with a predominance of birch, and in the spruce-oak forest - far from the footpaths, 2–3 m from the footpaths, and 1 m from the footpaths.

### 3 Results and Discussion

For the above-mentioned species, the separate stages of ontogenesis were identified and analyzed. The individuals of different ontogenic conditions were counted in the test plots, characterising the ontogenic spectra for coenopopulation. The findings were based on the premise that weeds' response to the external forcings, both natural and man-made, means the changing in their nature of growth, their lives and age conditions.

The study shows that 9–11 species of herbaceous forest plants per 100 m<sup>2</sup> were present under a weak recreational load in Bitsevsky forest park (stage of a recreational digression of SD I-II). At the initial stages of digression some sorts of plants have dominated such as: Bishop's-weed (*Aegopodium podagraria*), Sedge (*Carex pilosa*), Weaselsnout (*Galeobdolon luteum*), with a total projective covering of 60%. Under an average level of recreational load (SD III) their projective coverage consists of 15%, and they have almost completely disappeared on the actively visited areas (SD IV, V). The proportion of species, resistant to physical damage and soil surface compaction has increased towards SD IV, the plants as touch-me-not (*Impatiens vulgaris*), small-flowered balsam (*Impatiens parviflora*), herb bennet (*Geum urbanum*), big-sting nettle (*Urtica dioica*), bugle (*Ajuga reptans*), May lily of the valley (*Convallaria majalis*). At the Stage of V only the most resistant to the recreational species left: dandelion medicinal (*Taraxacum officinale*), Plantago major (*Plantago major*), Gravilite urban (*Geum urbanum*), and Imotiens small-flowered (*Impatiens parviflora*). At the first stages of digression a flowering phase was marked for most species, but at the stages III and IV plants have only vegetation. For that matter Floristic Jaccard similarity

coefficient for herbaceous plants at the different stages of digression stands at: SD II – 0.62; SD III – 0.56; SD IV – 0.24; SD V – 0.24 [11].

As to coenopopulation structure analysis for mentioned above species, May lily is a local forest species on the territory of the natural-historical park “Bitsevsky forest”, that grows massively in birch-spruce forest with a projective crown coating of 45–50%, and under the conditions of phytocenosis digression III-IV stages. When calculating the age composition of *Convallaria majalis* coenopopulation in the “Bitsevsky Forest Park”, it is revealed that coenopopulation is dominated by virginal partial shoots, developing from forked, long rhizomes (Table 1) Sprouts and juvenile specimens are not available. This is the evidence of suppressed seed resume, although the presence of small amount of immature shoots reflects the vegetative propagation material. A sufficient number of generative shoots proves the good prospects for seed breeding, but, unfortunately, these potencies are not implemented in view of a continuing anthropogenic press (Fig. 1).

**Table 1.** Ontogenic structure coenopopulation of May lily (*Convallaria majalis* L.)

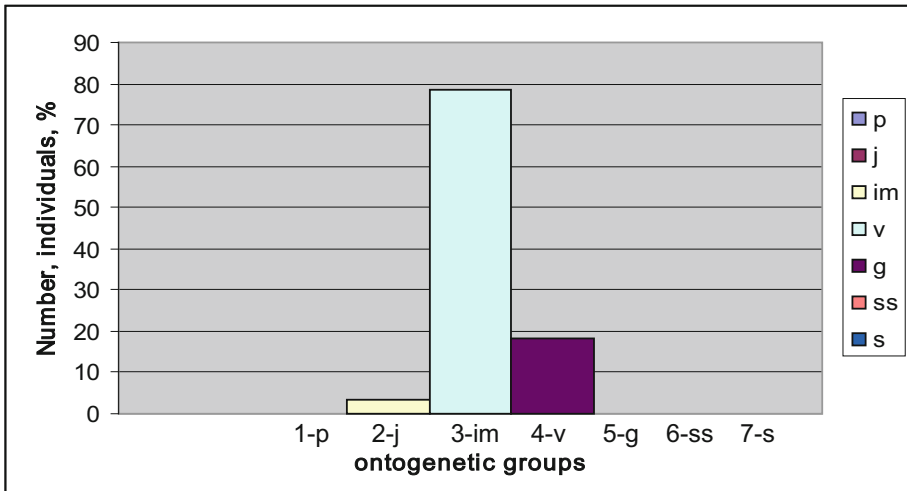
Stadies of ontogeny	p seedlings	j juvenile	im immature	v virginal	g generative	ss subsenile	s senile
Number of individuals	–	–	53	1248	289	–	–
Percents	–	–	3,3	78,5	18,2	–	–
rms	–	–	±0,5	±2,2	±1,1	–	–

Thus, under the influence of recreational load the age range of *Convallaria majalis* coenopopulation has changed in the comparison with the basic range: the number of young age individuals is significantly reduced, the state is almost non-existent seed resume with domination of poor virgin and generative, fewer growing rhizomes. The basic age spectrum of the May lily is characterized by the presence of two maxima. The first one - in the field of the immature and verniginal individuals, the second - in the field of generative individuals (flowering and forming mature fruits and seeds) [8.9].

In addition, the growth rate and the proportion of flowering shoots are being reduced, thus the dynamics of flowering is changing gradually, Lily-breaks between the years of mass flowering are becoming more, i.e. *Convallaria majalis* coenopopulation enters into the category of regressive.

In general, in the context of “Bitsevsky Forest Park”, the system organization of *Convallaria majalis* coenopopulation has broken under the influence of anthropogenic factors that is an essential condition for their stability. *Convallaria majalis* form defective (inferior) material, with a predominance of virgin individuals, characterized by low vitality elevated partial shoots of low density, low seed productivity. But in this situation, it may be due to the autonomic mobility kept long enough on occupied territory, adapting thereby to anthropogenic load.

Perennial grassy short-rhizomed *Polygonatum multiflorum* forms a coenopopulations, where the center influence on surroundings is individual. This species exists in “Bitsevsky Forest Park” scattered coenopopulation individual small loci, the age structure of which was carefully calculated [12]. Solomon’s seal grows in a linden-oak



**Fig. 1.** Ontogenetic structure coenopopulation of May lily (*Convallaria majalis L.*) in “Bitsevsky Forest Park” (1-p – seedlings; 2-j – juvenile; 3-im –immature; 4-v - virginal; 5-g – generative; 6-ss – subsenile; 7-s - senile individuals).

forest, with the projective crown coating of 65–75%, far from the pathways, under the conditions of the I-II stages of phytocenosis digression.

Location of coenopopulation loci on the territory of “Bitsevsky Forest Park” *Polygonatum multiflorum* is diffused, that can explain the drift seeds through birds and their random striking root. In all cases, *Polygonatum multiflorum* only meets oak-lime phytocenoses of “Bitsevsky Forest Park” forest, surrounded by broad-herbosa.

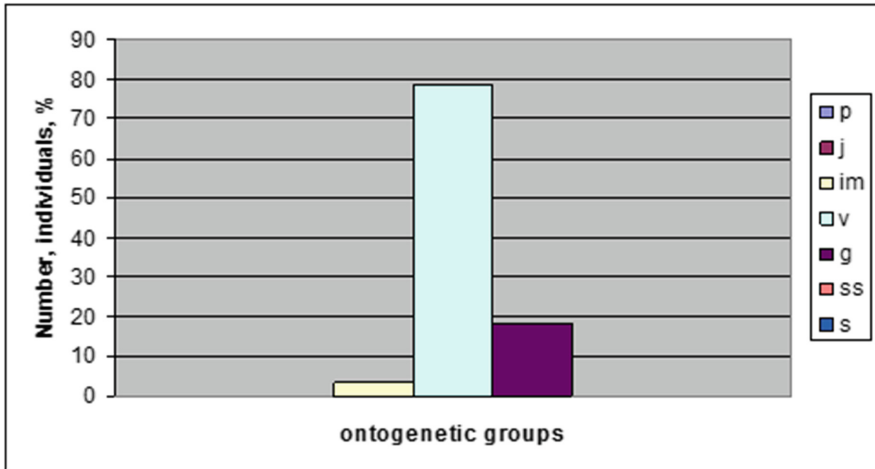
Age structure of coenopopulation loci *Polygonatum multiflorum* is almost full (Table 2), dominated by mostly virgin and generative beings that, most likely due to the predominance of vegetative propagation of *Polygonatum multiflorum* over seed (Fig. 2).

**Table 2.** Ontogenetic structure coenopopulation of Eurasian Solomon’s seal (*Polygonatum multiflorum*).

Stadies of ontogeny	p seedlings	j juvenile	im immature	v virginal	g generative	ss subsenile	s senile
Number of individuals	3	7	21	39	61	–	–
Percents	2,3	5,3	16,0	30,5	46	–	–
rms	± 1,3	± 2,0	± 3,5	± 4,8	± 6,0		

The presence of almost all State ontogenetic conditions in the age range of *Polygonatum multiflorum* presents on dynamic stability of material of this kind, in the studied phytocenosis. The predominance of the same virginal and young individuals of





**Fig. 2.** Ontogenetic structure coenopopulation of Eurasian Solomon's seal (*Polygonatum multiflorum*) in the forest "Bitsevsky Forest Park" (1-p – seedlings; 2-j – juvenile; 3-im – immature; 4-v – virginal; 5-g – generative; 6-ss – subsenile; 7-s – senile individuals).

the generative is a sign of the prospects for the development of these coenopopulations loci in the foreseeable future. Thus, as a rare species belonging to category 3, *Polygonatum multiflorum* in "Bitsevsky Forest Park" feels relatively well.

*Polygonatum multiflorum* increased status can be considered quite promising, but small vegetative mobility and poor seed reproduction of this species prevent it from taking a substantial position in the "Bitsevsky Forest Park". But if we take into account that individuals of *Polygonatum multiflorum* may be able to the secondary dormancy relatively long [12], then there is the possibility of a longer preservation of this species populations even on the area with increased anthropogenic impact. As a corollary to this, the impact - a decrease in population of loci *Polygonatum multiflorum* in the Park, especially near frequently visited sites, trails and tracks.

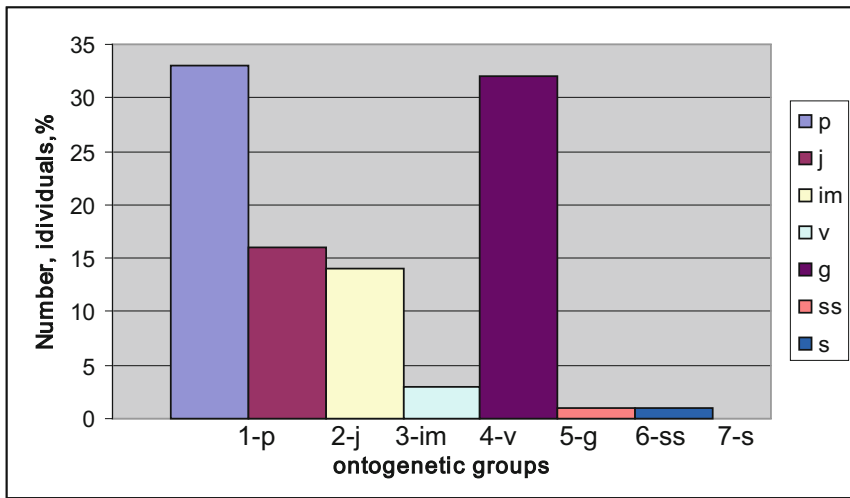
Speaking about *Sanicula europaea*, it represents itself before-glacial-period relic, mezofit, grows in deciduous, mixed and, less frequently, coniferous forests, mainly propagated by seeds [13]. This species occurs on the territory of protected the "Bitsevsky Forest Park" forest as small coenopopulation loci, which are located mostly along the network, owing to the specificity of its reproduction (exozoochoria). Sanicle grows in the Bitsevsky forest along the paths, on clearing in the woods, among trees with the projective crown coating of 50–65%. This species is resilient to trampling and blossoms under the conditions of III-IV stages of phytocenosis digression.

Age spectra of *Sanicula europaea* in broadleaf phytocenoses in the "Bitsevsky Forest Park" are almost full, with a maximum for species of pregenerative spectrum (Table 3). The second maximum is on generative stage's individuals. This is explained by the presence of good lighting near the sanicle coenopopulation. In population loci located closer to the forest roads subsenil and senil individuals are appeared. Thus, trampling has increased the number of subsenile and senile individuals of sanicle.

**Table 3.** Ontogenic structure coenopopulation of European sanicle (*Sanicula europaea*):

Stadies of ontogeny	p seedlings	j juvenile	im immature	v virginal	g generative	ss subsenile	s senile
Number of individuals	151	73	65	12	144	4	5
Percents	33	16	14,3	2,6	21,6	0,9	1,1
rms	± 2,7	± 2,0	± 1,8	± 0,8	± 2,6	± 0,4	± 0,5

The general age range of the population *Sanicula europaea* (Fig. 3) shows that the age structure of populations of this species and the reproductive health are dominated by the individual pregenerative stages, namely immaturn, juvenile and sprouts. This structure is a characteristic of coenopopulation types which are prone to r-strategy, i.e. explerent [14]. And, indeed, the observed coenopopulation *Sanicula europaea* sprouts, juvenile and immature plants grew in the most disturbed areas of grassy mole’s and mouse’s borrows, exposed areas of soil.



**Fig. 3.** Ontogenic structure coenopopulation of European sanicle (*Sanicula europaea*) in the forest “Bitsevsky Forest Park” (1-p – seedlings; 2-j – juvenile; 3-im –immature; 4-v – virginal; 5-g – generative; 6-ss – subsenile; 7-s – senile individuals).

Thus, the presence of all age conditions in the range of *Sanicula europaea* testifies its sustainability and the preponderance of young stages of ontogenesis, the prospects of development of these coenopopulation loci in the foreseeable future. That is, as a kind of rare, belonging to category 3, *Sanicula europaea* experiences in the “Bitsevsky Forest Park” forest relatively weak anthropogenic pressure and maintains stability of the population, despite the increased anthropogenic press.

## 4 Conclusion

The age structures of coenopopulations for three protected species show the differences in dependence on anthropogenic load. Under the influence of recreational load and anthropogenic press, the age range of coenopopulation for *Sanicula europaea*, *Convallaria majalis* and *Polygonatum multiflorum* has been modified, the number of individuals in a young age conditions has been reduced, the systematic organization of coenopopulations has been broken, and some of the material has been transferred to the category of regressive. But subject to certain security measures, sometimes quite minor, associated only with environmental education, it is possible not only to maintain but also to increase the number of these species in the natural-historical Park “Bitsevsky Forest Park”.

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# Modern Technologies of Ornamental Plants Cultivation in Vertical Structures

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**Abstract.** The history, the methods and general principles of vertical gardening, green walls, phytowalls, living walls are reviewed. These methods have been implemented using the latest designs and technologies of Russian and foreign companies. The application of new technologies for green walls construction is considered. Two fundamentally different technologies of green walls are compared and analyzed. The problems of aesthetic, ecological and rationalization character are discussed.

**Keywords:** Vertical gardening · Green walls · Phytodesign  
Ornamental gardening

## 1 Introduction

In the cities of Europe and Asia XXI century in conditions of high population density, lack of space and the violation of gas composition of atmospheric air, oxygen-depleted and contaminated with toxic products of combustion, vertical gardening has become one of the important methods to solve the problem of stabilization of environment quality, comfortable feeling and human life in the urban environment [1]. All the technology vertical landscaping walls are based on the principles and experimental study of soilless water culture.

In the second half of the XIX century primarily due to the works of Lieberg [2] misconceptions about the physiology of plant nutrition has been eliminated and showed the dominant role of mineral nutrition uptake by plants and incorporation into the metabolism of inorganic compounds of the main biogenic elements. These studies allow to grow plants in artificial conditions. German Wilhelm Knop (1817–1901), together with Julius Sachs (1832–1897) first found which chemical elements plants needed. They picked up the salt solutions, which have helped to grow plants without soil from seed germination to flowering and ripening of the new seeds.

In the 1930-ies Europe and United States already had setup for mass cultivation of plants in soilless culture on artificial media. In 1936 a professor of University of California William F. Gerik introduced the term “hydroponics” (from the greek. *hydor* – water and *pónos* – work, labor) to describe the cultivation of plants in aqueous medium with the dissolved salts. In Hungary in the same years, Professor Paul

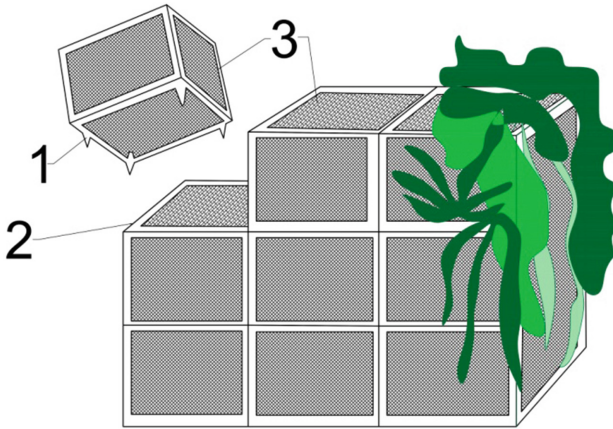
Roeschler developed a small automatic hydroponic system, the principle of which nowadays is used in many modular designs for vertical gardening. P. Roeschler system was designed for maximum automation of all processes for the care of plants. This setting could well be scaled and gave an opportunity to obtain good yields of various crops [3]. It is interesting to note that many modern Russian and foreign patents of modular structures for vertical gardening are practically duplicate this invention, made 80 years ago.

In 1940-ies in Western Europe a special method of growing plants in a vertical plane became well known; it was practiced in the Republic of South Africa – on the walls of coconut fiber or moss. The method was known in South Africa under the name “Tankfarming” and is still widely used in the country. In accordance with this method plants are grown not in pure nutrient solution or on an inorganic substrate but in an organic filler, i.e. on the appropriately prepared plant materials, periodically wetted with a nutrient solution [3, 4].

In the United States an associate Professor at the University of California, Berkeley, F. Gericke in 1929 conducted extensive experiments on this method of growing plants for the cultivation of vegetables in greenhouses [3]. Culture of plants on the walls of moss, in the so-called grow-bags, didn't find application in the industrial horticulture of European countries until now, but has been used in ornamental crop production [4–6]. According to the US patent office since 1937 several patent applications of phyto-walls were filed [7]. One of the authors of these patents was Elmer Gates. In 1938 Elmer Gates applied the invention of “Vegetation-Bearing Display Surface”, i.e. screen with the surface of plants. His system of vertical garden consists of individual blocks made of steel grating (Fig. 1).

Lattice blocks are made on the basis of cellular cells in a single structure, forming a vertical wall. As the substrate for filling the blocks it is proposed to use mineral wool or peat. This principle was modified by the engineers of the British company Bio Texture Ltd. and American GSky Plant Systems, and it is used today in USA by several companies which are involved in vertical gardening. For example, Ambius uses volumetric stainless steel panel measuring about 25 × 25 cm, which contains a blend of crushed composted bark, coconut fiber and lightweight mineral wool (AirLite) [8–11].

The most famous is the design and concept, which was invented by Professor of landscape architecture S. H. White (Stanley Hart White) at the American University of Illinois at Urbana-Champaign of Illinois in 1931–1938 S.H. White in the patent “Vegetation-Bearing Architectonic Structure and System” from 1937 describes a completely new at that time method of vertical gardening with the help of “Botanical Bricks” [11]. The primary use of S.H. White invention was creating the special architectural-landscape units, the visible surface of which planted with ever-evolving plants. Thus, using the modules “Botanical Bricks”, allow to get “architectural structure of any size, shape or height, whose visible or open surface is a permanently growing covering of vegetation”. The method was based on the principle of blocking – establishment using standardized units of walls and partitions of required height, shape, and, most importantly – the desired design, as each block with vegetation is portable and interchangeable. The vertical wall of blocks with plants could serve as an element of interior living spaces, or used at exhibitions and other functional objects [12]. The Invention S.H. White has become a challenge to the conventional notion of vertical



FLORAL WALL OF THE INDIVIDUAL ELEMENTS:  
 1- ANKER  
 2- GROOVE  
 3- THE SAME BUILDING ELEMENTS

**Fig. 1.** First-of-its kind vertical gardens system of individual blocks.

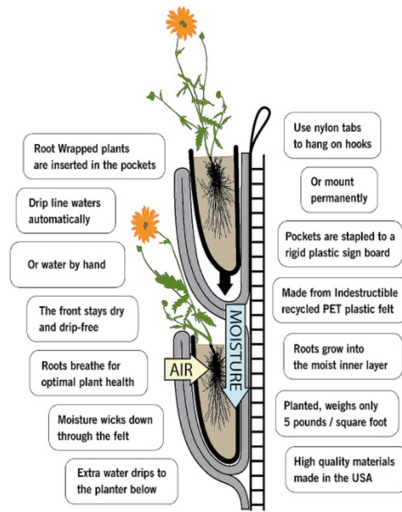
gardening, which meant that the vertical support structure served to accommodate only stems of basket or liana plants and their root system was fixed on a horizontal plane of the base construction. Now the entire surface of the wall became a space where plants are fixed, receive nutrition and grow [6, 11].

At the turn of the century a new method of vertical gardening was introduced into the practice of green building by extraordinary french botanist, member of the National research center of France Patrick Blanc.

P. Blanc has created a new technology of growing vertical gardens on the basis of the synthetic “carpet” with pockets filled with a minimal amount of soil substrate for plants (Fig. 2). This invention opens up tremendous opportunities in the greening of vertical surfaces [1, 13].

Thus, the traditional vertical gardening was limited to the use of liana and a basket plants as a green material [11, 14]. Tanks to the development of new agricultural technologies, vertical greenery is now mostly based on the application of constructions created with carpet or modular technologies that allow you to grow plants directly on a vertical surface.

In this case plants with different life forms can be used. Modern methods of vertical gardening allow to integrate a large mass of plants in the urban environment without requiring additional horizontal space both inside and outdoors. The development of production of various synthetic materials made this type of gardening more affordable and accessible [15, 16]. In highly urbanized areas, the use of vertical landscaping is



**Fig. 2.** “Carpet” or “pocket” phytowalls construction by P. Blanc

very appropriate, as it creates a favorable environment and gives anaesthetic appearance to buildings and the entire landscape [11, 13].

This type of external landscaping of buildings and constructions in most regions of Russia is limited by seasonal use and greatly complicated by the adverse climatic conditions of plants wintering; it is only beginning to be studied and tested [8, 9, 11, 17, 18]. However, some modern technologies can be used in greenhouses and in residential areas.

## 2 Types of Load-Bearing Structures

To refer to the load-bearing structures use the terms phytowalls, living wall, vertical gardens and phytomodule or phytopanel.

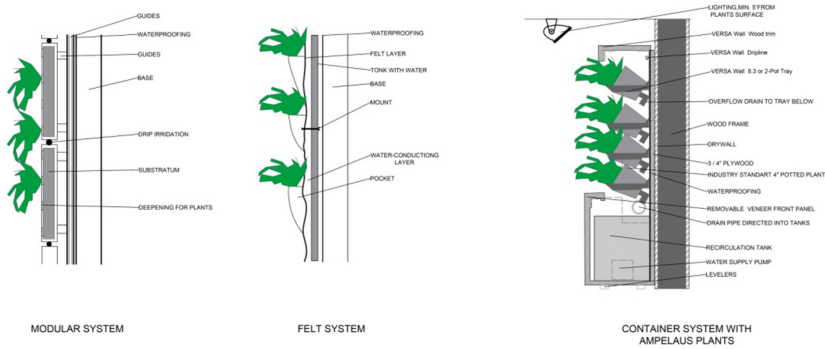
The diversity of phytowalls is conventionally divided into three types (Fig. 3):

- modular plastic construction;
- plastic carpet (felt) design [5, 8, 10, 19].
- pot (or container) structure.

The modular design is representing a frame and fasten containers, shelves or mats with a substrate that provides mechanical anchoring of the plants.

The second type of structures involves the fixing on the frame multilayer synthetic carpet material with pockets for plants, where a suitable for development of roots substrate is situated [14, 20–22].

The main problem of creating vertical structures for plants was the search and fixing the root-caring construction that will not crumble under the action of gravitational forces, wind and rain. In both principles of structures, the root system of plants



**Fig. 3.** Three fundamentally different types of vertical phytowalls

develops on the substrates which do not serve as a source of nutrition for plants. The plant receives nutrition not from the substrate but from nutrient solution. The substrate only serves to water retention and water conduction, optimum aeration and mechanical anchoring of the roots. Only in some types of modular structures a complete substrate is fitted in the container, to provides plants by mineral nutrition for some time [19, 23]. Despite the type of substrate the irrigation system bases on the achievements of hydroponics [1, 3, 10, 24]. Known in practice 6 basic types of hydroponic systems vary depending on the irrigation system and they all are used in vertical structures: periodic flooding (Ebb/Flow), drip irrigation (reversionary/not-reversionary) – dripSystem (recovery/non-recovery), nutritional layer (Nutrient Film Technique – NFT), aeroponika (Aeroponic), wick irrigation (Wick). There are many modifications of these basic systems [4, 25].

### 3 Vertical Gardens by Modular Technology

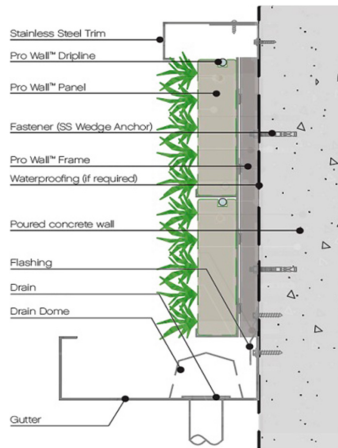
Modular system in a general form implies the existence of a supporting structure to which plastic or metal modules are attached, which are also called “phyto-modules”. They are mounted to the irrigation system (Fig. 4).

Most often a module is a box with a sloping bottom, or cabinet with the shelves beveled toward the back side. Anterior (front) wall of these structures is missing. Each drawer or cabinet is usually designed for multiple plants. The modular approach allows you to grow plants in hydroponic technology (without soil) and traditional method using different nutrient substrates [9, 19, 24].

According to our observations, an important advantage of such structures are:

- finding roots of plants in a relatively large volume which can be filled with natural soil, which increases their life cycle;
- ability to change the exposure by changing the modules order;
- possibility of installation on the wall modules with adult, deeply rooted plants;





**Fig. 4.** Construction of the vertical garden modular technology GSKy - versa wall.

- possibility of fast installation of the construction, except for the period which is necessary for rooting of the plants in the modules. The entire process from planting plants into containers to their mounting on the wall may take several months [10].

Negative features of modular phytowalls are the following:

- a large specific proportion, about 50–90 kg per m<sup>2</sup>;
- salinization of the substrate for a few years if watering with tap water with a high content of carbonates;
- difficulties with planting and care associated with possible contamination of surrounding surfaces and soil mixtures, in the case of their use [1, 10].

We can distinguish the following main types of substrates used in modular phytowalls:

**A. Bulk medium** – a substrate consisting of a mixture of soil, biological, mineral and synthetic components. The bulk medium is used in ground modules of plants [19]. The advantage of bulk medium is that the substrate may be selected in accordance with the requirements of the specific plants to acidity, air permeability, fractional composition and other indicators. Plants on these substrates can live 6–8 years without a transplant [10].

As example, we present the composition of the substrate: 2 pieces of leaf litter (leaf compost) to slightly acid reaction (pH 5–6) (by volume), 1 part of peat moss of medium decomposition degree (acidified to pH of 5.0–5.5), 0.5 parts of river sand (coarse river sand), 0.5 parts of pozzolanic material (crushed volcanic siliceous rock) and 0.1 part vermiculite.

There is a constant study and testing new components for the compilation of bulk substrates: a variety of water-retaining hydrogels, ionites, zeolites, granular silicates, ligno-humates, etc. [19, 23, 25, 26].

**B. Landless medium** – light non-nutrient materials such as coir (the mesocarp fiber of the nut of the coconut palm), perlite, vermiculite, crushed bark of larch or pine, claydite, mineral wool (Fig. 3).

**C. Fractional medium** is a special mineral, synthetic and natural materials, consisting of disjointed particles of the desired granulometric composition. The advantage of fractional media is that the grain size for strengthening roots may be selected in accordance with the needs of specific plants. In addition, most of its components are very available and not expensive. An example can serve as a substrate for epiphytic plants: pine bark of various fractions, sphagnum moss, lime, pumice stone, charcoal (5:2:0.5:0.5) [5, 27, 28]. The substrate, consisting of claydite of fraction 10–15 mm, sphagnum moss and shredded pine bark, all they are used in modern hydroponic modular walls, which are working on the principle of the P. Roeschler system.

Currently, a proliferation of several types of modular structures phytowalls.

A system GroVert is well known in the West design. The system consists of a plastic cabinet without front wall arranged with the shelves beveled toward the back side. Along the back wall laid a capillary mat (Moisture mat) [7, 10, 29]. In the planting cells a special substrate composition is placed. The requirements for this substrate are the following: slow decomposition (for plant material), moisture capacity, air permeability, durability (maintenance of the physical properties of the substrate for a long time), it must have prolonged fertility, should not contain pathogenic microflora. In addition, the substrate should have a good hold on the root system of a plant, so that with the growth of green mass the root system would not be pulled out from the pot, which is hanging horizontally. As an example, the following composition is given: coconut fiber (pH 5.8 to 6.5), chopped sphagnum moss, pine bark, volcanic silicate pumice and vermiculite in an approximate ratio (by volume) 1:0.5:0.5:0.5:0.2. In such a substrate an addition of ion exchange materials (ion-exchange synthetic resins, natural zeolites, etc.) is also recommended [25].

Water as needed is supplied through the upper tank-irrigator, wetting the mat inserted from the back side of the module, which provides uniform distribution of water to the boxes; hidden tray reservoir at the bottom collects excess runoff [12].

In Russia one of the first module system with a rare watering, in which the elementary cell was used the design of a plastic box with a skew angle of 60° was patented [19]. Here the plants are planted in the bulk medium, i.e., it is a modular phytowalls “on the soil”, in the bulk medium. On the bottom and on the back wall of each box sponge (floral foam) is stacked to allow a longer water retention in the substrate (each box can hold 2.5 L of bound water). Then fit the plastic grid and filter (synthetic felt) are fitted. Several (6 or more) boxes are composing phytomodule, which is mounted on a metal frame. The company Verticalsad have developed a special wall fastener, allowing you to create vertical gardens and orchards of different size, it also provides the possibility of mounting a decorative framing panels. The back frame is the layout of the drip irrigation system. In each block there is an entrance for hose with drip irrigation (top back wall), entrance for a front of drip leaves irrigation (top front edge) and a drain hole to drain excess moisture.

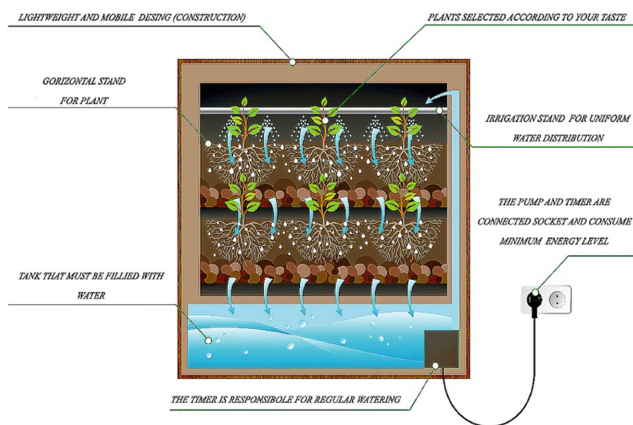
Problems of this system are: (1) the need to collect and build independently an auto-irrigation system and to install the pump for water reservoir each time; (2) the construction is noticeably heavier than other analogs, it cannot be installed in a

seismically unstable areas and at high altitude; (3) the boxes are very extensive unsightly plastic surface on the front side, making it difficult for decoration; (4) significant lateral width of the structure, a minimum of 200 mm can also complicate decorating [30].

The advantage of this system is the low dependence from energy, and other potential issues of auto-irrigation, as a reserve of moisture in the substrate of each box is enough for 4–6 days. To increase the supply of moisture and the nutrient properties of the substrate manufacturer (OOO “Vertical healing gardens”) recommends to mix agroionit into the substrate, it is a domestic natural material of Bondarskiy deposits of glauconite. It is produced as a universal supplement to the soil of container plants.

Also the operation of the system is greatly simplified by the absence of a return irrigation system that addresses many issues of hydroponic content of phytowalls: filters do not clog; clogging of the thin hoses, of droppers by build-up of salts and particles of the substrate does not occur; the roots of the plants do not grow into a synthetic felt; solutions to each module are delivered independently – there is no threat of the transfer of root rot throughout the system etc. [19].

More popular becomes a common domestic hydroponic modular construction, developed initially by the company Lafasad (Perm) [5]. The prototype became an autonomous P.Roeschler system [3]. The construction represents a sealed cabinet-phytomodule made of PVC (Fig. 5).



**Fig. 5.** Construction of a modular hydroponic phytowalls “Lafasad”

Slant shelves have a lateral width (depth) of only 15 cm. Below the construction a water tank that needs to be filled 1 time in 7–30 days is integrated. Built-in pump with programmable timer-relay automatically performs the circulation of the nutrient solution through the system. Water from the tank rises to the irrigation shelf through the special silicone tube. On the top, in the irrigation shelf the water is evenly distributed and through the holes goes directly to the first top shelf, and from there to the underlying shelves with plants. Containers-shelves are filled with claydite or sphagnum. Washed from the soil plant root system is wrapped in sphagnum, which is fixed in

addition, with coconut fiber, nylon mesh or sezal. This construction allows plants to grow and develop in a well air-permeable substrate with the automatic irrigation system.

Mineral nutrition of plants is realized by laying special tablets or filling of dry granular feeding for hydroponics into tank, for example, Lewat it is a long-acting fertilizer for hydroponics (BAYER Enterprise) [28]. Modern liquid fertilizer concentrates are very comfortable: Hydro Growth (Hesi), EtissoHydroVital, Greenworld “SpezialdungerHydrokultur” (a complex of fulvic and humic acids, which increases the ability of plants to absorb nutrients). The nutrient solution for the first time after planting until the plants are rooted, is changed once a week and its composition is controlled basing on the parameters: the total concentration of salts 600–700 ppm, electrical conductivity EC 0,9–1,0  $\mu\text{s}/\text{cm}$ , pH is 6.0–6.5 [31].

Also an ionite resin (ion exchanger) is recommend be used for such walls instead of claydite [19, 25]. This fine-grained granular polymer material, insoluble in water, reacts easily exchanging ions with the cultivated plants. When using this material the need to prepare the nutrient solution eliminates and you can water plants with clean water. However, the availability and cost of the ion exchanger is disproportionately higher in comparison with a mix of claydite and sphagnum moss and it has a number of disadvantages – small granulation, the trend of crust formation and loss of physical properties.

On a similar principle operates the system using a construction of Lafasad company, patented by Gsky (USA) [32]. There inside phyto-module on slanting shelves an automatic irrigation system is laid, using a trickling hose formicro-irrigation, and in some variations fiber medium is used instead of claydite (Fig. 4). The main feature (honours) of Lafasad construction is an efficient drenching of shelves from top and to the bottom by gravity flowing of the nutrient solution, and in a single monoblock of the shelves and their surrounding frame which has the same color. This frame is the stiffening rib, and the decorative frame at the same time.

Even the largest of the produced phytomodules,  $2 \times 2.5$  m, can be easily moved to any place in the case of the interior change, the weight of phytowalls is negligible (of the order of 50–90  $\text{kg}/\text{m}^2$ ).

The structure mounting is facilitated due to the fact that it's enough to fix it by bolts. Important advantage, in contrast to other systems is also constructions' impermeability. Plants in phytomodule can relatively easily be replaced without damaging the whole structure. Also there is no complex system of water distribution, in which nozzles can get clogged up with salt. A particular advantage is the absence of bulk soil substrate, and therefore littering of the room. The experience of operating such walls shows that plants of 3–4 years do not require transplantation and replacement of sphagnum.

Among not completely solved problems there is the possibility of lack of mineral nutrition for plants. With periodic flooding in this system there is no feedback—the needs of plants for additional power is not enough pronounced. In addition, dissolved organic matter and constant room temperature above  $20^\circ\text{C}$  promote the development of anaerobic microorganisms in the irrigation nutrient solution tank. This leads to the formation of gaseous reduced sulphur compounds ( $\text{H}_2\text{S}$ , mercaptans, etc.) having a bad flavor.

This problem is partly solved by the use of modern soluble fertilizer for hydroponics, such as BioSevia Grow (General Hydroponics Europe) that prevents the development of anaerobic processes in solution. A complex Bioponic Mix, includes soil bacteria *Trichoderma harzianum*, etc. which realize the process of decomposition of organic matter [22, 31].

One of the variations of modular structures is patented by Finnish NaturVention company technology FreshWall, operating on the principle of aeroponics [33, 34].

Aeroponic – a kind of hydroponics with periodic watering of plant roots with air-to-water suspension of the nutrient solution. It is the youngest, recently developed technology. Plants usually are suspended in baskets above the closed trough or cylinder. Since the roots are in the air, they receive the maximum possible amount of oxygen. The increased saturation of the root system with oxygen by this technique gives absolute improvement in growth. It has been proven that with this technic, the yield increases about 10 times compared with the substrate on the basis of soil [20]. Root systems are also developed very strongly and practically are not damaged by root rot.

This method provides for the recycling of the nutrient solution, excess solution which has not been absorbed by the roots, drains back into the tank and then recycle. The main objective of the operation of this system is preventing possible dehydration and loss of roots that optimum frequency of spraying [3, 10, 17, 20, 22].

A well known technology AeroSpring combines aeroponic with the possibility of dipping the roots in a deep reservoir with a nutrient solution in case of failure of the pump [21].

The system FreshWall is based on the temporary influx of the nutrient solution to the plant roots, and then its outflow back into the tank (Fig. 6).



Fig. 6. The scheme of phytowall “Freshwall” functioning

This method is called “method of inflow and outflow”. Plants are placed in small perforated boxes-pots (plastic cassettes) filled seramis (small porous pellets which are made of baked clay), vermiculite, and ionite resin (substrate performs the function of fixing the root system, holding moisture and nutrition). The pots are inserted horizontally into the holes in the hollow vertical structure. The setup tank the nutrient solution is preparing and on the flow of moisture through built-in irrigation system automatically turns on and then an automatic system controls the hydration of the roots. An important feature of this system is that all time through the root system of the plants from the bottom up passes the air which, is constantly supplied into the room by silent fan built into the top panel. In the process of purging air humidifies and cleans the system from contaminants. According to many studies, the system of FreshWall is a real alternative to indoor air humidifiers and helps cleaning it from impurities and dust [33–36]. So, according to research by *Ryan Hum, Pearl Lai* this type of phytomodules when installed in premises of public buildings can reduce the levels of toluene, ethylbenzene and form aldehyde in the air, which were identified as particularly harmful to humans. In the work of *B. C. Wolverson, Wolverson J. D.* indicates that simply having three small potted plants like *Chlorophytum* (*Chlorophytum* sp.) can significantly reduce (50–75%) the total level of hazardous volatile organic compounds in the air in a real office of 30–50 m<sup>3</sup>. If the room is large, like the atrium, only a phytowall with lots of plants and high density of planting can effectively reduce the levels of harmful impurities in the air. The indoor air cleaning process is more completely studied on the example of phytowalls of the NaturVention wall construction.

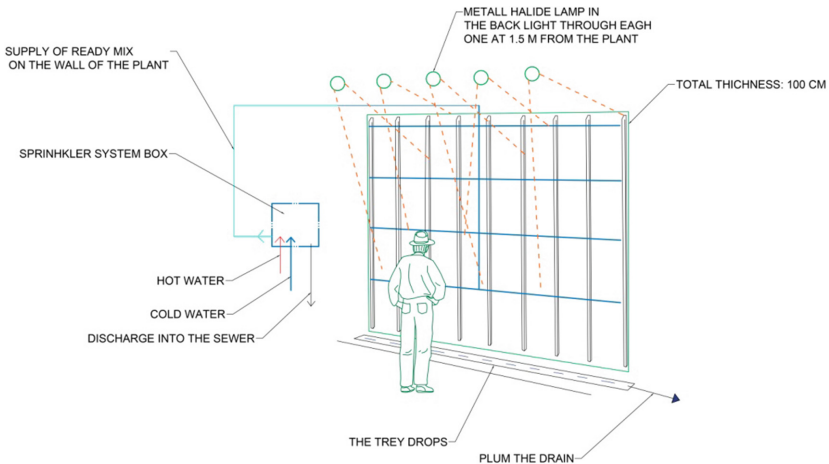
NaturVention constructions differ from the rest also with the fact that they are connected in a single network and controlled from a single general electronic center, i.e., the signals of the sensors of humidity, temperature, water level, etc., are installed on all connected into a single network constructions and are joined in one general control center. If necessary, by remote control you can change the watering program of every wall or just send a signal about necessity to add water. This system has many advantages and disadvantages, but it is not sufficiently tested by domestic experts, although already installed on several sites in St. Petersburg.

Among the disadvantages of this system the following should be noted:

- Since the roots are in the substrate, which isn’t able for a long moisture retain, in case of interruption of the process of hydration they can dry quickly.
- The indication of high-technical humidity sensors of root zone and the solution spray nozzles is not always sufficiently reliable and objective.
- As in other hydroponic systems, supply chain solution is controlled by the timer, but this system needs to have frequent cycles of paging, perhaps taking place every three to four minutes. The wear rate of the system with frequent swap cycles is probably very high.
- The possibility of landing only very young plants, because it provides very small cell container that reduces the aesthetic quality of the construction at first time after landing.

**Vertical gardens with the “carpet” technology** “Carpet” technology for the location of plants on the wall building designed by the P. Blanc, consists of a

supporting structure (plastic sheet with a thickness of about 10 mm) that serves as a moisture barrier, and synthetic felt (plastic felt) with disposed therein pockets for planting, which are attached to the plastic sheet [1, 35, 37] (Fig. 4). Between synthetic felt and a sheet of plastic the capillary carpet mat is attached, often a synthetic batting is used. As a result, a solid carpet, which retains moisture, is created. The described variant of phytocarpet is called Phytotextil® and patented by spanish company Slim Greenwall [1, 38]. However, there are variations without the capillary mat when the synthetic felt acts as a conductor of moisture to the root systems of plants (Fig. 7).



**Fig. 7.** Construction of the vertical garden with the “carpet” technology.

For planting are used young plants, which can easily recover from root damage during cleaning them from soil and gain a foothold in felt. After the transplant, the plants may need some time to grow to their normal size, so the wall in the first period does not look very decorative, because a large area is occupied by felt, which is usually of black or dark gray color. However, thanks to a microcapillary structure of the felt and light substrate, the plant roots receive optimum amount of oxygen and the root system growing in such conditions allows plants to form strong, healthy foliage and go in the generative phase of development quickly, which is important for flowering plants.

Substrate is a very light and well aerated blend aimed to provide plant nutrition during the first period of adaptation in the future to smooth out fluctuations in humidity of phytocarpet. The composition of the substrate can be about such: fibrous peat, vermiculite, coconut fiber, sphagnum moss, crushed charcoal in the ratio (by weight) 1:0.2:0.2:0.5:0.1.



Irrigation system is laid in the form of drip irrigation tubes. Typically, perforated pipe lays horizontally at the upper edge of the mat. Nutrient solution is pumped on the timer and dropwisely wets the carpet from the top.

The composition of the solution includes 13 major nutrients (nitrogen, phosphorus, potassium, magnesium, calcium, sulfur, etc.) selected in optimal proportions [4, 37, 38]. The composition of the feed solution was developed by P. Blanc in the process of a 30-year experiment with soilless plant cultivation, in addition, he suggested special filters for the automated irrigation system (so that the deposition of calcium carbonate from mineralized water doesn't block the tubes over time) [39]. Excess of moisture drains by gravity and gathers at the bottom. This requires a water tank (if the carpet size is not big) or removal of fluid that sometimes, especially in the indoor conditions, can be quite problematic.

According to some experts, a significant disadvantage of this construction is that pests and diseases spread quickly through the phytocarpets to neighboring plants, and even a small area of lesion is very difficult to remove from felt, some affected roots always remain. In addition, there is a high probability of damaging the felt material, and this leads to the need of structural repair right on the wall. Overall, all this may ruin the aesthetic condition of the green wall for some time [9, 11, 13].

In addition, in the process of operation in terms of indoor use, fungi are actively developing on the surface of the synthetic felt, as well as the evaporation of mineral solutions from the felt surface happens, all this badly affects the sanitary condition of the air [10].

However, this construction has absolute advantage: it weighs only 30–35 kg per 1 m<sup>2</sup> and a thickness of about 5–10 cm. Only carpet phytowalls allow to green irregular vertical area, such as columns. In addition, by eliminating the traditional substrate – soil, which have a large mass, reduce the expenses associated with its transportation.

Many experts note that the plants which are planted in felt pad don't need traditional care [12, 35, 38]. In our experience, care really comes down to low-cost procedures, trimming and forming, periodic washing of leaves, foliar feeding, treatment against pests and diseases (Table 1).

To create a “carpet” phytosystem modern material Epiweb can be used. This material on 70% consists of recycled plastic polyethylene terephthalate. Epiweb is one of the best materials available on the market for creating phytowalls. It is hygroscopic, does not rot, does not decompose under the action of ultraviolet light, chemically neutral. Epiweb holds the moisture (up to 76% of body weight) and has a neutral gray color. It is important for designers creating color compositions. The material thickness is 20 mm. Roll material Epiweb is a complete basis for the roots of plants, it is possible to cut independently or sew on little pockets to fix the plants. The plants easily root in it. Plasticity but also rigidity and stability of the material allow to create variety of forms [10].



**Table 1.** A comparison of two basic technological principles of the organization of living Wallson Key parametrs.

	Carpet by Patrick Blanc	Modular	Potted "Agostini"
The proportion of plants	35-50 кг/м.кв.	45...95 кг/м.кв.	35...92 кг/м.кв.
Term of achievement mature after planting of decorative compositions in a medium interior illumination	20-45 days	30-45 days	15-30 days
The presence on the market structural elements and components	+ -	+ -	+ -
East installation	+	+	+
The need of automatic irrigation and drainage tray	Necessery	In some model eou can do without	In some model eou can do without
Easy planting	-	+	+
Planting density	35...45 pca/m.	40...55 шт./м.кв.	30...81 шт./м.кв.
Stress resistance	-	+	+
gidroponic/soil	+ / +	+ / +	+
Demand (frequency) to the care treatments	once in tens days	once in tens-fifteen days	once in tens-fifteen days
Phytoncide activity and cltans the air	+ -	++	+
Ease of replacement plants	-**	+	++
<p>*There is information that carpeted vertical gardens hydroponics may be used only outside residential areas, as when used wet the surface of the substrate evaporates water together with chemical elements of the nutrient solution, which can negatively affect people's health. In addition, a large area of the wet Mat can accommodate various fungi, which can produce toxic or bad-smelling volatile compounds.</p> <p>** With the exception of technologies with pockets in the skirt. (нап. <a href="http://vertiflor.com/">http://vertiflor.com/</a>)</p>			

## 4 Conclusions

There is an enormous potential in creating green vertical structures in modern cities, which is implemented using the latest constructions and systems of the Russian and international companies.

The most simple, affordable, replicable and close to practical implementation in the indoor conditions are modular-type constructions like *versa wall* by Gsky company (USA) and different variations of modular hydroponic systems like "Lafasad" (Russia). They are not difficult to install, mobile, require a minimum energy (except the systems of illumination of plants, if applicable). The most important thing is that the installation of these structures is possible even where such green areas were not originally planned.

"Carpet" technology is simple in implementation and operation as well, especially on small areas. However, in cases when a green area is more than 2 square meters the implementation of this technology is limited by the complexity of the organization of drainage and underdevelopment of the components market in Russia. While taking the decision about its installation, should be considered more factors (drainage, sealing of

the back wall, cleaning of the floor after using a “soil” substrate), but benefits such as less weight and a smaller lateral thickness are not always taken into attention as strong selection criterions.

The use of new technologies in the creation of green walls, such as micro drip irrigation system, synthetic biomats like *hygrolon* and *epiweb*, complex biomineral fertilizers for hydroponics, new synthetic components of substrates (zeostrat, etc.) enhances the use of various types of phytowalls and helps to adapt them to different conditions and operating modes.

The use of technology for growing plants in vertical plane doesn't only create comfortable, beautiful and environmentally friendly space, but also contributes to sustainable development of the city ecosystem, which is especially needed in the urban development of megacities, when other type of landscaping is often impossible because of the lack of horizontal area.

From the point of view of phytowalls operating in the open “ground” in the middle Russia, there are a number of scientific and technical issues to be explored and solved. Most suitable for practical application are “potted” or “containerized” phytowalls like Verticalsad constructions. Box-container that holds the root system should be large enough and therefore not so susceptible to temperature changes and atmospheric phenomena. Although until now the range of plants with frost resistant root system are not matched, especially which are also suitable for growing in the carpet or modular structures. Research for identification of reasons for the degradation of many plant species when growing in phytowalls and search for new types, growing well on vertical structures should be carried out. Also need to improve the sensors that would remotely monitor humidity, temperature and other parameters of substrate and nutrient solution to facilitate maintenance.

“Live” walls is a relatively new technology and is currently on the market, so their price varies depending on the execution at about \$ 800–1500/m<sup>2</sup>. In addition, many organizations after the installation of these systems decide to include in the operating cost of about 8,000/year \$ for the care of plants and services, which include pruning of plants or striping, fertilizing, plant health, etc.

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# Spatial Heterogeneity of Some Soil Properties of the Botanical Garden of Lomonosov Moscow State University

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**Abstract.** The analysis of the spatial distribution of soil organic carbon (SOC) and the actual acidity of the topsoil of the botanical garden created 65 years ago on the campus of Lomonosov Moscow State University was performed. It has been revealed that the sectors of the botanical garden, differentiated by a set of cultivated plants and a system of agrotechnical practices (arboretum, orchard, flower parterre, etc.) were characterized by significant differences in SOC and pH. Trends in the spatial distribution of these indicators have been revealed, which makes it possible to estimate the degree of anthropogenic load on the territory.

**Keywords:** Urban soils · Soil organic carbon · pH · Digital soil mapping  
Anthropogenic load

## 1 Introduction

Urbanization is the key trend in modern land use. Urban ecosystems develop in conditions different from the natural environment, significantly affecting the soil cover. Urban botanical gardens are unique artificial ecosystems that compensate for the negative impact of the urban environment and create a high level of biodiversity [1]. In urban conditions, botanical gardens are a refuge for a number of living organisms. They are of great value featuring plant collections and highly fertile soils with relatively low level of contamination [1]. In megacities botanical gardens serve as convenient sites for long-term ecosystem research due to a limited regime of visits and the stability of the territory care. Thus, the study of soils in botanical gardens is a valid task.

Soils of botanical gardens are affected by a number of factors: natural climatic conditions, anthropogenic impact typical for urban areas, and applied agricultural practices. The degree of the impact of these factors varies depending on the location, age of the garden, the use of specific sectors and the duration of anthropogenic impact [11]. The combination of these soil-forming factors determines the variety of soil

properties of urban botanical gardens and allows one to investigate the influence of various factors on soil properties.

The structure of the soil profile, the chemical properties and the composition of the soil biota of botanical gardens differ from the soils of urban forests and parks [2]. The profile of botanic garden soils can be split into three parts: the surface organo-mineral layer; the middle layer, most transformed due to the urban impact; and the lower layer, represented by natural soil horizons [1].

Topsoil characterizes the current state of the territory and can have a variable composition, defined by the applied agricultural practices, as well as the origin and properties of the material brought to the location. In botanical gardens it can be represented by the material of the urbic horizon or of the natural weakly disturbed humus-accumulative horizons, compost-peat mixes, etc. Thus, a high variety of properties of the surface layer, in particular, pH and organic matter content, which can be considered as a criteria of quality of the urbanized territory, may be observed in soils of botanical gardens [3].

In most cases, the pH of urban soils is higher than that of natural soils in the taiga forest zone [4, 5]. This is due to the use of carbonate-containing materials in house-building, industrial wastes, soil contamination with surface runoff and dust-borne anti-ice reagents, salts and oxides of heavy metals and liming [3–5]. The pH values under these conditions decrease with depth.

In the deeply disturbed soils of botanical gardens, the middle part of the profile, often slightly alkaline, has the maximum pH values, while the upper and lower parts of the profile have lower values. There is also a directly proportional correlation between the depth of the maximum pH value and the duration of cultivation [1]. Thus, the study of pH of soils in botanical gardens is of great interest in terms of analyzing the intensity of modern aerial fallout.

Accumulation of organic matter in the city depends on the other factors. On the one hand, the content of organic matter increases because of the organic pollutants of complex composition [6]. They get into the urban soil both in the form of thin aerial particles, and with garbage [4]. Among aerial fallout, carbonaceous particles, soot and other products of incomplete combustion of solid and liquid fuels are of the greatest importance [7]. Organic garbage includes food waste, sewage sludge, plastic [8]. In addition, urban soils are enriched with carbon as a result of slowing the mineralization of plant residues under the influence of heavy metal contamination [8] and increasing the productivity of vegetation due to the specific urban climate (higher temperatures), high carbon dioxide content in the air, and care of green plantations [7].

On the other hand, the carbon content decreases as the result of reducing carbon stocks of microbial biomass (because of the soils thickening due to construction and high recreational loads); lower return of carbon to the soil (due to cleaning lawns from leaves in the autumn period) and lower fertility of urban soils in response to severe chemical contamination [9–11].

In comparison with background soils an increase in organic carbon content is often observed in urban soils in the taiga forest zone. The content and properties of organic matter depend on the type of functional use [4, 5, 7].

The purpose of this study was to investigate the distribution of soil organic carbon (SOC) content and the water pH of the soil surface layer of the Botanical Garden of Lomonosov Moscow State University on Vorobyovy Gory.

## 2 Objects and Methods

The study area was a part of the territory of the Botanical Garden of Lomonosov Moscow State University on Vorobyovy Gory with an area of about 20 ha. The order of the Rector of Lomonosov Moscow State University on the Foundation of the Botanical Garden was signed on October, 6 1950 and the main activities on territory: planning and planting, were conducted in 1951–1953.

The study was conducted in 2016. The sampling covered several sectors: an Arboretum; an Orchard; “Rare Plants of Central Russia” (hereinafter “Rare Plants”); “Useful and Medical Plants;” “Decorative Plants” (hereinafter referred to as “Flower Parterre”); “Display of decorative decoration methods;” and part of a Forest Protective Belt (Fig. 1).

The soil texture of all sectors was medium- and heavy-loamy with the exception of the “Flower Parterre” section with light-loamy soils, where regular grits of coarse-grained ( $d > 1.5$  mm) river sand were common [2]. The soil forming material of the territory was a mantle of silty clay and loam with inclusions of brick, glass, coal, wood, etc. Anthropogenic inclusions were distributed unevenly both in the area and in soil profiles. The thickness of the filled grounds varied from 0 cm to 120 cm [2] and was not homogeneous within the same sector. The topsoil thickness was also heterogeneous within the sectors and ranged from 15 cm to 40–50 cm.

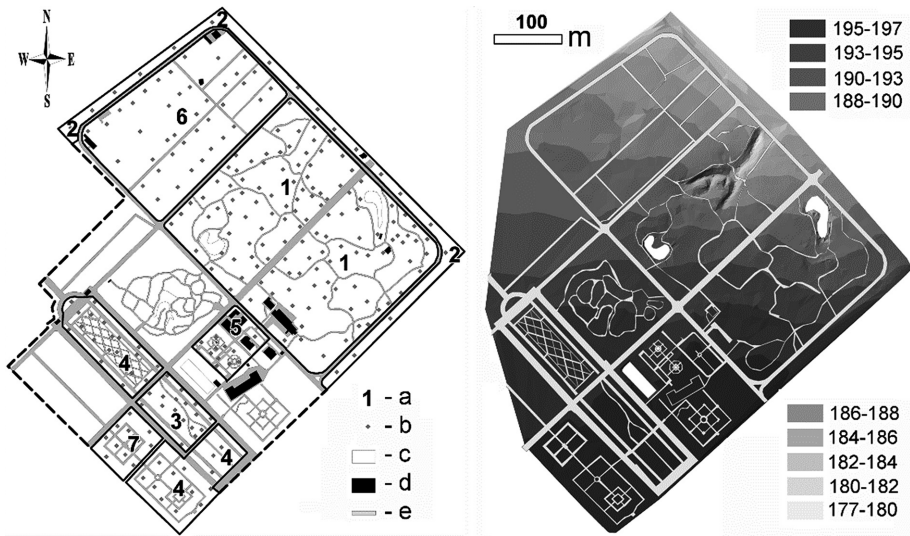
The selected sectors had different sets of cultivated species and agrotechnical practices of soil treatment, different elevations (Fig. 1).

For further analysis, 255 samples of the topsoil horizons were taken from the depth of 0–15 cm with a soil drill (Fig. 1). Despite the heterogeneity of the topography, the study area was more or less evenly covered by sampling points.

Soil analyses were performed by routine methods: the water pH was determined potentiometrically, the content of SOC was determined by the Tyurin method with a photometric determination of the carbon concentration.

The distribution of the SOC was checked for normality, so average and standard deviations were calculated for each sectors of the botanical garden. One-way ANOVA was done for multiple comparisons of SOC values. To test the applicability conditions, the homogeneity of the variances was preliminarily evaluated. Variances comparison was carried out by the criterion  $F_{max}$ .

The pH distribution does not follow the normal distribution, which was verified by the preliminary analysis, so medians were used to estimate the middles of distributions, and the difference between the percentiles was 0.75 and 0.25 was used to characterize the variability. For multiple comparisons of pH values, there was Kruskal-Wallis ANOVA & Median test applied. The statistical analysis was made with Statistica 10 package. All the hypotheses were tested with a significance level of 0.05, exceptions were described separately.



**Fig. 1.** Study areas (left) and digital elevation model (right) of the Botanical Garden of Lomonosov Moscow State University on Vorobyovy Gory. a – sector number: 1. “Arboretum”, 2. “Forest Protective Belt”, 3. “Rare Plants of Central Russia”, 4. “Decorative Plants” or “Flower Parterre”, 5. “Display of Decorative Decoration Methods”, 6. “Orchard”, 7. “Useful and Medical Plants”; b – sampling points; c – water; d – buildings; e – roads

To create the SOC map, the ordinary kriging method was applied, first order drift was removed. The inverse distances method was applied to create the pH map. The digital elevation model was constructed using TIN interpolation deriving from GPS data. All maps were developed using ArcGIS 10.

Since the study area is located in the central part of the Moscow metropolis, average values for Moscow were used as reference pH values and SOC content, according to Prokofieva et al. [12].

### 3 Results and Discussion

#### 3.1 Soil Organic Carbon

The average content of SOC in the topsoil of the botanical garden was  $2.43 \pm 0.01\%$  ( $n = 244$ ), which was slightly lower than the average values of the urban soils in Moscow.

According to Prokofiev et al. [12] the average content of SOC in urban soils of Moscow lied in the range of 2.7% to 3.3%. The spread of values is significant: the minimum value (0.04%) was observed in the Arboretum, the maximum value (7.65%) was noted in the Orchard (Table 1).



**Table 1.** Statistical characteristics of SOC of the Botanical Garden sectors.

Sector name	Sample size	Average	Variance	Min	Max
“Rare Plants”	17	2.12	0.58	0.8	3.3
“Arboretum”	121	2.23	1.06	0.0	4.6
“Useful and Medicinal Plants”	10	2.50	1.32	0.7	4.8
“Flower Parterre”	31	2.55	1.46	0.7	5.4
“Forest Protective Belt”	15	2.55	0.96	1.1	4.4
“Orchard”	39	2.84	2.34	0.8	7.6
“Display of Decorative Decoration Methods”	11	2.94	2.46	0.2	5.1

ANOVA and LSD-test showed that with a confidence level of 90%, three groups can be identified in SOC content. Arboretum and the sector of “Rare Plants” formed the first group, they were characterized by lower SOC values (2.1–2.2%). The second group - the Orchard and the sector of the “Display of decorative decoration methods” were characterized by the highest values (2.84–2.94%). The remaining sectors took an intermediate position along the average SOC.

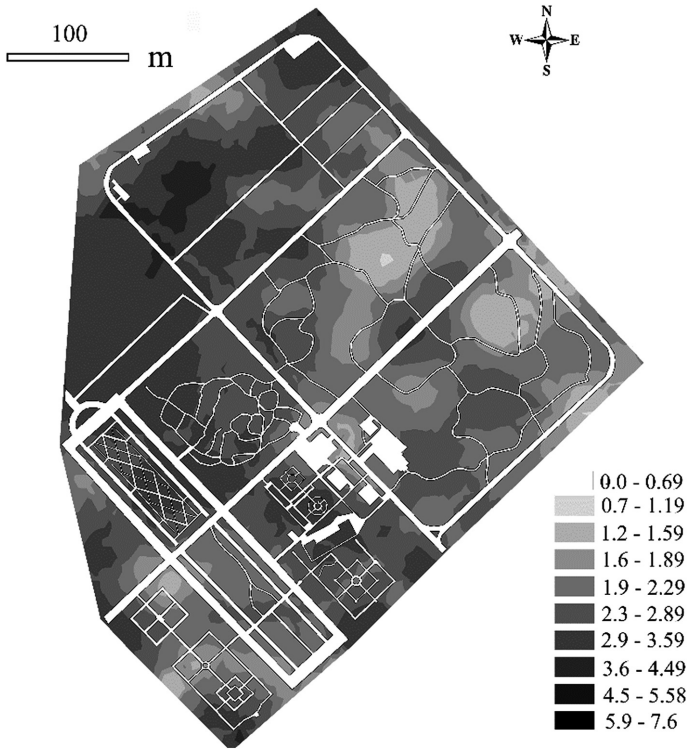
The impact of texture heterogeneity on the SOC content was not detected. The evidence was the fact that the Flower Parterre with the lighter texture was not allocated to a separate group, and got into the third group. Most likely the lighter texture was “counterbalanced” by the regular application of fertilizers and composts.

The first group was formed by sectors where the reservation conditions were conducted. When creating the collection of the Rare Plants sector, the carbonate rubble was used for some plant species as additives to the ground. After the formation of the collection, the agrotechnical activities carried out on the territory of the Arboretum and Rare Plants sector were reduced to the irrigation only in cases of extreme weather conditions. The SOC content in these sectors was comparable, for example, to the soils of the Summer Garden in St. Petersburg (2.0%), the first regular French garden in Russia [13].

The second group united the areas with the most intensive treatment: regular application of nitrogen-phosphorus-potassium fertilizers, watering and usage of compost–peat mixes. The third group was heterogeneous in terms of treatment intensity and periodicity of plants handing. So, for example, plots with regular application of fertilizers and areas of lawn, where fertilizer was not applied, were combined within the Flower Parterre.

SOC varying, judging by the variance, differed by almost 4 times for the extremes and grew in the series: “Rare Plants” - “Forest Protective Belt” - “Arboretum” - “Useful and Medicinal Plants” - “Flower Parterre” - “Orchard” - “Display of Decorative Decoration Methods”. However, these differences are not statistically significant for the given sample sizes.

Analysis of scientific publications showed that these trends were not typical for all botanical gardens of the taiga forest zone [1, 14]. So, the soils of Sprygin Botanical Garden of Penza, were characterized by lower average values of SOC - 1.7%.



**Fig. 2.** Map of SOC content (%)

At the same time, the maximum SOC content in Penza botanic garden was identified in the arboretum, and the area of ornamental plants was characterized by a minimum content: 2.6% and 0.8%, respectively. These results the authors also have associated with the features of the agrotechnical treatment: regular weeds removal and no fertilization in the area of ornamental plants [15]. Similar trends of SOC decreasing in ornamental plants sector in comparison with arboretum were found in botanical garden of the Far Eastern branch of the Russian Academy of Sciences in Vladivostok: 4.7% and 5.1%, respectively [16].

Figure 2 shows the SOC content map. The prediction error in the areas, where sampling was performed, was on average 0.45%.

Comparative analysis of SOC content map and of the digital elevation model of the Botanical Garden showed that the lowest values were in the ravine slope in the Arboretum. This may be due to the processes of soil erosion. The site of accumulation of material in the lower parts of the slopes and at the bottom of the ravine was not marked on the map, since in these positions samples were not collected because of the reserved status of the site. Areas with the highest SOC content were typical for the western part of the Orchard, where the remains of the fruits yield were traditionally stored before being removed for disposal.

### 3.2 pH

On average, the topsoil of the Botanical Garden had a neutral reaction: the median for pH was 6.67, which corresponded to the lower boundary of the surface horizons of urban soils in Moscow: pH values from 6.7 to 7.5 [12]. The minimum values of pH correspond to the natural background soils [17] and were confined to the weakly disturbed area - the preserved upper part of the ravine in the Arboretum. The maximum values of pH were found on the sector of Rare Plants, where, as already noted, carbonate crush-rock pad was done.

**Table 2.** pH values of soils of the botanical garden areas.

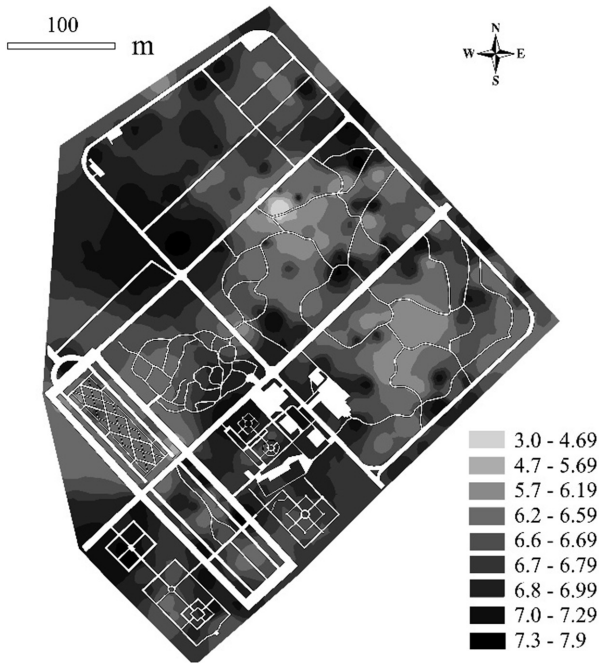
Sector name	Sample size	Median	Percentiles 0.25	Percentiles 0.75	Min	Max
“Flower Parterre”	31	6.51	6.32	6.81	5.06	7.37
“Arboretum”	126	6.60	6.19	6.99	5.47	7.77
“Forest Protective Belt”	18	6.78	6.53	7.01	5.84	7.18
“Orchard”	41	6.79	6.58	7.06	6.17	7.77
“Rare Plants”	17	6.82	6.60	7.06	5.97	7.93
“Display of Decorative Decoration Methods”	11	7.02	6.81	7.21	6.40	7.37
“Useful and Medicinal Plants”	11	7.12	6.76	7.29	6.60	7.70

The pH medians for the soils of the Arboretum and the Flower Parterre (6.5 and 6.6, respectively) differed significantly from the soils of the “Useful and Medicinal Plants” sector with pH value of 7.12. The other sectors occupied an intermediate position (Table 2).

The lower pH values of the topsoil of the Flower Parterre were probably connected to the regular application of sand, wood scraps, and manure. The Arboretum was not exposed to any agrotechnical treatment. Compared to the other sectors the lowest pH values of the Arboretum were identified in the botanical garden of Vladivostok: pH value of 5.2 for Arboretum, pH value of 7.0 for ornamental plants [16].

The sector “Useful and Medicinal Plants” was the smallest in the area of the surveyed sites; there were no natural soils; soil-forming materials were represented by technogenic deposits; fertilizing was done regularly. In addition, it was an open area without woody vegetation capable to acidify the soil.

The sector of Rare Plants was included in the group with average pH values due to the fact that a large part of the soil of the territory lied within the neutral - slightly acidic pH values that was more typical for soils of the South taiga zone; the plants collection was represented in the sector.



**Fig. 3.** Map of pH values

The greatest variance in pH values were found in the Arboretum that was the most heterogeneous in terms of the elevation changes and the soil disturbances. The remaining sectors were characterized by lower pH variability.

Most of the territory featured neutral soils (Fig. 3). The built-up area was located on the site of the Arboretum as it was shown at the map of 1952 [18]. According to previous studies the alkalization of the middle and lower part of the soils profile was typical for this area [2]. However, the spatial distribution of the pH values of the topsoil of the Arboretum did not reflected the impact of the historical land use on the soil cover disturbance. Two large contours with a weakly acid reaction were clearly distinguished in the center of the both parts of the Arboretum, separated by a wide asphalt path. These weakly acid contours followed to the periphery by areas with neutral and slightly alkaline values. Such distribution can be associated with the shielding effect of the Forest Protective Belt and the crowns of trees of the Arboretum.

The largest contour of alkaline pH values was located in the South-Western part of the Orchard and was connected with the peculiarities of landuse of adjacent territory: a place for burning wood residuals was located nearby.

A trend was observed in the pH values of the forest protective belt topsoil: there was a decrease in values from slightly alkaline to neutral from the corner point of the intersection of Universitetsky and Michurinsky avenues, located in the Northern corner of the map. Interestingly, that along the Mendelejevskaya street (along the South-Eastern border of the map) the distribution of values did not have any pattern.

Thus, it was revealed that the aerial transfer of silt particles containing carbonates, the features of technogenic soil-forming materials, and the peculiarities of agricultural practices led to a shift in the pH values towards neutral and alkaline values typical to urban areas. The age of the Botanic garden soils of 50-60 years was not sufficient to ensure that the spatial distribution of topsoil pH reflected the specific character of plant communities, rather than the impact of the urban environment.

## 4 Conclusions

The topsoil of the Botanical Garden of the Lomonosov Moscow State University on the Vorobyovy Hills was under lower anthropogenic loads than the average in Moscow. The average value of pH and SOC content were slightly below the average value of those for urban soils in Moscow, but different sectors were heterogeneous in these indicators and significantly differ from each other. A minimum set of agrotechnical treatments or a complete absence of those has resulted in minimal pH and SOC values. Spatial distribution of pH and SOC values of the topsoil can serve as an indicator of the level of modern anthropogenic impact on the territory.

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# Contrast of Soil Cover as a Factor of Land Suitability for Agricultural Production

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**Abstract.** Urbanization implies an increase in settlements areas at the expense of productive land, primarily, agricultural. In these circumstances, an important issue is the identification and protection of especially valuable agricultural land. In this research we analyzed existing approaches to classification of productive land, its reference to especially valuable land and suggested approaches for consideration of the soil cover heterogeneity in the classification.

**Keywords:** Soil fertility · Contrast of soil cover · Land-capability classification  
Value of land

## 1 Introduction

The Russian land legislation sets a priority for protection of lands as the environment's important component and as means of production in agriculture, and the priority for preserving especially valuable lands, according to which transition of the use of valuable agricultural land to another uses is limited or prohibited. Protection of land implies activities carried out by government bodies, local governments, legal entities and individuals and aimed at preserving land as the environment's important component and as a natural resource.

The value of productive land is determined on the basis of the land-capability classification for agricultural purposes. This grouping based on consideration of soil characteristics that influence their qualities to have similar potentialities and including limitations or hazards.

The international practice demonstrates an example of the US SSURGO (Soil Survey Geographic Database) [1], where land is classified according to its ability to support cultivation and crops growth for a long period of time without depletion. The data about soils in SSURGO is divided into sections and components. Each section

covers one or several components of soil of different agricultural land value. As a result of mapping, the prevailing type of land value on a plot is chosen.

High intra-field variation of soil cover quality under conditions of homogeneous agrotechnological background reduces the yield of agricultural crops and the efficiency of undifferentiated application of technologies by several times.

All possible solutions to this problem are: optimizing the formation of fields and working sites in the order of land management, fertility equalizing, use of agricultural technologies and intelligent agricultural machinery for precision farming will only reduce the negative impact of qualitative heterogeneity of soils, but will not “transform the nature” [2]. The soil cover variegation is a stable, hard-to-regulate factor that reduces the value of agricultural land and requires development of ways and norms for land valuation, taking into account the factor of in-loop variation of soil characteristics, of soil cover contrast degree and soil fertility within the field. Therefore, this factor should be taken into account when classifying land [2].

The purpose of this research is to determine, based on many years of experience, the criteria by which the complexity of soil cover can be taken into account when determining the value of a particular land plot.

## 2 Materials and Methods

Heterogeneous complex soil cover is widespread in all natural zones of Russia. In the European part of the country, more than 20% of the arable land area is occupied by complex soil cover, in the area of gray forest soils – more than 25%, in the forest-steppe zone of chernozems – about 20%, in the dry steppe zone – more than 70%.

Many research and design organizations have studied agricultural lands’ soil cover in the Russian Federation. The main organization carrying out that work for decades was RosNIIzemproekt (with the participation of the authors of this paper), which conducted a systematic research of the soil cover of each plot of agricultural land and of the results of agricultural activities on that land plots.

For the purpose of this research works of a number of authoritative Soviet pedologists [3, 4] were also studied. They researched the contrast and complexity of the soil cover and the influence of that factor on prolificness of agricultural crops.

The main ideas and knowledge on the assessment of soil fertility and its influence on plants growth and development are set in the Methodic Guidelines for Conducting Integrated Monitoring of Soil Fertility in Agricultural Land [5] and in the Methodic Guidelines for State Cadastre Valuation [6].

## 3 Results

The variety of properties (belonging to the genetic subdivision, granulometric composition, degree of erosion, etc.) by which soil cover components can differ causes great difficulties for selection of quantitative methods for contrast assessment.

One of those who first studied the influence of soil cover heterogeneity on production processes in agriculture was Malandin [3]. He proposed to classify the soil



cover microcomplexity (complexity due to the site microrelief) by two main characteristics: 1 - the ratio of soil components and 2 - their contrast and degree of its manifestation.

Currently, while carrying out calculations of the normative crop yield of agricultural crops within cadastral valuation of agricultural land, special attention is paid to assessment of the agroecological contrast of the soil cover of land parcels reflecting the variegation of the crop within the plot. By agroecological contrast we mean presence of components (types of soils) with negative features (for example, excessively moistened, saline, eroded soils, etc.) along with the zonal soils in the soil cover structure of land parcels. In areas with a contrasting soil cover, the normative yield and, ultimately, the unit indicator of cadastral value is determined for each soil type, taking into account presence or absence of a particular soil type's negative properties reducing the yield, and then it is weighed. In a similar way land quality indicators are calculated in works on land classification according to their suitability for use in agriculture.

However, in some cases, such valuation methods can provide significantly over-estimated results, for example, in cases of assessment of land with pronounced microrelief, where, against a background of zonal soddy-podzolic soils of heavy granulometric composition, gleyed (excessively moistened) soils are developed in varying degrees along depressions. The time needed for different soils at such sites to be ready and available for processing and sowing works can vary by 5–10 days or even more. In such cases often the soil in the hollows and saucers happens to be not ready yet while the rest of the area has already dried up. No matter when it is possible to sow spring crops on such a plot, the plants will in any case be in unfavorable conditions.

At the same time, it is well known that well-timed planting dates are in most cases the most important agrotechnical measure to be taken. The delay of this measure due to late ripening of certain contrasting components of the soil cover can sharply reduce the yield of the entire land plot. This means that different lengths of periods of excessive moistening of various soil cover components is itself a negative feature of soil cover at the site, which further reduces the yield of the entire area. Based on the experimental data obtained by Markitantova [4], it has been identified that a day of delay in sowing grain crops reduces their yield by 2% in average.

## 4 Discussion

All mentioned above leads to a logical conclusion that the contrast of the soil cover is an independent factor that must be taken into account while assessing the quality of land, its suitability for use in agriculture and the allocation of especially valuable land. Scientists and practitioners have long noticed that a heterogeneous (contrasting) soil cover reduces the effectiveness of arable farming, since it excludes the possibility of timely application of an optimal agricultural technology for all its components.

The most objective assessment of the quality of land plots with a heterogeneous soil cover structure can be provided by direct calculation and consideration of crop yields, produced with observance of the rules of an experimental case. However, in the conditions of carrying out mass works on land classification or cadastral valuation of agricultural land, such consideration is only lowly accessible.

Taking into account the studied results of earlier research works of different authors and practical and experimental data on the influence of soil cover contrast on the under-field variation in the yield of agricultural crops obtained during land management of agricultural organizations, we can assume that the degree of negative impact of agroecological contrast in land plots' soil cover on agricultural crops yield is determined by two main factors:

1. the ratio (share participation) of soil components.
2. soil components contrast and degree of its manifestation.

## 5 Conclusion

Summarizing the literature review, in order to take into account the contrast of soil cover while allocating land plots with especially valuable productive lands we suggest that an integrated indicator – the proportion of the prevailing component of the soil cover of the land plot (crop rotation, work area, hayfield or pasture area) – may be used. The area of the predominant component should be at least 60% of the total area of the site when soil components of its soil cover are comparatively similar, and not less than 80% when the soil components are represented by variants of different genetic types of soil formation.

Consideration of this criterion when identifying the suitability of a land plot for conducting agricultural activities will increase the objectivity of the method of classifying productive agricultural lands as especially valuable lands, the use of which is prohibited or restricted for other purposes.

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# Spatial Model of Electron-Ionic Concentrations Distribution of in Low-Temperature Air Plasmoid Over Strong Radiation Contamination of Soils and Territories

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**Abstract.** When developing radar monitoring systems for soils and territories in radiation-dangerous urban ecosystems [1, 2], it is often necessary to model the spatial electron-ionic distributions of low-temperature air plasmoids that are formed over highly contaminated soils and territories with radionuclides. Such a model should reflect the unique spatial characteristics of the distribution of electron-ionic concentrations, through which it is possible to reliably identify strong radionuclide contamination of soils and territories. Under the strong radioactive contamination of soils and territories we understand those, in which even a short stay is deadly on human. Such contamination, for example, can occur, when nuclear reactors are destroyed.

**Keywords:** Monitoring the soils and territories  
Radiation-hazardous urban ecosystem · Air ionization

## 1 Introduction

In this paper we consider a simplified model of contaminated territory, above which a round center of ionizing radiations (above a destroyed nuclear reactor) and elongated elliptical radioactive trace, created in the direction of the wind of distribution and radionuclide subsidence in soils, have been formed. Above this configuration of the territory of radioactive contamination, low-temperature weakly ionized plasmoids are formed in the air. These plasmoids are created as a result of continuous gamma

radiation from radionuclides. Their shape, size and ionization characteristics will depend on the size of the radioactive contamination of the terrain, the flux density of gamma photons and their energy.

Ionization of atmospheric air from radioactively contaminated terrain is not fundamentally steady. In general, electron-ionic concentrations are proportional to the activity (radiation dose rate) of radionuclides distributed on the earth's surface. Spatial-power relationships can take various forms.

The main contribution to the ionization of the atmosphere for this case is made by secondary Compton-electrons produced owing to the interaction of gamma radiation with the air. Beta-radiation is completely absorbed by a layer of air of a few meters high, and alpha-radiation is absorbed by a layer of air of a few centimeters high. Therefore, we can assume that the ionization of the atmosphere is stipulated only by gamma radiation. In the cases of the nuclear reactor destruction over an open reactor zone, intensive neutron radiation will be present, which is absorbed by the air layer of several kilometers high.

The free path length of gamma photon in standard atmosphere depends on its energy and air density and this length is limited to a value of 500–1000 m. Electron-ionic concentrations in the given range of the heights will depend on the flux density of gamma radiation and vary smoothly in accordance with the law of attenuation of gamma radiation by the air layer.

## 2 Materials and Methods

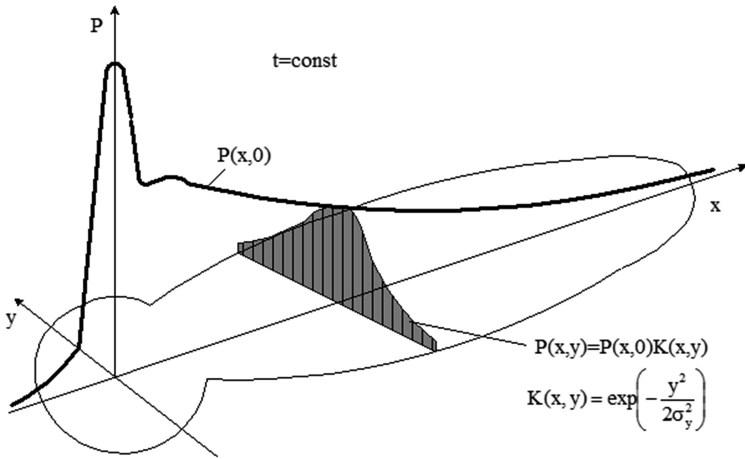
Figure 1 shows the dependence of the gamma radiation dose rate of on the trail of the radioactive cloud on the spatial coordinates on the terrain. In this dependence, the averaged values of the atmospheric wind are taken, which faintly reflect the entire dynamics of settling the radioactive cloud on the soils. However, to simplify the further modeling of plasmoids, these assumptions can be justified, since the uniqueness of spatial characteristics of plasmoids lies in the regularities in the distribution of electron-ionic concentrations from the surface of contaminated soils to heights, at which the ionization of air ceases.

For clarity, the area with contaminated soils near the destroyed reactor can be approximated by a circle with a given radius. In this case, the modeling of plasmoids will be simpler, since in this case the movements of the air masses can be completely neglected.

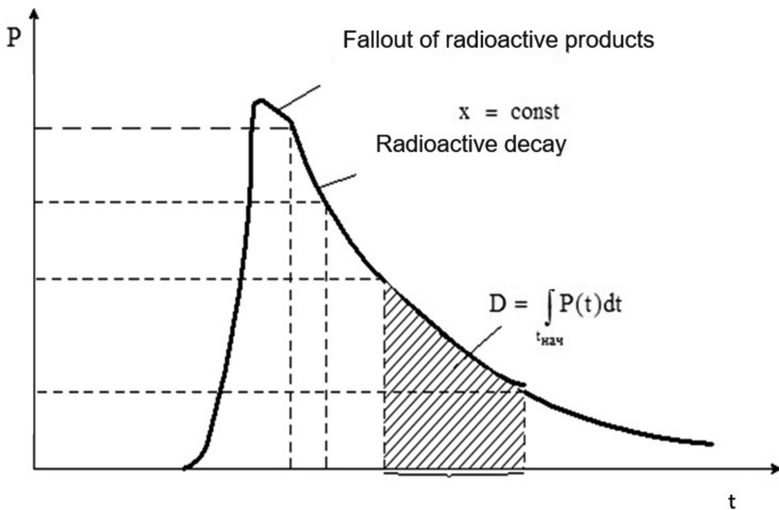
Figure 2 shows the known dependence of the gamma radiation dose rate on the time. This dependence corresponds to the law of radioactive decay and accurately reflects the processes on the trail of the radioactive cloud; these processes were studied in the test nuclear explosions [3]. Despite the different radionuclide composition when compared with radioactive contamination caused by the destruction of nuclear reactors, such a time dependence can only be taken into account in the model without specific time indices.

Considering the fact that the electron-ionic density in the elementary air volume depends on the dose rate of ionizing radiations in the same volume, and the dose rate varies in space according to the graph depicted in Fig. 1, then the conditional form of

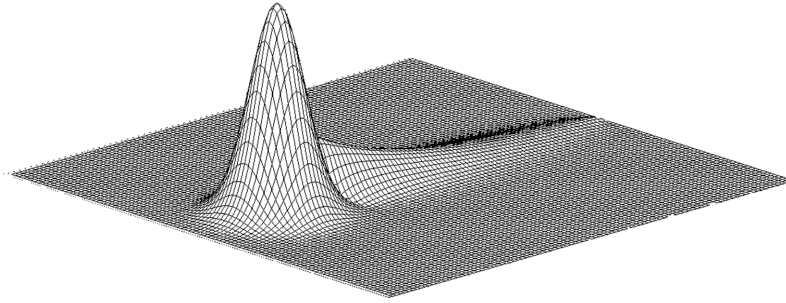
the plasmoid in the space above the radioactive cloud trace, corresponding to the assumptions described above, will take the form shown in Fig. 3. Figure 4 shows a simplified form of the plasmoid for a circular model of the contaminated area near a destroyed nuclear reactor. Such forms are very conventional, since the electron-ionic density inside such plasmoids is distributed unevenly, and this density decreases with height and horizontal distance from the destroyed nuclear reactor.



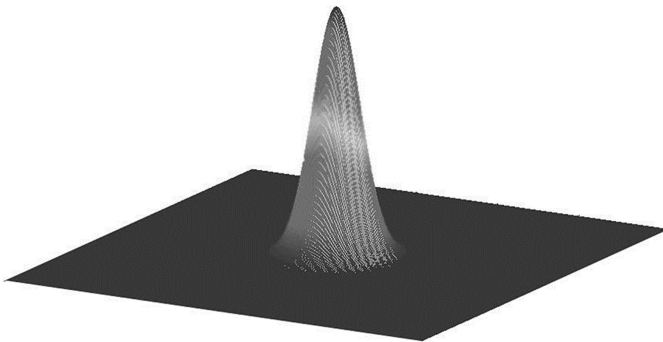
**Fig. 1.** Change in the dose rate of gamma-radiation on the trail of the radioactive cloud.



**Fig. 2.** Change in dose rate of gamma-radiation during the time at the point on the trail of the radioactive cloud.



**Fig. 3.** Conditional form of the plasmoid near the nuclear reactor and above the trail of the radioactive cloud.



**Fig. 4.** Conditional form of the plasmoid for the circular model of the contaminated area near destroyed nuclear reactor.

### 3 Results

To illustrate the internal structure of such a plasmoid, it is necessary to take into account the complex processes of interaction of gamma-radiation with molecules and air atoms.

Figure 5 shows the electron-ionic density in the section of the plasmoid over the destroyed nuclear reactor, obtained by mathematical modeling, taking into account the attenuation of gamma radiation depending on the altitude and the distance. It is believed that the dose rate in each elementary volume of the spatial plasmoid is reduced to one moment of time. The resulting spatial gradient of electron-ionic concentrations has a special practical significance for identifying radioactive contamination of soils and territories with remote sensing radar by secondary characteristics, because it has a unique spatial distribution inherent only in radioactive contamination of the terrain.

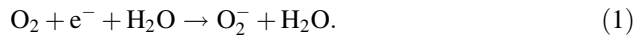
The electron-ionic density in Fig. 5 is of an illustrative nature and this density is denoted in relative units from 0 (natural concentration to perturbation in the atmosphere) to 1 (the maximum electron-ionic density at the surface in the middle of the zone of a ground or low airborne nuclear explosion).

Depending on the nuclear event in the contaminated zones near the destroyed nuclear reactor, the dose rate of gamma radiation can reach 105 R/h. Taking into account the results of [4], where the main plasma-chemical equations for operating the atmospheric plasma with allowance for recombination under the influence of ionizing radiation are shown, it can be identified, that at such high quantity of the dose rate, even with allowance for transient recombination in a dense normal atmosphere, plasmoids with an electron density of  $10^{10} \text{ cm}^{-3}$  are formed. This density corresponds to the resonant frequency for waves in the centimeter range (for the most common radar stations). For electromagnetic waves in the meter range, the resonance frequency corresponds to even lower concentrations. In this case, the vegetation and the upper layers of the soil become transparent. A large number of works are devoted to the study of the principles of propagation of electromagnetic waves in plasmas [5, 6]. Most of these principles are based on modern methods of plasma diagnostics.

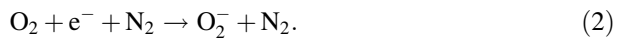
The plasma frequency at an electron density of  $10^{12} \text{ cm}^{-3}$  corresponds to millimeter waves, and the concentration in  $10^{19} \text{ cm}^{-3}$  of particles corresponds to infrared radiation. It is true, that such ( $10^{12}$ – $10^{14} \text{ cm}^{-3}$ ) high values of electron concentrations can reach only under the condition of thermonuclear reaction with a temperature of  $10^8 \text{ K}^{14}$ .

It should also be noted that the distribution of electron-ionic concentrations in air plasmoids strongly depends on the meteorological characteristics of the atmosphere itself. Thus, when the humidity in the atmospheric air changes, where the radionuclide plasmoids under study are formed, the electron concentration also changes. And with a change in humidity  $q$  in the range from  $10^{-6}$  to  $10^{-1}$  of the mass fraction of air decreases several times [7].

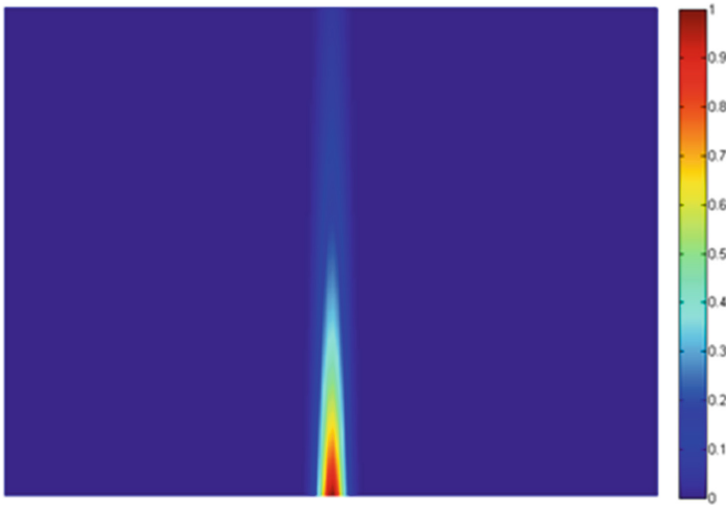
Such a drop in the electron concentration is due to an increase in the contribution to the loss of free thermal electrons because of the triple attachment reaction to molecular oxygen with the participation of water



With a moisture content of more than  $10^{-3}$ , the contribution of this reaction exceeds the contribution of electron loss due to the traditional reaction



In the temperature range from 200 to 1500 K, the electron concentration drop is 10–20 times, and at a higher temperature this drop is only 4–8 times. This is due to the fact that below 1500 K the dominant process of electron concentration formation is direct ionization of atmospheric components, the velocity of which is practically independent of the moisture content. In the conditions of temperature above 1500 K, the rate of electrons detachment from certain negative ions depends on the moisture content.



**Fig. 5.** Electron-ionic concentration in the plasmoid near a destroyed nuclear reactor.

## 4 Conclusion

A spatial model of the distribution of electron-ionic concentrations at a low-temperature air plasmoid, formed over strong radioactive contamination of soils, reflects the unique properties that will help to reliably identify strong radionuclide contamination of the soils and the territories with appropriate processing in remote sensing systems.

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# Ecotoxicological State of Urban Soils of the Arctic with Different Functional Load (Yamal Autonomous Region)

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**Abstract.** Soil chemical properties are essential for the functioning of soils in the polar biome. This study aimed to evaluate ecotoxicological state of urban soils of Yamal region. At 17 sites 39 soil samples were collected and analyzed. Trace elements were detected with X-ray fluorescent analyzer “Spectroscan-MAX”. The values obtained were compared with the Approximate Permissible Concentrations and Maximum Allowable Concentrations adopted in Russia. The highest median values for Cu were found in Kharp, for Pb - in Aksarka and Labytnangi key plot, for Zn and Ni – in Nadym. Calculated *p* values for Cu, Zn, Ni, and Mn are lower than 0,05 significance level. Pb contents showed no significant differences. Statistically significant differences in Ni and Cu contents in soils were found only between Kharp and each of the rest settlements. Predicted Arctic warming will lead to degradation of permafrost, which could affect the rates of accumulation, transformation, translocation, leaching and transportation of trace elements and other pollutants within the permafrost-affected landscapes.

**Keywords:** Trace elements · Settlements of Yamal · Urban environments

## 1 Introduction

The functioning of the polar biome strongly relies on its soils. The geochemical regime directly connects soils with their function as agent for accumulation, migration and transformation. In addition, soils play very significant role for various ecosystem services [8]. In fact, Trace metals naturally present in parent materials and soils occurring mainly in the form of oxides, carbonates, sulfides and silicates [3]. Trace metals are considered as one of the major anthropogenic contaminants in soils. A number of studies, showed that trace metals sources in the high Arctic can have both anthropogenic and natural origin [1, 2, 4, 11, 13, 16]. Metallurgical and energy industries are usually accompanied by the emission of acid-forming substances. These substances can be transported over long distances and can contribute leaching of such labile elements as aluminum, cadmium, zinc [10].

Studying of pollutant behavior in both urban and natural soils seems to be one of the most important issues for investigations in further decades. Such investigations could be used for making accurate risk assessments concerning such aspects as human health and

long-term ecological effects. Approaches to establishment of limit values and identifying priorities concerning the remediation of contaminated sites could be also developed [7]. Data concerning the trace elements content in soil of the Arctic is limited and should be state as insufficient. Evaluation of anthropogenic impacts on Arctic ecosystems requires not only background levels of trace metals, but also landscape distribution of elements in permafrost-affected soils in relation to soil properties [3].

## 2 Materials and Methods

This study was conducted on the territory of Yamal autonomous region within the settlements - Aksarka, Kharsaim, Kharp, Labytnangi, Salekhard and Nadym. Soil classification was conducted according to “Classification and diagnostics of Russian soils” [15] and World Reference Base for Soil resources [18] (Table 1).

**Table 1.** General field information on studied key plots.

Key plot	Geographical coordinates	Functional zone/landscape description	Name of the soils in WRB (2014); Russian soil classification system (2008)
Aksarka	N 66°33′ 54,3″ E 67°48′04,8″	Recreational functional zone	Urbic Technosol; Urbanozem
Kharsaim	N 66°35′ 54,7″ E 67°18′34,2″	Recreational functional zone	Urbic Technosol; Urbanozem
Salekhard	N 66°33′ 31,9″ E 66°34′07,2″	Residential functional zone	Urbic Technosol; Urbanozem
Labytnangi	N 66°40′ 01,1″ E 66°20′59,6″	Industrial functional zone	Urbic Technosol; Technozem
Kharp	N 66°48′ 34,0″ E 65° 47′ 08,0″	Industrial functional zone	Urbic Technosol; Technozem
Nadym	N 65° 32′ 39,9″ E 72° 28′ 56,4″	Town and surroundings	Histic Cryosol; Eutrophic peat soil underlain by permafrost

Ecotoxicological state of Russian Arctic cities is underestimated. That is why this study was aimed to investigate trace metals content in soils of both Yamal and Murmansk urban environments, and to deduce profile trends of distribution trace metals in permafrost-affected soils of studied urban areas. During the investigation 17 sites in

Yamal region were studied and samples were taken from a depth of 0–5 cm and 5–20 cm (in southern Yamal) and from the whole soil profile in Nadym. Soil samples have been collected in industrial (Labytnangi, Kharp), residential (Salekhard), recreational functional zones (Aksarka, Kharsaim, Nadym). Laboratory analysis was conducted in the Komi Scientific Centre Laboratory of the Russian Academy of Sciences. Trace elements contents (Pb, Cu, Ni, Zn, Mn) were determined with an X-ray fluorescent analyzer “Spectroscan-MAX”. The values obtained were compared with the permissible concentrations and maximum allowable concentrations adopted in Russia named in GN 2.1.7.2511-09, GN 2.1.7.2041-06 and SanPin 42-128-4433-87 [5, 6, 14]. Statistic was conducted according [12].

### 3 Results and Methods

Results on trace elements content for investigated key plots in urban environments of Yamal region are summarized in Table 2 and compared with maximum allowable concentrations for sandy-loamy soils [5, 6]. The highest concentrations for Cu were found in the Kharp key plot which seems to be caused by existing chrome-processing factory. The highest median values for Pb were found in soil samples from Aksarka and Labytnangi key plots. The highest median values for Zn and Ni were found in soil samples Nadym key plot. This can be explained by geological origin and high regional background concentration element for this trace element [9].

As it was discussed previously natural soils of Yamal region show usually the highest contents of trace elements occur in Histic topsoil horizons or on the biogeochemical barriers (which can developed on the active layer-permafrost border or in redoximorphic conditions) [17].

Chemical elements concentrations were analyzed at least in triplicate ( $n = 3-6$ ). Calculated mean concentrations were provided with standard deviations ( $a \pm b$ ). One-way ANOVA was used in order to identify relationships between obtained data. This method is based on estimation of the significance of differences of the average values between several independent groups of data combined by one factor. Fisher LSD test was used for detailed evaluation of averages differences significance. Differences were considered to be significant if  $p < 0,05$ . All calculations were done in STATISTICA 10.0.

The most contaminated soils were located in Kharp settlement (exceeding on maximum allowable concentrations for Ni, Zn and Cu). This could be related to intensive mining activity and transportation of excavated grounds in surroundings of this settlement. Exceeding of Ni maximum allowable concentrations was fixed also for topsoils of Nadym city, accumulation of Pb and Zn was fixed also for Kharsaim settlement. So, moderate contamination is typical for topsoils of Nadym and Kharsaim, while strong and deep pollution evident for Kharp settlement.

Obtained probabilities for One-way ANOVA revealed statistically significant differences between concentrations of chemical elements analyzed in soils of urban sites (Table 2). Calculated  $p$  values for Cu, Zn, Ni, and Mn are lower than 0,05 significance level. Pb contents showed no significant differences. Significance of differences for each analyzed chemical element was additionally checked using Post Hoc Fisher LSD test.

**Table 2.** Trace metals content in soils of studied urban areas, mg kg<sup>-1</sup>

ID/Soil horizon (depth, cm)	Cu	Pb	Zn	Ni	Mn
<i>Kharsaim</i>					
Km1/O (0–5)	10.5 ± 1.1	36 ± 7.6	143 ± 35.6	13 ± 1.4	599 ± 83
Km1/G (5–20)	8 ± 0.5	7 ± 01.2	27 ± 4.9	16 ± 4.2	538 ± 74
Km2/O (0–5)	1.6 ± 0.2	2.3 ± 0.5	5.7 ± 1.1	4 ± 0.8	339 ± 61
Km2/Gtur (5–20)	1.6 ± 0.1	2.3 ± 0.6	5.4 ± 0.9	4.4 ± 0.7	87 ± 17
<i>Aksarka</i>					
Aks1/O (0–5)	3.8 ± 0.3	4 ± 0.8	11.6 ± 3.1	8.3 ± 2.6	262 ± 44
Aks1/G (5–20)	9.1 ± 3.2	7.6 ± 0.9	25 ± 5.7	15 ± 4.9	392 ± 52
Aks2/O (0–5)	5.5 ± 1.2	10 ± 0.9	17 ± 6.9	12 ± 2.8	425 ± 69
Aks2/G (5–20)	6 ± 0.1	150 ± 29.6	17 ± 6.9	14 ± 1.5	419 ± 67
<i>Salekhard</i>					
Sal1/W (0–5)	7.1 ± 0.7	8,9 ± 2.4	27 ± 8.3	9 ± 0.9	497 ± 65
Sal1/C (5–20)	7.5 ± 0.9	8,9 ± 3.7	25 ± 7.4	9 ± 0.9	499 ± 71
Sal2/W (0–5)	6.3 ± 0.8	6,2 ± 0.7	20 ± 6.6	10 ± 3.9	649 ± 93
Sal2/C (5–20)	7 ± 1.5	6,7 ± 0.6	24 ± 6.6	11 ± 3.8	1520 ± 245
<i>Kharp</i>					
Kh1/W (0–5)	73 ± 8.5	7,9 ± 0.9	56 ± 11.1	50 ± 11.1	1745 ± 311
Kh1/C (5–20)	80 ± 12.5	3 ± 0.5	46 ± 14.7	19 ± 2.1	1886 ± 356
Kh2/W (0–5)	74 ± 10.8	4,2 ± 0.7	49 ± 16.9	28 ± 3.2	1799 ± 374
Kh2/C (5–20)	86 ± 15.6	3,9 ± 0.8	49 ± 11.3	30 ± 1.1	557 ± 79
<i>Labyangani</i>					
Lab1/W (0–5)	9 ± 3.4	9,1 ± 1.6	31 ± 10.4	13 ± 0.9	402 ± 42
Lab1/C (5–20)	6 ± 1.9	6,1 ± 0.7	19 ± 3.9	10 ± 0.9	449 ± 45
Lab2/W (0–5)	6,2 ± 0.8	6,6 ± 0.7	19 ± 3.9	9 ± 0.6	1632 ± 288
Lab2/C (5–20)	7,4 ± 0.9	7 ± 1.1	21 ± 2.4	12 ± 0.9	1432 ± 221
Lab3/W (0–5)	9,5 ± 2.7	7,3 ± 1.1	27 ± 3	17 ± 2.4	456 ± 64
Lab3/C (5–20)	11,2 ± 3.2	7,7 ± 0.9	28 ± 3	17 ± 2.4	476 ± 65
<i>Nadym 16-1</i>					
O 0–3	15,05 ± 4.2	1,40 ± 0.2	57,37 ± 13.7	6,83 ± 1.1	165,35 ± 23.4
TO <sub>1</sub> 3–15	14,70 ± 3.6	1,30 ± 0.2	45,87 ± 10.3	8,81 ± 2.2	304,54 ± 45.6
TO <sub>2h</sub> 15–30	7,75 ± 1.3	2,15 ± 0.9	50,70 ± 10.6	9,65 ± 1.5	293,75 ± 35.9
TO <sub>3</sub> 30–50	18,57 ± 6.8	5,15 ± 0.8	87,46 ± 14.4	11,99 ± 3.9	310,59 ± 53.6
Permafrost 50↓	–	–	–	–	–
<i>Nadym 16-2</i>					
O 0–3	9,8 ± 3.2	3,9 ± 1.3	46,5 ± 12.8	28,8 ± 5.1	397,8 ± 68.5
TO <sub>1</sub> 3–18(20)	16,3 ± 4.6	3,5 ± 1.3	59,4 ± 14	23,8 ± 3.2	583,7 ± 3.2
TO <sub>2h</sub> 18(20)–35	10,1 ± 2.1	3,9 ± 1	71,2 ± 22.6	10,5 ± 0.9	300,3 ± 3.4
Permafrost 35↓	–	–	–	–	–

(continued)

**Table 2.** (continued)

ID/Soil horizon (depth, cm)	Cu	Pb	Zn	Ni	Mn
<i>Nadym 16-3</i>					
O 0–3	3,2 ± 0.2	8,9 ± 0.7	48,8 ± 9.6	21,7 ± 3.9	195,9 ± 33.5
TO <sub>1</sub> 3–15	3,5 ± 0.3	8,9 ± 0.7	45,1 ± 10.8	19,4 ± 7,1	148,7 ± 29.2
TO <sub>2h</sub> 15–50	3,5 ± 0.2	6,2 ± 1.1	46,8 ± 11.7	17,3 ± 8.6	149,4 ± 27,6
Permafrost 50↓	3,4 ± 0.2	6,7 ± 1.4	43,9 ± 10.4	10,8 ± 7.1	214,8 ± 35,4
<i>Nadym 16-4</i>					
O 0–3	–	–	–	–	–
TO 3–10(15)	7,3 ± 2.2	2,2 ± 0.3	35,7 ± 11.1	14,2 ± 4.4	105 ± 11.9
TO <sub>2h</sub> 10(15)–35	7,4 ± 1.4	2,2 ± 0.3	38,4 ± 12.5	17,4 ± 2.7	285 ± 45.1
Permafrost 35↓	–	–	–	–	–
<i>Nadym 16-5</i>					
O 0–3	–	–	–	–	–
TO <sub>1</sub> 15–35	14 ± 1.8	4,6 ± 0.7	31,1 ± 10.1	26,2 ± 4.3	821,7 ± 112.5
TO <sub>2h</sub> 10(15)–35	12,3 ± 5.9	3 ± 0.6	38,1 ± 8.9	14,9 ± 5.6	264,8 ± 65.1
Permafrost 35↓	8,9 ± 3.8	2,5 ± 1.1	40,4 ± 5.3	13,2 ± 1.1	153,2 ± 41.5
<i>Maximum allowable concentrations (MACs) [4, 5]</i>	<b>33</b>	<b>32</b>	<b>55</b>	<b>20</b>	<b>1500</b>
<i>ANOVA, P</i>	<b>&lt;0,05</b>	<b>0,06</b>	<b>&lt;0,05</b>	<b>&lt;0,05</b>	<b>&lt;0,05</b>

The results show that statistically significant differences in Ni and Cu contents in soils were found only between Kharp and each of the rest settlements.

## 4 Conclusions

The highest median values for Cu were found in Kharp, for Pb - in Aksarka and Labytnangi key plot, for Zn and Ni – in Nadym. Calculated *p* values for Cu, Zn, Ni, and Mn are lower than 0,05 significance level. Pb contents showed no significant differences. Statistically significant differences in Ni and Cu contents in soils were found only between Kharp and each of the rest settlements.

Degradation of permafrost could alter the behavior of trace elements in soils. It will affect the rates of accumulation, transformation, translocation, leaching and transportation of trace elements and other pollutants within the permafrost-affected landscapes. Consequently, ecosystem services provided by urban soils should be investigated in context of predicted climate change.

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# Anthropogenic and Natural Soils of Urban and Suburban Parks of Saint Petersburg, Russia

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**Abstract.** The aim of the present study was to characterize soils and soil cover of urban and suburban parks of Saint Petersburg. Soils were classified according to the Russian soil classification system and WRB 2014. The studied urban soils are characterized by alkaline pH, high concentrations of organic carbon and available phosphorous. The thickness of anthropogenic layers and soil pH were significantly different in urban and suburban parks, while soil organic carbon, available phosphorous and available potassium varied greatly even in the same profile.

**Keywords:** Urban soils · Saint Petersburg · Urban parks · Buried natural soils

## 1 Introduction

Urban and suburban parks are cultural landscapes influenced by human activity. Park development is commonly accompanied by significant purposeful transformation of the initial landscape: filling of depressions, creation of artificial hills and terraces, drainage construction, etc. Natural vegetation is partly or completely substituted by deciduous tree cultivars, ornamental shrubs and lawns. Anthropogenic transformation of soil cover depended on initial landscape features and architecture style and aimed to create and maintain the appropriate edaphic condition for ornamental vegetation as a part of landscape design. In addition, the litter of deciduous trees is richer in biogenic elements and conditions for its decomposition are preferable in comparison with natural coniferous forest, because the drainage promotes not only better aeration but also better heating of soils.

Soils in urban area, including park soils, are subject to trace metal contamination from industrial and traffic emissions. The degree of urban impact on soil cover in different parks depends on their location and size. Numerous studies were conducted on parks and other urban green areas primarily for environmental assessment and contamination control [1]. There are only a few papers where genesis and evolution of park soils were considered [2–6]. The objective of the present study was to characterize soils and soil cover of urban and suburban parks of Saint Petersburg.



## 2 Study Area

Saint Petersburg is situated in the north-western part of Russia. The climate is humid continental, the average annual temperature is 5.8 °C and average annual precipitation is about 660 mm. Its natural conditions correspond to the southern taiga subzone. There are eight landscape regions within administrative boundaries of Saint Petersburg (1439 km<sup>2</sup>). They are distinguished by landform, soil-forming materials and moisture regime [7]. The main part of the city lies on a terraced lowland. The first terrace (0–3 m above sea level) formed by The Littorina Sea (the last stage of the Baltic Sea evolutionary development) several thousand years ago. The historical part of the city is situated on this terrace and is divided by numerous rivers (the Neva and its distributaries, the Fontanka, the Moyka and others). The soils tend to be waterlogging due to the flat terrain and water-bearing surface deposits, combined with the wet climate conditions.

Saint Petersburg is a young city; its history began about 300 years ago, but numerous settlements started in the 17<sup>th</sup> century with areas of arable land along rivers Neva, Fontanka and others.

## 3 Study Sites and Methods

The studied parks were located at the different distances from the city center. These include the urban parks of 18<sup>th</sup> century located in the central part of Saint Petersburg (Polish Garden, Summer Garden, Sheremetev Garden), urban parks of 20<sup>th</sup> century (Internationalists Park, Yablonevy Garden), and the suburban parks of 18–19<sup>th</sup> centuries (Angliiskiy Park, Pavlovsk Park) (Table 1). Morphological description of selected soil profiles (up to 1–2 m deep) was performed. Samples were taken from the identified horizons in the profiles.

Soils were identified using Russian soil classification system [8] considering additions proposed by Prokofieva et al. [9] and according to the World Reference Base [10]. A set of traditional analytical methods was used to obtain chemical characteristics of soils [11]. Organic carbon content was determined titrimetrically by dichromate oxidation, pH was electrometrically measured in an aqueous suspension at a ratio of soil to water = 1 to 2.5; carbonate content was determined using the alkalimetric method, and exchangeable bases content was determined using the complexometric titration method after extraction using 1N NaCl solution. The content of plant available potassium (K) and phosphorus (P) compounds were determined using a 1% solution of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> in a ratio of soil to solution = 1:20, and the pH = 9 – for alkaline soils and 0.2 N solution of HCl in a ratio of soil to solution = 1:5 for acid soils. P was measured photometrically (FEK-3) in an extract tinged with ammonium-heptamolybdate and ascorbic acid reagent. Potassium was determined by photoelectric flame photometry. Exchangeable bases content was determined in the samples that lacked free carbonates (i.e. samples that did not exhibit “fizz” reaction when a drop of 10% hydrochloric acid is applied).

The statistical processing of the results was performed with PAST 3.16 [12].

**Table 1.** Characteristics of studied parks.

Park	Location	Period of foundation	Area, ha	Share of anthropogenic soils, %	Parent materials	Total number of described profiles	№ of profiles*
Sheremetev Garden	59°56′ 11.1′N 30°20′ 45.3′E	the beginning of 18 <sup>th</sup> century	0.75	100	Littorina marine loamy sand	12	1
Summer Garden	59°56′ 41.2′N 30°20′ 08.3′E	1703	11.30	100	Littorina marine loamy sand	13	2
Polish Garden (garden of Derzhavin manor)	59°55′ 07.3′N 30°18′ 37.4′E	the end of 18 <sup>th</sup> century	2.63	100	Littorina marine loamy sand	11	3
Internationalists Park	59°51′ 38.0′N 30°24′ 16.9′E	1985	45.0	80	Varved clay	17	4
Yablonevy Garden	59°51′ 53.7′N 30°21′ 48.2′E	1949	14.8	100	Varved clay	1	5
Angliiskiy Park	59°52′ 55.1′N 29°53′ 00.7′E	1779–1780	176.0	25	Limnoglacial sand and clay, moraine loam	12	6
Kolonistsky Park	59°52′ 37.5′N 29°54′ 30.0′E	1840s	29.0	100	Cambrian clay	10	7
Pavlovsk Park	59°41′ 11.9′N 30°27′ 05.6′E	1777	600.0	30–90 (depends on the area)	Limnoglacial sand, moraine loam, Cambrian clay, alluvial sand	234	8

\*The numbers of profiles presented in the Tables 3, 4 and 5

## 4 Results and Discussion

### 4.1 Soil Cover

Soil cover of the urban parks in the central part of the city (Prinevsky landscape region) consists mainly urbostratozems (Urbic Technosols). The natural soil cover of this area is usually hidden under the cultural layer. The most abundant buried native soils in the central part of Saint Petersburg are grey-humus gley soils (Umbric Gleysols). The parent material for these soils are Littorina marine loamy sand. Traces of the initial

layout of the garden, remains of a fountain on the central walkway and the natural alluvial grey-humus gley soils (Umbric Fluvisols), buried at the depth of 92–94 cm, were found in the Sheremetev Garden.

Anthropogenic soils also predominate in urban parks of 20<sup>th</sup> century. Nevertheless, natural soils (Stagnosols and Gleysols on varved clay) occupy about 20% of area in Internationalists Park. Soil cover of suburban parks usually have significant share of natural soils (Table 1).

#### 4.2 Soil Morphology

There is a series of anthropogenic layers with various amounts of artifacts in the upper part of urbostratozems. Urbostratozems (Urbic Technosols) of Summer Garden have anthropogenic layers with entire thickness of 68–150 cm (p. 2). In Polish Garden the native grey-humus gley soils were also found under anthropogenic layers with entire thickness of 130–145 cm (p. 3). Urbostratozems and stratozems in suburban parks usually have thinner anthropogenic layer in comparison with urban parks (Table 2).

**Table 2.** Characteristics of anthropogenic soils in different parks.

Parks		Thickness of anthropogenic layer, cm	pH H <sub>2</sub> O	Total organic C, %
Urban parks of 18 <sup>th</sup> century (Polish Garden, Summer Garden, Sheremetev Garden)	N	34	178	169
	Mean	115	7.7	2.39
	Median	120	7.9	2.14
	St. dev.	30	0.5	1.53
	Min.	60	6.1	0.17
	Max.	177	8.9	8.72
Urban parks of 20 <sup>th</sup> century (Internationalists Park, Yablonevy Garden)	N	10	32	25
	Mean	82	7.5	2.79
	Median	62	7.4	2.73
	St. dev.	32	0.5	2.09
	Min.	56	6.3	0.12
	Max.	140	8.5	9.77
Pavlovsk Park	N	55	28	28
	Mean	62	6.3	1.83
	Median	57	6.2	2.12
	St. dev.	18	0.8	1.03
	Min.	40	4.9	0.17
	Max.	105	7.8	3.60

St. dev. – Standard deviation

Min. – Minimum

Max. – Maximum

The humus horizon of buried grey-humus gley soils is characterized by dark grey color with a steel shade, and it sometimes contains fragments of roots and stems of marsh plants. The lower horizons are heavily moistened and gleyed. Redoximorphic features expressed in the form of rusty ocher and bluish mottles are abundant with ferrugination along root traces. In the courtyard of the Sheremetev manor (p. 1), buried native soil is located at the depth of 175 cm, and it has a dark brownish-grey humus horizon (31 cm in thickness). The soil forming material is bluish gray loamy sand. Several wooden stakes, charcoal pieces, and an iron pin were found in the humus horizon. Presumably, in the 18<sup>th</sup> century the soil was on the edge of the small harbor of the river Fontanka where boats moored in front of the main entrance.

### 4.3 Selected Chemical Properties of Soils

Anthropogenic soils in all urban parks have alkaline reaction. pH in the soils of urban parks of 18<sup>th</sup> century is higher than the parks of 20<sup>th</sup> century, due to longer period of urban influence (Tables 2, 3 and 4). Generally, anthropogenic soils in suburban parks of Saint Petersburg have lower pH in comparison with soils of urban core (Tables 4 and 5). The content of available phosphorous in studied soils of urban and suburban parks is high; the potassium concentrations strongly varied from high to low, but lower values prevail. The spatial heterogeneity of urban soils was shown previously [13, 14]. The concentrations of organic carbon (SOC) are variable not only in the soils of different parks, but within the same profile (Tables 3, 4 and 5). This observation confirm the previous data by Kovyazin et al. [4] for parks of Saint Petersburg. Nevertheless, the average SOC content (Table 2) is rather similar in different parks. Ufimtseva et al. [15] reported that the SOC content in urban soils of central Saint Petersburg was in the range from 1.70 to 5.32% (mean content is 3.24%). The wide range of SOC content (from 1.6–1.8 to 6.9–8.8%) was also reported for soils of urban parks in Prague and Ostrava (Czech Republic) [16] and for Moscow urban soils (2–7%) [17].

**Table 3.** Selected properties of anthropogenic soils in the parks of 18<sup>th</sup> century located in the central part of Saint Petersburg.

Horizon	Depth, cm	pH H <sub>2</sub> O	SOC, %	CaCO <sub>3</sub> , %	Mobile forms, mg/kg		Particles <0.01 mm, %
					K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	
p. 1 - Urbostratozem on buried grey-humus gleyed soil (Urbic Technosol (Calcaric, Arenic) over Umbric Gleysol (Arenic))							
UR1	0–31	7.4	3.30	0.61	178	170	16
UR2	31–44	7.9	1.76	4.10	92	840	13
UR3	44–64	7.9	1.52	0.87	70	280	13
R1	140–150	8.0	0.72	1.69	N/d		9
UR7	150–160	8.1	0.97	1.14	N/d		12
UR8	160–175	8.0	1.00	2.26	N/d		11
[AY]	175–206	7.9	1.39	0.44	N/d		13
Cg	206–216	7.8	0.16	0.10	N/d		8

(continued)

**Table 3.** (continued)

Horizon	Depth, cm	pH H <sub>2</sub> O	SOC, %	CaCO <sub>3</sub> , %	Mobile forms, mg/kg		Particles <0.01 mm, %
					K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	
p. 2 - Urbostratozem on buried grey-humus gleyed soil (Urbic Technosol (Calcaric, Arenic) over Umbric Gleysol (Arenic, Technic))							
UR1ay	0–18	6.7	4.01	8.8	144	157	23
UR2	18–34	7.2	1.92	4.5	40	146	18
UR3	34–55	7.5	1.63	0.8	32	66	13
UR5	98–118	6.3	0.64	1.1	32	110	10
[AYur]	118–127	7.8	0.93	1.9	32	97	15
Cg	127–140	7.9	2.67	2.6	26	80	15
p. 3 - Urbostratozem on buried grey-humus gley soil (Urbic Technosol (Calcaric, Arenic) over Umbric Gleysol (Arenic))							
UR1ay	0–15	7.2	5.37	2.9	164	203	26
UR2	15–47	7.8	3.17	2.7	132	126	10
UR3rt	47–60	7.9	6.92	4.6	228	168	13
UR4	60–99	8.2	2.67	2.9	320	156	15
UR5rt	99–112	8.3	5.22	4.3	400	151	19
[AY]	155–170	7.7	1.94	1.3	105	696	15
CG	171–176	8.2	0.52	1.5	N/d		14

SOC –soil organic carbon, N/d - Not determined

**Table 4.** Selected properties of anthropogenic soils in the parks of 20<sup>th</sup> century located in the southern part of Saint Petersburg.

Horizon	Depth, cm	pH H <sub>2</sub> O	SOC, %	CaCO <sub>3</sub> , %	Mobile forms, mg/kg		Particles <0.01 mm, %
					K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	
p. 4 - Urbostratozem on buried post-agrogenic soddy-eluvial-metamorphic soil (Urbic Technosol (Loamic) over Stagnosol (Siltic))							
AYur1	0–7	7.2	3.31	3.5	316	128	30
UR1	16–35	7.4	2.73	4.5	173	78	28
UR2 g	45–50	7.4	5.52	4.4	237	125	40
UR3	55–60	7.6	2.09	3.5	221	32	75
[AYpa]	65–75	7.4	3.83	6.0	173	110	56
EL	80–90	7.6	0.58	2.7	149	2	83
BM	110–115	7.5	0.40	2.1	173	15	92

(continued)

**Table 4.** (continued)

Horizon	Depth, cm	pH H <sub>2</sub> O	SOC, %	CaCO <sub>3</sub> , %	Mobile forms, mg/kg		Particles <0.01 mm, %
					K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	
p. 5 - Urbostratozem on buried soddy-eluvial-metamorphic soil (Urbic Technosol (Loamic) over Stagnosol (Loamic))							
UR1	0–5	6.6	3.49	–	332	130	33
UR2	5–21	7.2	3.43	2.0	205	78	43
UR3	21–56	7.2	2.73	1.5	157	108	36
[AY]	56–63	7.1	2.33	1.9	125	108	49
EL	66–72	7.2	0.29	1.5	94	51	50
BM	72–97	7.1	0.41	2.2	125	58	53
C	120–130	7.0	0.12	1.7	141	5	59

SOC –soil organic carbon

**Table 5.** Selected properties of anthropogenic soils in the suburban parks of 18-19<sup>th</sup> centuries.

Horizon	Depth, cm	pH KCl	SOC, %	ΣCa <sup>2+</sup> Mg <sup>2+</sup> mmol(+)/100 g	Mobile forms, mg/kg		Particles <0.01 mm, %
					K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	
p. 6- Stratozem gleyed, underlain by moraine loam (Umbric Glesol (Loamic))							
RY1	0–8	3.9	2.06	6.2	N/d		16
RY2	8–26	4.3	0.80	8.3	N/d		17
RY3 g	26–52	5.7	1.23	15.2	N/d		19
G1	52–74	5.5	0.66	9.0	N/d		25
G2	74–86	5.4	0.22	8.5	N/d		29
p.7 – Stratozem (konstruktozem), underlain by Cambrian clay (Urbic Technosol (Ruptic, Siltic))							
RU1	0–20	4.9	6.69	27.5	225	268	39
RU2	20–28	5.0	10.23	37.1	100	196	40
RY	28–38	6.2	0.76	26.5	75	257	61
RU3	38–48	4.6	3.43	40.8	115	200	35
RYur	55–68	5.3	0.23	4.2	35	240	6
Cg	95–100	5.9	0.17	9.6	75	68	69
p.8- Stratozem on buried alfehumic agrozem (Technosol over Entic Podzol (Arenic))							
AY	0–8	5.1	2.09	6.0	107	89	N/d
RY	15–20	4.7	0.87	3.6	32	38	N/d
[AY]	35–53	6.1	1.10	7.1	10	168	N/d
BF	53–65	6.4	0.35	2.6	10	450	N/d
C	96–120	6.3	0.23	1.8	13	500	N/d

SOC –soil organic carbon, N/d - Not determined

The chemical properties of Saint Petersburg urban soils are rather similar to the properties of soils in other cities. Alkaline pH, increased concentrations of phosphorus in urban soils are typical for urban environment [18].

The light texture of urban park soils in the historical center of Saint Petersburg corresponds to the loamy sand texture of the native parent material. Urbostratozems in Internationalists Park and Yablonevy Garden have the highest percentage of clay due to the properties of parent material (varved clay).

## 5 Conclusion

Soil cover of parks, especially of large suburban parks, is unique natural and anthropogenic phenomenon. There is considerable share of natural soils in the soil cover of large suburban parks. Soil cover of suburban parks in Saint Petersburg varied in components and spatial patterns due to natural pedogenic factors and the history of park development. The anthropogenic soils of suburban parks have thinner anthropogenic layers and lower pH than the soils in urban parks. The study of park soils can contribute to soil conservation and resolving of urban environmental problems.

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# Heavy Metals in Soils and Plants of Arid Zones of Russia

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**Abstract.** The Astrakhan region at the Caspian lowland, characterized by semi-arid climate, is one of the most important regions in the agricultural sector of Russia. However, due to contamination of soils with heavy metals, there is not only a decrease in productivity, but also an increased threat from toxic products. The present study was conducted to analyze the content of heavy metals and their accumulation in irrigated light-brown soils of the arid zones of Russia and the content of heavy metals accumulated in the biomass (stems and leaves) of medicinal and forage plants cultivated in these conditions. The safety or toxicity of these plants was assessed by comparison to the antipollution standards. Results showed the distribution and content of heavy metals in soil horizons: zinc, manganese, nickel and chrome accumulated in the upper layers of soil, strontium in carbonate-illuvial horizons, while lead was uniformly distributed over the soil profile. The role of irrigation in decreasing active forms of certain heavy metals was also noticed. In the study, the selective capability of various plants to accumulate heavy metals was also illustrated.

**Keywords:** Light-brown soil · Heavy metals · Phytomass · Arid zone

## 1 Introduction

The Caspian region is one of the most complex agro-ecological regions in the semi-desert southern regions in Russia. The Caspian region itself is the region adjacent to the Caspian Sea, and is divided into four regions located in Kazakhstan, Turkmenistan, Dagestan, Azerbaijan, Russia and Iran. In Russia, the Caspian region includes two regions – the Astrakhan region and Kalmykia.

The studied region – the Astrakhan region is situated in the south-east of the Eastern-European plain within the Caspian lowland, and features a temperate continental semi-arid climate with cold winters and hot summers. The main economic branches in the regions are the oil and gas industry and chemical industry. The area is rich in chemicals, fuel, energy sources and minerals. Agriculture is also one of the main

contributors to the economy of the Astrakhan region being one of the largest Russian vegetable producers [1].

Despite the importance of the agricultural sector, productivity of natural and cultivated plants in the zone continues to diminish because of low level of precipitation, high moisture evaporation, frequent cases of drought, increased disinflationary area, salinity, loss soil humus and environmental contamination [2–4]. Environmental contamination can be caused by soil erosion of metal ions and leaching of heavy metals and metal evaporation from water resources to soil and ground water [5]. Each year due to climate change and environmental contamination, plants, animals and humans find themselves in new environmental conditions with hardships to adapt [3].

These environmental factors significantly affect the elemental chemical composition of plants [6, 7]. Plants are one of the most sensitive indicators of changes in the environment, and they can also accumulate harmful to animals and humans, concentration of chemical elements. Plants absorb heavy metals from the soil and accumulate them in their tissues or on the leaf surface, becoming an intermediate link in the pathway “soil - plant - animal - humans” [8–10].

The uptake of heavy metals by plants from soil poses the greatest threat [8]. Heavy metals such as mercury (Hg), lead (Pb), zinc (Zn), cobalt (Co), copper (Cu), chromium (Cr), iron (Fe), nickel (Ni), manganese (Mn), cadmium (Cd) etc., with a large atomic weight, have anthropogenic dispersion in the environment and are toxic to living organisms [5, 11]. In animal and human body, with consumed plants (medicinal herbs or feed), a complex of biologically active substances comprising macro- and microelements is absorbed. And along with it, there are possibly toxic chemical compounds. Therefore, the problem of ecological purity of medicinal and food plants is particularly relevant and highlights one of the most pressing problems - reinforcement of the quality control of vegetable raw materials, considering threat from heavy metals [12–14]. Thus, it is necessary to estimate the reaction of plant vegetation to dangerous elements present in the environment [8, 14–16], which is the aim of this study. In this article, we provide the analysis of heavy metals in irrigated soils and in different plants cultivated on these soils.

## 2 Materials and Methods

### 2.1 Study Area

The experimental site was located in the fields of the Caspian Research Institute of Arid Agriculture, located in the southeast of the European part of Russia at the Caspian lowlands. The topsoil contains the light brown alkaline soils. Based on to the sodium content in the plough-layer (4.1% of the sum of alkali absorbed), the studied soil belongs to slightly alkalized soils. Studied plants were also cultivated on the site. Characteristics of studied soils are shown in the following table (Table 1). In Table 1., humus content was analysed by the Tytin method [17], while the concentration of  $\text{NO}_3$ ,  $\text{P}_2\text{O}_5$  and  $\text{K}_2\text{O}$  was determined by the Kirsanov method [18].

**Table 1.** Characteristics of studied soils.

Humus content, %	pH	$\Sigma$ of alkali absorbed, mg-eq./100 g	NO <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O
			mg/100 g soil		
0.91–1.1%	6.7–7.2	18.4–18.7	0.47	2.29	25.03

## 2.2 Soil Sampling

The investigated soils were irrigated up to 30 cm. Soil sampling was conducted in accordance with the state standard of soil sampling with a total and local contamination – GOST 17.4.3.01-83 (Nature protection. Soils. General requirements for sampling), GOST 17.4.4.02-84 (Nature protection. Soils. Methods for sampling and preparation of soil for chemical, bacteriological, helminthological analysis) and GOST 28168-89 (Soils. Sampling) [19–21].

Additional sampling methodology were taken from the Guidelines on agrochemical analysis of agricultural lands [22] and the Guidelines on conducting field and laboratory research for the control of metal contamination [23].

Soil samples were taken twice a year, in the spring (after snow melt) and autumn (during harvest). A mixed sample was composed of at least 5 spot samples taken from the test site. The sampling was performed at regular intervals along the transect in accordance with GOST requirements, adopted in the Russian Federation [19–21].

## 2.3 Plant Sampling

Plant samples were collected at the same sites as the soil samples. For a combined plant sample weighing 0.5–1 kg at natural humidity. Eight to ten points were selected. The combined sample consisted of samples taken from the aboveground plant parts (stems and leaves), collected using a sharp knife.

## 2.4 Heavy Metals Analysis

Assessment of total content of heavy metals was performed by atomic absorption spectroscopy using an atomic absorption spectrometer MGA – 915 [24–26]. For analysis of toxicity, obtained results on the content of heavy metals in plants phytomass were compared with the maximum permissible concentration from the antipollution standards [27].

# 3 Results and Discussion

## 3.1 Salinity and Heavy Metals in Soil

For soils analysis, we firstly studied the qualitative characteristics of soil salinity, given its importance in plants nutrition [6] (Table 2).

Irrigation leads to the accumulation of salts, and their toxicity varies depending on the nature of cations and anions. Results showed that in the upper layer the amount of cation and anions of easily soluble salts increased by 9.31 mEq and 6.71 mEq respectively.

**Table 2.** Qualitative characteristics of soil salinity.

Horizon, cm	$\frac{\text{Cl}^-}{\text{SO}_4^{2-}}$	$\frac{\text{HCO}_3^-}{\text{Cl}^- + \text{SO}_4^{2-}}$	Salinity due to anions	$\frac{\text{Na}^+ + \text{K}^+}{\text{Ca}^{2+} + \text{Mg}^{2+}}$	$\frac{\text{Mg}^{2+}}{\text{Ca}^{2+}}$	Salinity due to cation	Dry materials, %	Soil salinity
A 0-19	21.16	0.04	Chloride	1.80	0.61	calcium-sodium	3.12	alkali soils
AB 19-32	17.08	0.02	Chloride	1.30	1.23	magnesium-sodium	1.87	alkali soils
B1 32-52	17.72	0.03	Chloride	1.95	1.75	calcium-sodium	1.48	alkali soils
B2 52-90	22.50	0.02	Chloride	2.23	1.92	sodium	1.72	alkali soils
B3 90-135	23.41	0.01	Chloride	2.27	1.88	sodium	2.25	alkali soils
B4 135-210	2.15	0.01	Chloride	0.84	0.78	magnesium-calcium	2.34	alkali soils

Chlorine anions have the greatest accumulation in soils of agricultural landscapes. So, its content in the upper layers increases to 18.14 mEq compared with rain-fed soils. With depth, the chloride content is significantly reduced. Also irrigated soils marked a decrease in the amount of sulfate ions. The maximum accumulation of soluble salts of cations observed in the upper layers. The greatest increase observed for the sodium content is by 2,65–11,10 mEq. Magnesium and calcium accumulation is observed in the upper layers of 1,05–3,50 and 0,68–2,64 mEq respectively.

A significant increase of the Mg exchangeable form (from 10–20 to 40–50%) was observed on the background of Na exchangeable form decrease. As part of the exchange cations significant amount of Ca is observed, which is evenly distributed along the profile. In irrigated soils is it increases in the nearly the entire profile, but the maximum accumulation is observed in the upper 50–60 cm (1.5–2 times).

The content of heavy metals in soils was also analyzed, and the results are given in Table 3. The accumulation of the majority of the studied elements in the soils' horizons, as presented in Table 3, can be explained by the high content in these layers of organic matter and clay particles, and also by the high content of Fe and Mn, which oxides and hydroxides are capable of accumulating metals.

**Table 3.** Total content of heavy metals in soils, mg/kg.

Horizon, cm	Sr	Pb + 2As	Zn	Ni	Fe %	Mn	Cr
A 0-19	313	32	61	60	3.65	569	129
AB 19-32	353	27	52	51	3.02	400	82
B1 32-52	348	28	45	48	2.76	395	93
B2 52-90	328	24	48	48	2.9	463	110
B3 90-135	305	27	49	49	3.03	451	110
B4 135-210	333	28	59	55	3.53	459	131
LSD.05	8.3	1.5	2.2	1.2	0.1	77	6.5

The active forms of zinc, lead and nickel, and their dynamics and radial distribution in soils (Table 4) were investigated.

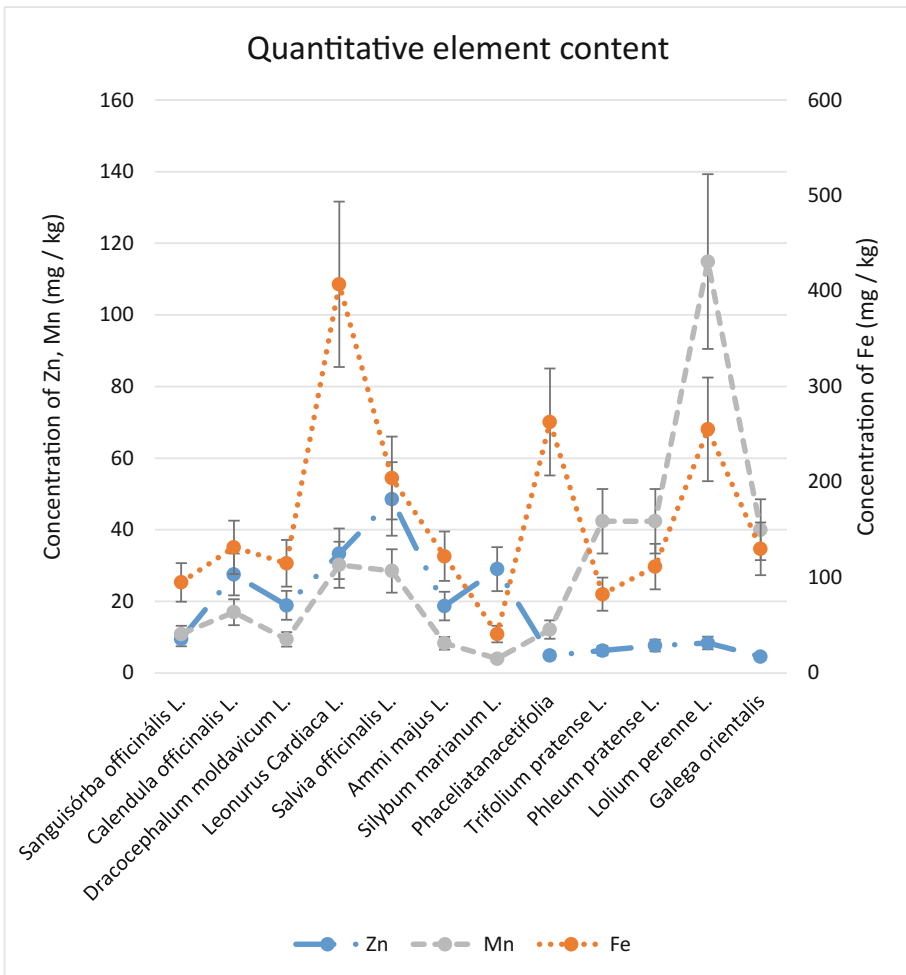
The analyses of active zinc forms, lead and nickel, their dynamic and radial distribution, showed that in irrigated light brown soils active forms of lead and zinc are predominant in the humus-accumulative, transition and gypsic-illuvial horizons. Irrigation leads to zinc redistribution in the upper horizons and soil layers. Active nickel forms in the upper layers of light-brown soils of non-irrigated soils were almost absent and irrigation significantly reduced nickel mobility.

### 3.2 Heavy Metals in Plants' Samples

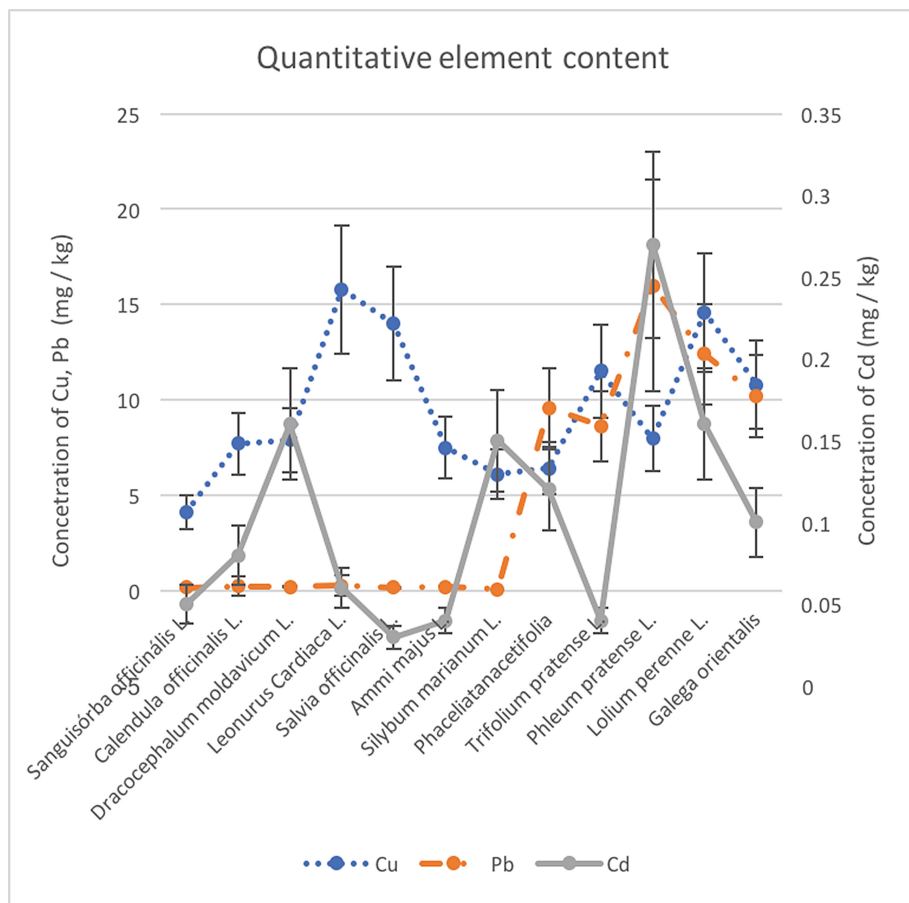
Concentration of Fe, Mn, Zn, Cu, As, Sr, Ni, Co, Cr, Pb and Cd, elements conventionally combined into a group of heavy metals, in plants cultivated on irrigated soils were analyzed by atomic absorption spectroscopy, and the results are given in the following figures (Figs. 1, 2 and 3).

**Table 4.** Active forms of metals.

Horizon, cm	Zn, mg/kg	Pb, mg/kg	Ni, mg/kg
A 0-19	–	–	–
AB 19-32	–	–	–
B1 32-52	1.1	–	–
B2 52-90	3.2	–	0.2
B3 90-135	–	–	–
B4 135-210 (135-145)	2.4	–	–
B4 135-210 (200-210)	–	–	–
LSD.05	0.02		0,001



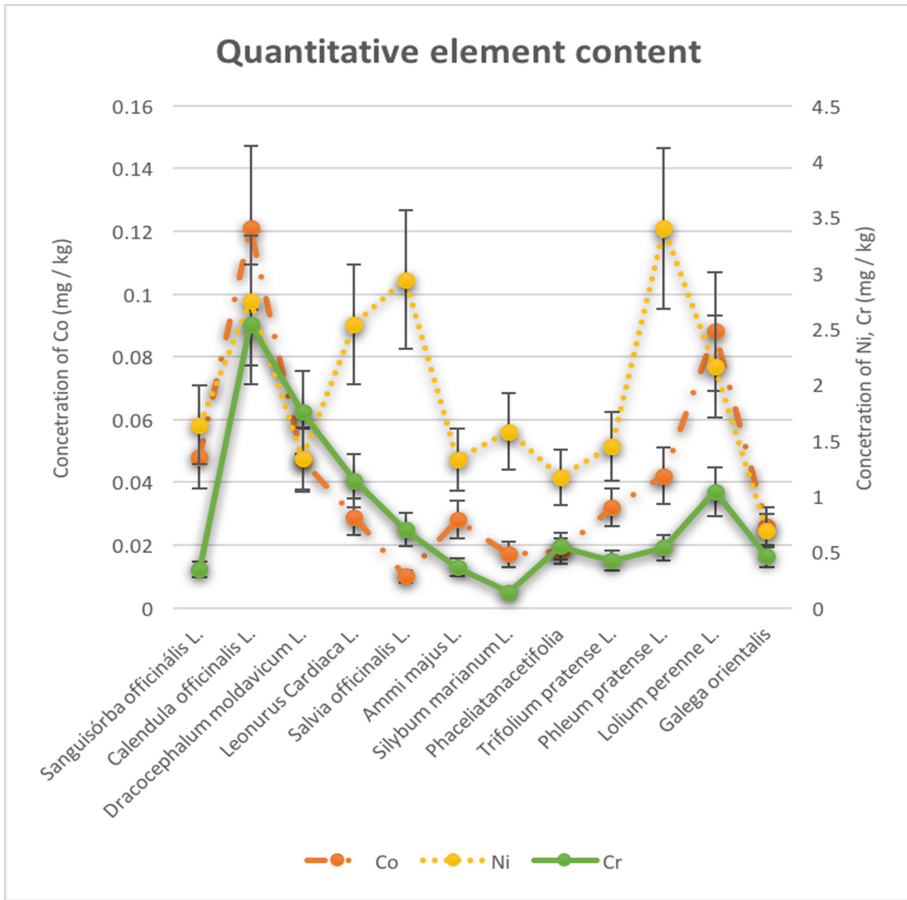
**Fig. 1.** Zn, Fe, and Mn content in medicinal and forage plants biomass.



**Fig. 2.** Pb, Cu, and Cd content in medicinal and forage plants biomass.

The total content of Fe in phytomass samples of different plant species ranged from 407.2 mg/kg (*Leonurus Cardiaca*) to 40.8 mg/kg (*Silybum marianum*) with a mean of 143.6 mg/kg (Fig. 1). The total Fe content in phytomass samples correspond to natural background concentrations, and, total Mn concentration in plant samples ranged from 84.9 mg/kg (*Lolium perenne*) to 4.0 mg/kg (*Silybum marianum*), mean – 30.0 mg/kg, which is lower than in the same phytomass from other regions (101.5 mg/kg). A direct correlation was found between Fe and Mn content in plant biomass: increased total content of one entails increase of the other (Fig. 1).

Total Zn content varied from 48.6 mg/kg (*Salvia officinalis*) to 4.58 mg/kg (*Galega orientalis*) (Fig. 1). The average total Zn concentration was 18.1 mg/kg, which is twice lower than average heavy metals content from other regions (36.8 mg/kg). The capability of the majority of studied plants to accumulate increased amounts of Zn in, mainly in above-ground organs was also noticed.



**Fig. 3.** Ni, Cr, and Co content in medicinal and forage plants biomass.

The content of Cu in plant raw samples varied from 4.1 mg/kg (*Sanguisorba officinalis*) to 15.8 mg/kg (*Leonurus Cardiacus*) with a mean 9.5 mg/kg lower than average Cu concentration values (12.2 mg/kg) in plants.

Determination of Pb and Cd content in plants elements of the 1st category of toxicity and the main components of the environment chemical pollution allowed us to estimate the degree of plants contamination, the content of Pb in the samples varied from 0,06 to 16,0 mg/kg and was at minimum *Silybum marianum*, and maximum in *Phleum pratense*. The average lead concentration in the vegetable raw material was 4,8 mg/kg, which is below the maximum permissible concentration by 1,2 mg/kg [27].

Cd – element extremely high toxicity. Cadmium salts have mutagenic and carcinogenic properties and pose a potential genetic danger. Cd content in the phytomass samples of medicinal plants varied from 0,03 mg/kg in *Salvia officinalis* to 0,27 mg/kg in *Phleum pratense*, with the maximum allowable concentration at 1,0 mg/kg [27].



The highest concentration of Cr in the phytomass was observed in the studied species *Calendula officinalis* 2,54 mg/kg and the lowest 0,14 mg/kg in *Silybum marianum*. The average concentration was 0,83 mg/kg, in all plant samples Cr concentration was below the average index.

Ni concentration in investigated phytomass samples varied from 0,69 mg/kg in *Galega orientalis* to 3,40 mg/kg in *Phleum pratense*. Average total Ni concentration did not exceed approximately permitted concentration (20,0 mg/kg).

The Co content in the plant biomass samples was minimal in *Salvia officinalis* - 0,010 mg/kg. High levels of Co were observed in biomass of *Calendula officinalis* - 0,121 mg/kg.

From obtained results, we remarked that different plant species have the selective ability to accumulate heavy metals, which made us able to divide them by the total concentration of heavy metals into 2 groups:

1. Species – accumulators of very high concentrations of heavy metals - Fe, and Cu - *Leonurus Cardiaca*, Mn - *Lolium perenne*, Zn - *salvia officinalis*, Co, Cr - *Calendula officinalis*, Ni, Pb, Cd - *Phleum pratense*;
2. Species containing low concentrations - Pb, Fe, Mn, Cr - *Silybum marianum*, Cd, Co - *Salvia officinalis*, Zn, Ni - *Galega orientalis*, Cu - *Sanguisorba officinalis*.

## 4 Conclusion

The results of the studies show that qualitative and quantitative can be altered in distribution and content of heavy metals due to agrogenic exposure. Zinc, manganese, nickel and chrome are accumulated in the upper layers of soil, strontium in carbonate-illuvial horizons, lead is distributed uniformly over the soil profile. Irrigation in those lands decreases the active forms of lead and nickel and the active form of zinc moves from the upper layers in the middle layers.

Results of heavy metals in plants' assessment showed a selective absorption characteristic of heavy metals in various plant species, despite which, their concentration in the grown on light chestnut arid soils in the Russian zone (Caspian), forage and medicinal plants does not exceed the allowed concentration. Therefore, these plants and their raw materials are not harmful to human and animal health, and can be recommended as ecologically clean.

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# Heavy Metals and Fluorine in Soils and Plants of the Minusinsk Basin

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**Abstract.** Heavy metals and fluorine are priority industrial pollutants that significantly affect the environment. The levels of heavy metals and fluorine in soils, carbonate soil formations and plants of the Minusinsk Basin are determined in this study. The high content of such heavy metals as zinc, lead, cobalt, nickel, vanadium, chromium in soils and carbonate pendants is probably due to the anthropogenic factor. High strontium and hafnium contents in soils and carbonate pendants are associated with lithogenic factor. The fluorine content in the soils and plants near the Sayanogorsk aluminum smelter impact reaches maximum concentrations of 10–12 ppm near the plant.

**Keywords:** Soil · Heavy metals · Fluorine · Carbonate pendants

## 1 Introduction

In recent decades, the volume of mining has increased significantly, the number of industrial enterprises has increased, and the technogenic impact of pollutants on ecosystems and soil has increased substantially, in particular. One of the polluters of the environment is the aluminum industry.

The aluminum industry is the source of pollutants entering the atmosphere, such as fluoride compounds and heavy metals. This is due to the peculiarities of the technology of aluminum production, during which raw components such as fluoride salts, sulfur coke and coal tar pitch are used. Due to the Increase of pollutants, it becomes extremely necessary to study the migration of pollutants in specific landscape components. The high toxicity and chemical activity of fluorine and heavy metals makes it important to study the transformation of pollutants in these landscapes.

Soils and carbonate soil formations act as sinks for many heavy metals and fluorine. The high content of fluorides and heavy metals in the soil can lead to accumulation of fluorine in plants, which is an acute problem of pollution for agroecosystems. High mobility of some of the pollutants in soil can lead to contamination of groundwater, which makes the water unsuitable for domestic use. The physiological effect of fluoride and heavy metals is manifested in the negative effect on the mucous membranes of the upper respiratory tract, lungs, central nervous system, skin, and at high concentrations they can cause damage to the teeth and bones and disrupt the metabolism in cells. The need for scientific research is also confirmed by the designation of specially protected

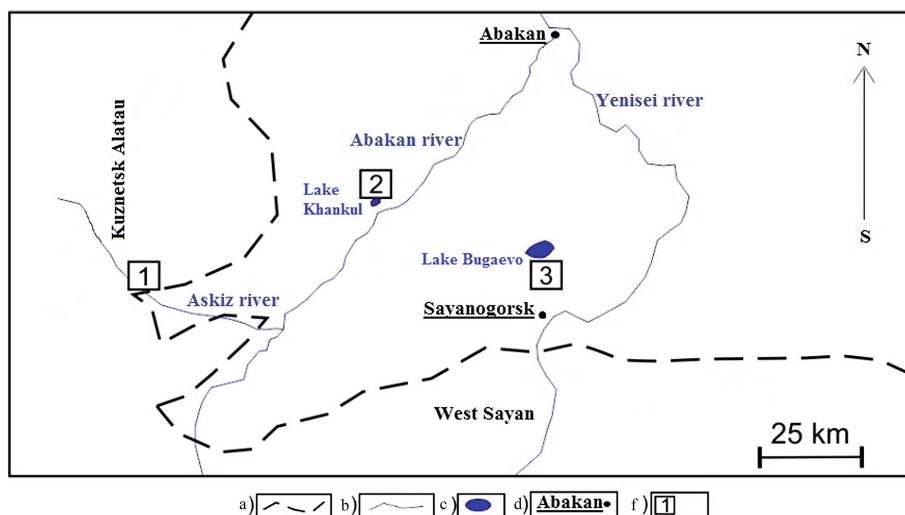
natural areas near the Sayanogorsk aluminum plant, whose purpose is to preserve the natural ecological systems and biodiversity of the region.

In the study area, fluorine content in soils and water was previously studied. Studies of fluorine in soil water obtained by the Ishcheyakov-Komarova method were carried out for the first time. Also, for the first time, heavy metals in soils and carbonate neoplasms was determined near the aluminum plant and in the background areas of the Kazanovka Khakass state national reserve and Lake Khankul.

The purpose of this study is to determine the levels of heavy metals, fluorine in soils, soil solutions, carbonate pendants and plants of the Minusinsk Basin.

## 2 Materials and Methods

Three study sites were investigated: the Sayanogorsk aluminum smelter area, and lake Khankul and the Kazanovka Khakass state national reserve, selected as the background site (Fig. 1).



**Fig. 1.** Setting of study area. (1) Kazanovka Khakass state national reserve (2) Khankul lake (3) Sayanogorsk aluminum smelter area. Map symbols (a) Minusinsk basin boundaries; (b) rivers; (c) lakes; (d) cities; (e) cities; (f) key sites.

The aluminum plant is located 15 km north of the city of Sayanogorsk, which is located 75 km south of the capital of the Republic of Khakassia, Abakan, on the west bank of the Yenisei River. The background site - the Kazanovka Khakass state national reserve, is located 120 km south-west of the city of Abakan and more than 100 km west of the Sayanogorsk aluminum smelter area, on the west bank of the Askiz river. The other background site Lake Khankul is located 50 km south-west of the city of Abakan and 75 km north-west of the Sayanogorsk aluminum smelter. The separation

of two background areas was necessary for studying as a steppe and forest landscape, as a saline landscape that are locally encountered in the territory of Lake Khankul.

The West Sayan Mountains surrounds the Minusinsk basin from the south and the Kuznetsk Alatau Mountains surrounds from the west.

The climate of this territory is characterized by cold and little snowy winter and the moderately warm dry summer, and the large variability of all meteorological values with sharp contrasts of annual, monthly and diurnal variation of air temperatures. The basin relief of the study area determines the characteristics of the atmospheric circulation: predominance of the south-west wind direction, high frequency of low-clouds, calm, or with weak winds of the weather and frequent cases with surface inversion of temperature. Frequent temperature inversions, forming air stagnation, prevent dispersion of industrial emissions and self-cleaning of air. Annual precipitation varies between 250–450 mm. The least amount of precipitation is observed in winter, while the maximum precipitation falls in the summer season. In July and August more than 50% of precipitation falls.

The study area is represented by desertified, tussock grassland, meadow, stony and solonchaks steppes. Desertified steppes have a limited distribution. They are noted fragmentarily along the southern slopes. Larch and pine forests with an admixture of birch are developed in the foothills of the Kuznetsk Alatau and the West Sayan Mountains.

Soils in this area are characterized by medium and light loamy chernozems and kastanozems. Often there are solonetz and solonchaks in depressions and at the outcrops of saline rocks. Under forest vegetation, greyic phaeozems are formed. The outcrops of carbonate rocks in the foothills of the West Sayan and the Kuznetsk Alatau form rendzic leptosols eutric.

The content of major elements and minor elements in soils, soil solutions and carbonate neoformations was measured with inductively coupled plasma mass spectrometry (ICP-MS). Mobile forms of some heavy metals were extracted with ammonium acetate buffer, followed by measurements with atomic absorption spectrometry. Samples of topsoil and subsoil were used for chemical analysis. Samples of carbonate neoformations were selected from carbonate soil horizons for chemical analysis.

Soil solutions displacement method by displacing fluid of Ischeryakova-Komarova was used. Ethanol was used as the displacing fluid. Determination of fluorine in the resulting soil solutions was carried out using the method of ion chromatography.

In addition, the content of water-soluble and acid-soluble fluorine forms in soils was determined by the potentiometric method using an ion-selective electrode. The content of fluorine in plant samples was determined by wet digestion of samples followed by the potentiometric method.

### **3 Results and Discussion**

#### **3.1 The Content of Heavy Metals in Soils and Carbonate Neoformations**

Sayanogorsk aluminum smelter is one of the biggest industrial enterprises in the Minusinsk Basin. Most studies of anthropogenic pollution in the aluminum industry

zone of influence are related to F and Al content, as well as Na, Ca Mg [1, 2]. The contents of heavy metals (HM) in soil is also an important indicator for ecological assessment. The lithology of the Minusinsk Basin is heterogeneous, and we consider that not only anthropogenic anomalies are important but also the sources of HM, which are parent rocks and especially locally exposed Devonian rocks [1]. The pollution is estimated by hygienic standards adopted in the form of maximum permissible concentration (MPC) of compounds [3, 4].

In soil minor elements absolute values Ba, Sr, V, Cr, Zn, Zr, Ni, Co, As, Hf, Yb, Cd prevail, In Sayanogorsk the content of Ba, V, Cr is greater relative to the two other sites; Sr and Zr content is the highest in soils of Lake Khankul area. The highest clarks of concentration [5] of elements in comparison with natural abundance of elements in igneous rocks by Vinogradov [6] are marked for As (2,2–7,9 ppm), Hf (1,75–5,01 ppm), Yb (4,4–7,4 ppm), Cd (2 ppm). Minory exceeded MPC for soil are noted for V, in Sayanogorsk the content in soils is 161 ppm and MPC is 150 ppm. The median content of heavy metals in soils and carbonate neoformations are given in Table 1.

**Table 1.** The median content of heavy metals in soils and carbonate neoformations of the Minusinsk basin (elemental concentrations in ppm).

Site	Object	Ba	V	Cr	Sr	Zr	As	Hf	Yb	Cd	Zn	Pb	Ni	Co
Sayanogorsk	Topsoil	439	136	87,1	166	75,2	7,4	2,5	2,2	0,2	73,8	32,2	63,1	12,4
	Subsoil	442	142	116,8	465,5	69,3	6,1	1,7	1,9	0,1	71,5	12,4	55,4	13,8
	Carbonate pendants	207	26,6	31,6	531,6	21,5	3,1	0,5	0,8	0,1	32,7	4,7	34,7	7,5
Kazanovka reserve	Topsoil	411	162	99,7	264,6	83,9	10,6	2,5	1,8	0,2	30,7	7,1	26,4	7,5
	Subsoil	359	150	82,2	260,4	90,2	15,0	2,3	1,8	0,2	28,4	6,0	24,9	5,6
	Carbonate pendants	380	16,7	11,5	405,0	33,8	3,8	1,4	0,7	0,1	17,4	4,9	14,1	3,6
Lake Khankul	Topsoil	346	55,2	17,2	334,0	114	5,3	3,3	2,0	0,2	61,7	13,7	9,4	4,6
	Subsoil	300	44,4	7,0	364,3	161	3,9	5,0	2,5	0,1	65,9	16,2	11,2	4,1
	Carbonate pendants	2626	12,6	810,6	1110	27,8	3,5	0,8	0,7	0,2	20	4,6	14,8	4,0

In the area of influence of the Sayanogorsk aluminum smelter a number of heavy metals - specific pollutants for the area is identified. They are zinc, lead, cobalt and nickel. Background zinc content in soils is 84,7 ppm. The maximum total concentration of Zn in the soil reaches 270 ppm, and the maximum mobile forms of Zn 33,9 ppm was observed in the impact zone of the Sayanogorsk aluminum smelter. MPC for total Zn in soil is 100 ppm, for mobile forms of Zn it is 23 ppm. Thus, the content of zinc exceeds the hygienic standards 1,5–2 times in soils near the plant.

Spatial distribution of lead in the soils of the study area can be mapped according to the distance from the industrial complex. The highest concentration of total Pb is observed near the smelter and is up to 80 ppm. Background concentration of Pb in soils is 13,1 ppm. The maximum mobile forms of Pb in soils near the plant is 1,5 ppm. MPC

for total Pb in soils is 32 ppm. Therefore, the content of lead exceeds the hygienic standards 3 times in soils near the plant.

In the area of influence of the Sayanogorsk aluminum smelter the maximum nickel concentrations in soils is 140 ppm. Background values of total Ni concentrations is 39,4 ppm. The maximum content of mobile forms of Ni is 1 ppm. MPC for total Ni in soils is 85 ppm, the content of nickel exceeds the hygienic standards 1,5 times in soils near the plant.

The maximum concentrations of total forms of cobalt in soils is up to 50 ppm. Local background cobalt content in soils is 14,2 ppm. The maximum value of the content of mobile forms of Co reaches 2,4 ppm.

In carbonate pendants Sr and Ba prevail. The content of these two elements is maximum in the saline landscapes of Lake Khankul, exceeding the content of the Sayanogorsk and Kazanovka 2–10 times. Ba, Zr, Ni, Zn predominate in Kazanovka and Khankul, while in Sayanogorsk – Ba, Sr, Ni, Zn, Cr, V prevail. Also Sayanogorsk area compared to other areas is characterized by higher Co content. Highest clarks of concentration of elements in carbonate neof ormations compared with natural abundance of elements in carbonate rocks [7] in the three key sites are observed for Pb (60–302,5 ppm), Ba (17–262 ppm), Co (32–26 ppm), Hf (11–48 ppm). The content of Sr is also high (273–810 ppm) and it is close to the natural abundance of this element in carbonate rocks.

The elemental composition of soil solutions obtained by the Ishcheyakova-Komarova method is determined. In general, in soil solutions Sr, Br, Ba, B, Zn, Al, Fe, V prevail, and the content of Sr, Ba, Br, Al is the highest in Sayanogorsk soils. In the plant's exposure area, heavy metal concentrations are higher than in the background areas. For example, in soil solutions from Sayanogorsk the Ba content is 339,2 ppb and 69,9 ppb and in Kazanovka, the content of Sr is 1588,9 and 538,1 ppb, respectively (Fig. 2).

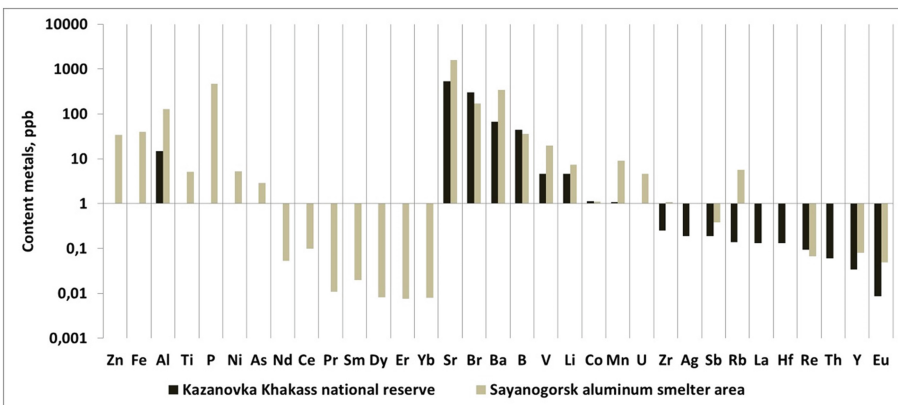


Fig. 2. Content of metals in soil solutions (elemental concentrations in ppb).



### 3.2 Fluorine Content in Soils, Soil Solutions and Plants

To assess the degree of soil contamination with fluorine it is necessary to know its background content, the initial amount in the soil or the natural level. Based on this study, the background content of water-soluble fluorine forms in the study areas is 1,7 ppm in topsoil and 1,2 ppm in subsoil. In soils, sanitary and hygienic standards for water-soluble forms of fluoride are regulated by the maximum permissible concentration, which is 10 ppm. The water-soluble fluorine content in the soils in the area of the Sayanogorsk smelter impact reaches maximum concentrations of 10–12 ppm in the topsoil and 5–8 ppm in the subsoil near the plant in the direction of the prevailing west and south-west winds.

Accumulation of fluorides is directly correlated to the distribution of the carbonate in the profile. Below the carbonate horizon, the fluorine content decreases to 1,5–2,0 ppm.

The content of mobile acid-soluble forms of fluorine is distributed along the soil profile with maximum in the upper humus horizons (270 ppm) and mid-carbonaceous horizons (470 ppm) in the area of the Sayanogorsk smelter. It is associated with the technogenic intake of fluorine in landscapes and the binding of fluorides with calcium. In the background areas – Kazanovka reserve and Lake Khankul, content of mobile acid-soluble forms of fluorine reaches up to 103 ppm and 82 ppm in the topsoils, 56 ppm and 77 ppm in the subsoils, respectively (Table 2).

**Table 2.** The median content of water-soluble ( $F_w$ ) and acid-soluble ( $F_a$ ) forms of fluorine in soils of the Minusinsk basin. Soil water obtained by displacing replacement liquid by the method of Ishcheryakov-Komarova. (elemental concentrations in ppm).

Site	Object	$F_w$	$F_a$
Sayanogorsk	Topsoil	8	205
	Subsoil	4	415
Kazanovka reserve	Topsoil	1.7	103
	Subsoil	1,2	56
Lake Khankul	Topsoil	0.8	82
	Subsoil	1.3	77

The content of fluorine in the soil water from soils of Sayanogorsk aluminum smelter area obtained by displacing replacement liquid by the method of Ishcheryakov-Komarova is 0,3–0,4 ppm. The maximum content of mobile forms of fluorides is in the topsoils. The minimum content of mobile forms of fluorides in soil solutions is noted in the carbonate horizons 0,1–0,15 ppm. But the fluorine content in soil solutions from soils of Kazanovka reserve and lake Khankul is higher due to the lithogenic factor and reach 0,8–1,2 ppm.

As it is known, fluorine is a bio-essential element for plants, but it can be a toxic element even at low concentrations for certain plant species. The biological accumulation of fluorine in plants depends not only on the absorption of the element from the atmosphere, but also on the content of the water-soluble form of the element available

in the soil. In this study, elevated content of fluorine in cereal plant species, in comparison with background values, was detected within a radius of 5 km from the plant (maximum content in the plant is 145 ppm; background – 2,3 ppm of dry matter).

Investigations of changes in fluoride concentrations in the pine forest make it possible to draw some conclusions about the influence of aluminum plant. The results of the chemical analysis indicate that in the needles and one-year-old shoots of the pine forest the fluorine content varies within 1,3–19,2 ppm of dry matter. For the background areas, the range of fluoride content is 1,4–3,3 ppm dry matter. Although the level of fluorine in the needles and shoots of the pine forest near the aluminum plant was on average low (6,8 ppm), it nevertheless 2–5 times higher than that in the background area Kazanovka reserve, which indicates the effect of aluminum plant emissions on the vegetative coniferous cover.

## 4 Conclusion

The conclusions are the following: (1) The high content of V, Cr, Ba in soils and carbonate pendants in Sayanogorsk compared to clarks and the MPC, is probably due to anthropogenic factor; (2) Excess Al and V relative to the background content in soil solutions also shows the human impact; (3) High content of Hf and Nb compared with clarks in carbonate pendants and in soils may be associated with Devonian rocks, some of which are enriched by these trace elements [2] high Sr content but not exceeding clark is also associated with lithogenic factor; (4) The fluorine content in the soils in the area of the Sayanogorsk smelter impact reaches maximum of 10–12 ppm at a distance of 1,5 km from the plant and also zinc, lead, cobalt and nickel are identified as major pollutants in the vicinity of the plant; (5) The fluorine content in soil water is higher in the background area due to the lithogenic factor; (6) Biological accumulation of fluorine in plants was detected within a radius of 5–7 km from the enterprise and reached 145 ppm of dry matter.

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# Rapid Screening of Bioaccessible Pb in URBAN Soils Using pXRF

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**Abstract.** U.S. EPA method 1340 (Bioaccessibility assay of lead in soils) requires well-equipped laboratories that are capable of measuring Pb in extract solutions using advanced instrumentation such as ICP-MS with high precision. In this study, we propose a new approach for low cost and rapid assessment of soil Pb bioaccessibility that can be conducted in the field using a portable X-Ray Fluorescence (pXRF) analyzer. Air dried soil samples were extracted with a soil: extract ratio of 1:10 for one hour at room temperature, and the filtered extractant was directly measured in cups by pXRF. Results showed that pXRF can measure Pb directly in liquid samples. The pXRF readings were consistently ~15% higher than expected. There was no significant matrix effect. The results of bioaccessibility of Pb determined by the simplified acid leaching methods with glycine solution at pH 1.5, 1 N HNO<sub>3</sub> and 1 N HCl were deviated from those determined with the standard EPA method 1340. More research is needed to find the best protocol that can utilize the pXRF and yield similar results to the EPA method 1340.

**Keywords:** X-ray fluorescence · Liquid samples · Urban soils  
Lead · Bioaccessibility

## 1 Introduction

Soil is a sink for many pollutants such as lead (Pb) [1] and is an important source of contamination in urban environments. Exposure can occur through direct ingestion and inhalation and via food chain transfer. Chronic ingestion of Pb is especially hazardous to children as their neurological systems are more susceptible to the negative consequences of Pb. However, not all Pb in soil is bioavailable. Bioavailable Pb in soils is a better measure of the actual health risk compared to total Pb. Standard *in vivo* tests for contaminant bioavailability are based on animal trials [2–4] whereas *in vitro* gastrointestinal extraction tests are available to measure bioaccessible Pb as a predictor of bioavailable Pb content. One of the challenges of the existing methods for soil Pb bioaccessibility measurement is that they all need to be conducted in well-equipped

laboratories that can measure Pb in extractant solutions using advanced instrumentation such as Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

Field Portable X-ray Fluorescence (pXRF) Spectrometry has the ability to conduct nondestructive, non-contact analysis of solid and liquid samples. It requires minimal sample preparation, high repeatability, and little operator training [5]. Several chemical and physical extraction techniques have been proposed to facilitate XRF analysis of liquid samples [5]. Preconcentration may be necessary and may include simple evaporation or freeze drying for samples of low salinity or hardness, but very often a more tedious and fallible chemical preconcentration is needed [6]. Eksperiandova et al. [7] proposed usage of gelatin (agar) to produce preconcentrated thin agar films that could be analyzed for trace metals by XRF with good repeatability due to the homogeneity of the agar films [8]. Moriyama [9] effectively used Ultracarry filter paper and an Ultradry vacuum dryer for sub ppm level analysis of hazardous heavy elements in wastewater and river water with the XRF method. Therefore, a preconcentration technique is commonly recommended before the XRF analysis, including solid- and liquid-phase extraction [5].

Direct analysis of liquid samples using XRF has often been considered problematic because liquid samples have a high X-ray scatter background, which often leads to low signal-to-noise ratio [5]. Liquid samples can be challenging depending on the composition and stability [10] and issues such as evaporation, stratification, and precipitation. The liquid may attack or be absorbed by the window film, wick up and out of the cup. Because of these difficulties, liquid samples should be freshly prepared, preferably directly before analysis. Solutions should be well mixed before transferring them into an XRF cup.

The need to develop fast, affordable methods for total Pb and bioaccessibility is driven by the observed high variability of Pb in urban soils and the high variability in bioaccessibility. The capability of pXRF for directly measuring metals in liquid samples have been advertised by manufactures, but there is scarce scientific literature on the topic. Therefore, part of this study was designed to evaluate the reliability of such measurements in terms of reproducibility, stability, matrix effect and accuracy. The second part of this study is to compare the pXRF bioaccessible Pb results on soil extractants with different acids/solutions, and with the results obtained with the standard U.S. EPA protocol (method 1340). This is the first study that explores the use of pXRF to measure liquid solutions for bioaccessibility of Pb.

## 2 Methods

### 2.1 Bioaccessible Metal Concentrations Using Standard EPA Protocol

Bioaccessible Pb was quantified following a modified version of the standard U.S. EPA Method 1340: *In Vitro* Bioaccessibility Assay for Lead in Soil [11]. This method was modified by using extraction with 0.4-M glycine solution at pH 2.5 rather than at pH 1.5, according to the protocol. All samples were oven-dried for 24 h at  $T = 105^{\circ}\text{C}$ , sieved through  $<250\ \mu\text{m}$ , and extracted at  $T = 37^{\circ}\text{C}$  after 1 h rotation on the temperature-controlled shaker. Standard Reference Material 2710a was used as the

external standard for bioaccessible Pb and was included in each extraction batch. Each extraction batch consisted of 20 samples. Bottle blank, blank spike and matrix spike samples were included in each batch along with two replicates for quality control. Extracts were analyzed by ICP-MS for Pb.

## 2.2 Simplified Acid Leaching

Twelve urban garden soil samples, with total Pb content ranged between 250 and 5500 mg kg<sup>-1</sup>, were air dried and passed through <1 mm sieve in the lab for this experiment. Sieving could be done in the field if necessary. Five grams of each sample were thoroughly mixed with 50 ml of 0.4-M glycine at pH 1.5 for 1 min to achieve homogeneity. The mixtures were left at a room temperature ( $T = 20^{\circ}\text{C}$ ) for 1 h. The samples were further filtered with a syringe filter of 0.45  $\mu\text{m}$  diameter. The resulting leachates were transferred into XRF cups and measured by the pXRF analyzer. In order for pXRF to be quantitative, samples must be at least 15 mm thick for liquid samples [12]. Each measurement was performed with one beam of 30-s duration in three replicates. The Inverted cup was placed on top of the XRF beam, a technique employed to avoid the bias from air bubbles in the liquid.

The same urban garden soil samples were used for leaching with 1N HCl or 1N HNO<sub>3</sub>. The samples were air dried but not sieved to mimic field conditions. Five grams of a soil sample were extracted with 25-mL 1N HCl or 1N HNO<sub>3</sub> for 30 min. The samples were further filtered with a syringe filter of 0.45  $\mu\text{m}$  diameter. The resulting leachates were transferred into XRF cups and measured with the pXRF. Each measurement was performed with one beam of 30-s duration in three replicates. Overall, the proposed XRF method requires 2–4 h of operation in field conditions, while standard EPA protocol requires 2–3 days with sample preparation, extraction, and ICP-MS analysis.

## 2.3 Quality Control

In order to examine the accuracy of XRF measurements for Pb in liquid samples, standard additions of 0, 20, 50, 100, 150, 200 ppm of Pb were added into DI water, measured by the XRF and further analyzed with more accurate ICP-MS. To study potential matrix effects on the XRF measurements, Pb spikes of 0, 20, 50, 100, 150, 200 ppm were added to the filtered solutions of two samples after the extraction and measured by pXRF. The same quantity of Pb was also directly added to the same soil samples prior to the extraction to assess the recovery of Pb during the extraction process. Standard Reference Material 2710a was used as the external standard for bioaccessible Pb.

## 2.4 Data Processing

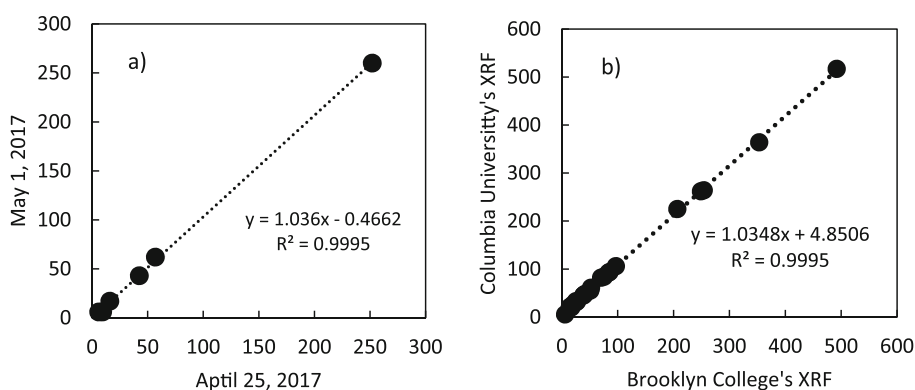
The Student's t-test was utilized to compare data sets measured at different time or with different XRF analyzers. The data sets were considered not statistically different if the probability value was  $>0.05$ . The data sets analyzed by XRF for glycine solution at pH

1.5, 1 N HNO<sub>3</sub> and 1 N HCl, and EPA method 1340 with ICP-MS at pH 2.5 were compared using One-way ANOVA with post-hoc Tukey HSD Test.

### 3 Results and Discussions

#### 3.1 The Ability of Portable XRF to Measure Pb in Liquid Solutions

Six extracted samples were analyzed twice with pXRF for Pb, at the initial extraction and one week later. The results were almost identical (Fig. 1a), suggesting that the extraction solution is rather stable and the pXRF measurements can be performed both in the field and in the laboratory reliably over at least one week period. In another trial, twenty three extractant samples were measured by two different XRF analyzers (Olympus Delta Classic 4000 from Brooklyn College and Delta InnovX Premium from Columbia University) and the results were found to be reproducible (Fig. 1b).



**Fig. 1.** (a) Stability of leachate samples ( $n = 6$ ) one week apart and; (b) Reproducibility of leachate samples ( $n = 23$ )

Standard additions of 0, 20, 50, 100, 150, 200 ppm of Pb were added into de-ionized water. There was a perfect correlation ( $R^2 = 1.000$ ,  $p < 0.001$ ) between expected Pb concentration and pXRF results, however, the latter was about 15% higher. It is not clear as to why the pXRF results are systematically higher, and this should be further investigated. This could be related to the software that was used in this study – it was mainly for the solid environmental samples rather than liquid samples. To our knowledge there is no pXRF software specifically developed for liquid solution samples available. It should be noted, however, that pXRF has largely been a screening tool rather than for highly precise quantitative analysis. According to Kalnicky and Singhvi [13], field-portable XRF measurements are reliable when precision is within 20% when target elements that have concentrations more than 10 times the XRF detection limit.

Two different samples (SCG and DF) were chosen to determine potential soil matrix effect on pXRF measurements of Pb in liquid solutions (Fig. 2a). There was

good correlation between expected Pb and pXRF measured Pb, however, again the latter was 17% and 22% higher respectively for these two samples. Because of the 15% bias from pXRF, as described earlier, the net matrix effect (2–7%) is rather small, if it indeed exists.

In a separate experiment, Pb spikes were added directly into the two soil samples prior to the extraction (Fig. 2b). The pXRF readings of the extracted solutions were much lower than expected, and this is contradicted to the pXRF reading bias (i.e., pXRF readings should be higher than expected) as discussed earlier. This indicates that part of the Pb spike was likely precipitated and was not able to be leached during the extraction. This was especially remarkable for the SCG sample, which has very high total P concentration ( $>4000 \text{ mg kg}^{-1}$ ) and high TOC ( $>20\%$ ). Lead has a tendency to bind with phosphates and organic matter forming stable complexes in soil.

### 3.2 Assessment of Soil Pb Bioaccessibility Using Different Extraction Methods Followed by pXRF

In this study, we followed a simple procedure for soil Pb bioaccessibility determination: air dried soil samples sieved to  $<1 \text{ mm}$ , a soil:solution ratio of 1:10, extraction time of 1 h at room temperature, and measurement of Pb in filtered extractant with pXRF.

U.S. EPA 1340 method typically uses soil:solution ratio of 1:100 [11]. This was used to reduce effects of metal dissolution that have been noted by Sorenson et al. [14] when low ratios (1:5 and 1:25) were used [15]. With the pXRF method, a higher concentration in the liquid was necessary due to the detection limit of the instrument. For pXRF, concentrations of  $>100 \text{ ppm}$  show peaks clearly, concentration of 0–100 ppm limit of detection (critical zone), concentrations of  $<10 \text{ ppm}$  show any peaks [16]. With a soil:solution ratio of 1:10 and a soil Pb content of  $100\text{--}5000 \text{ mg kg}^{-1}$ , there expected to be sufficient Pb concentrations to be detected and quantified by pXRF.

We also experimented with different acids/solutions (1N  $\text{HNO}_3$ , 1N HCl, 0.1N HCl, and 0.032N HCl) for extracting bioaccessible Pb in soil. The pH of extracting solution is a critical parameter for soil Pb bioaccessibility determination. It should maintain a pH range of  $1.5 \pm 0.05$  according to the standard EPA protocol [11]. In this study, different extraction solutions were tested to find the best solution for maintaining at a proper pH level (Table 1). Among four different extraction solutions (1N HCl, 0.1N HCl, 0.032N HCl, and 0.4 M glycine with initial pH 1.5), only the 0.4 M glycine solution showed the expected results. Other concentrations were too acidic and 0.032N HCl resulted in very high pH (4.22) for the SCG sample, likely due to its high carbonate content.

Figure 3 showed comparison of data sets analyzed by pXRF for glycine solution at pH 1.5, 1 N  $\text{HNO}_3$  and 1 N HCl, and EPA method 1340 with ICP-MS at pH 2.5. It should be noted that the pXRF readings were consistently  $\sim 15\%$  higher than expected. Keeping this fact into account, the 1N  $\text{HNO}_3$  extraction (air dried soil, 1:5 solid:acid ratio, 30 min leach at room temperature, pXRF measurement) yielded similar amount of Pb as the EPA standard protocol. The 1N HCl extraction (air dried soil, 1:5 solid:acid ratio, 30 min leach at room temperature, pXRF measurement)



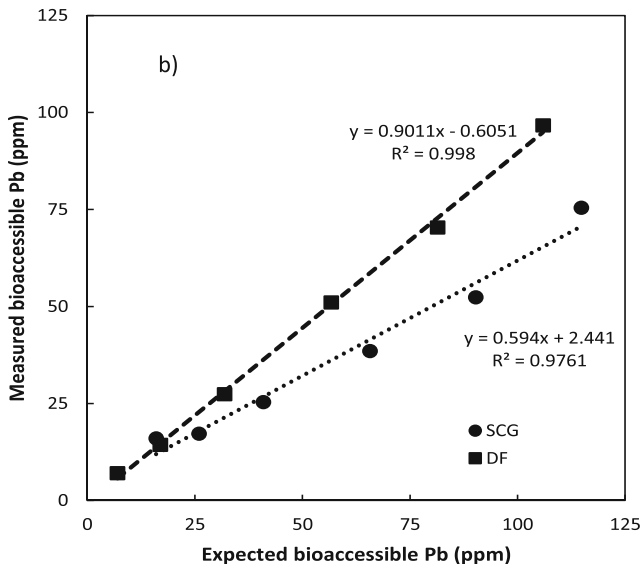
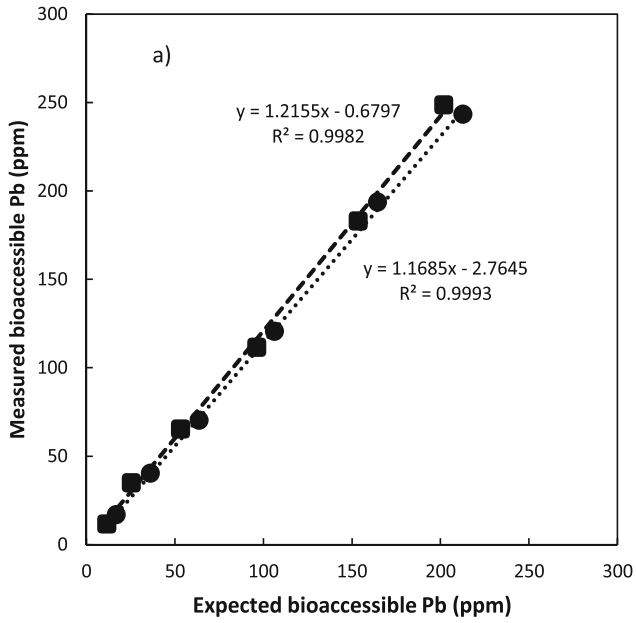
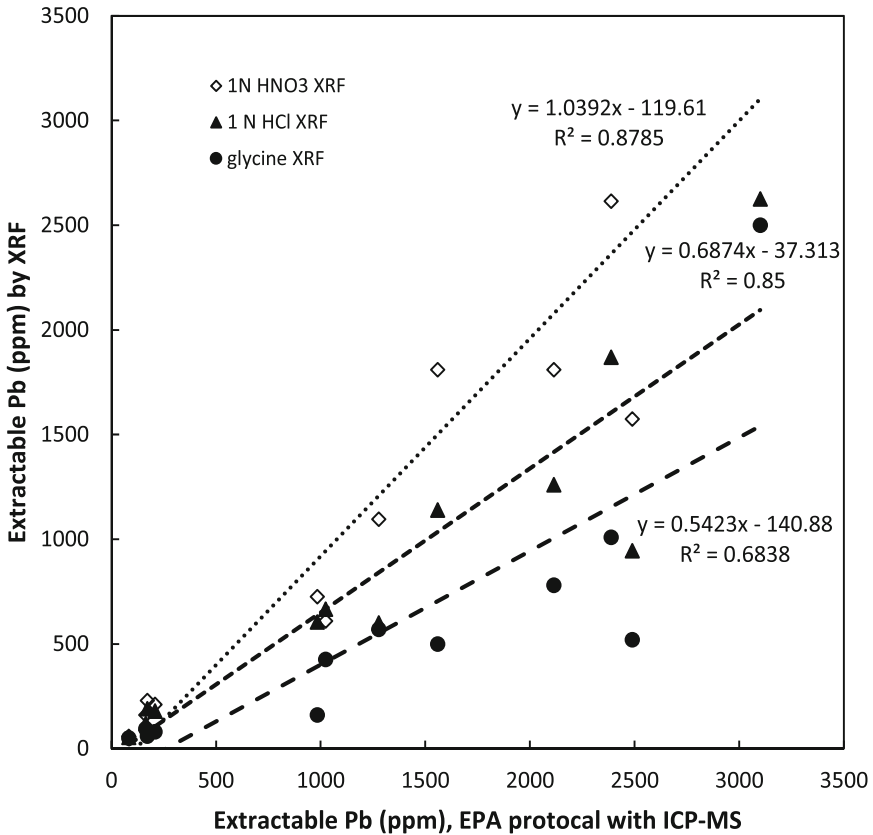


Fig. 2. (a) Soil matrix effect and (b) sorption effect

**Table 1.** pH of different extraction solutions

	1 N HCl	0.1 HCl	0.032 HCl	0.4 M glycine pH 1.5	Required pH
<i>pH before extraction</i>	0.84	1.35	1.68	1.47	pH 1.5 ± 0.05
<b>Sample ID</b>	<i>pH after extraction</i>				
SCG	0.82	1.41	4.22	1.80	pH 1.5 ± 0.5
DF	0.83	1.13	1.66	1.53	
S0214-6B	0.78	1.15	1.68	1.55	
S0412-48A	0.79	1.16	1.65	1.53	
S0712-1B	0.77	1.18	1.71	1.55	



**Fig. 3.** Comparison of data sets (n = 12) analyzed by XRF for glycine solution at pH 1.5, 1 N HNO<sub>3</sub> and 1 N HCl, and EPA method 1340 with ICP-MS at pH 2.5

yielded ~30% less Pb than the EPA standard protocol. The 0.4 M glycine solution extraction (air dried soil, <1 mm, 1:10 solid:extract ratio, 1 h leach at room temperature, pXRF measurement) yielded only about half the Pb than the EPA standard protocol. It should be noted that the lower extracted Pb could be due to a number of

factors, such as particle size differences – it is known that smaller particles can contain much higher Pb content [1]. With a larger solid-extract ratio, less Pb is extracted from the soil. The consistently lower extracted Pb (despite a higher reading bias with pXRF) suggest that some modification of the proposed simplified protocol is needed.

## 4 Conclusions

A screening method for soil Pb bioaccessibility using an XRF analyzer is proposed. This method allows for rapid, economical and field applications. A preliminary examination of the reliability and feasibility of this method was conducted. Results showed that pXRF can be used to measure Pb directly in liquid samples, albeit the readings were about 15% higher than expected values. A correction factor can be used if this bias is confirmed to be consistent for a large number of samples and across different pXRF instruments. No significant matrix effect was observed. More research is clearly needed to optimize the specific protocol for this proposed screening method, and evaluate the accuracy of results with those based on the standard EPA protocol.

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# Use of Tomographic Methods for the Study of Urban Soil Properties

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**Abstract.** Physical properties and their dynamics under anthropogenic impact are important for the rational use of urban soil and its fertility management. However, standard methods and procedures are hardly usable for the modern urban soil science. New methods from other areas of knowledge, such as computer microtomography widely used in geology, biology, and medicine, need to be searched and adapted.

The objects of the study are SUITMA soils of Rostov agglomeration and their physical properties, transformed under the effect of industrial, residential, and recreational zones, as well as margin city areas, which were affected by agricultural use. According to the results of studies since 1998, urban soils were grouped into morphological classes of (1) natural-structure soils without urban disturbance, (2) natural-structure soils overlaid by anthropogenic sediments, and (3) soils overlaid by water-impermeable layers.

3D scanning of soil samples was performed on a SkyScan 1172 X-ray scanner at the Dokuchaev Soil Science Institute. Image resolution was 16  $\mu\text{m}/\text{pix}$  for the study of internal structure. We used DataViewer and CTan to analyze the images. The samples had natural water content and structure during scanning. Soil samples were then placed in special plastic containers 3 cm in diameter and sealed. Modern analytical methods allow us to analyze separate structural elements, calculate their volume, surface area, amount, and orientation inside of the sample without disturbance. We also can gain data on soil pores (general porosity, open and closed porosities in  $\text{mm}^3$  or %, pore size and volume and their relationship, pore amount, connectivity).

For urban territories in the steppe zone, a comparison of humus-accumulative horizons (A, Asod, Ap, and buried [A] horizons) made it possible to trace tendencies in changes of surface soils under different technogenic and anthropogenic impacts and in the buried and sealed soils. Tomographic data allow us to acquire not only quantitative data, but also visual information.

**Keywords:** Urban soil · Urbanized area · Technosols · SUITMAs  
Calcic Chernozem · X-ray microtomography · Soil structure · Pore space

## 1 Introduction

Land use in cities and urbanized regions is characterized by increased exploitation intensity; therefore, almost all soils within the city are more or less subjected to physical degradation due to different excessive technological loads [1, 2].

Information about the physical properties of soil and consideration of their dynamics under anthropogenic impacts are necessary for the rational use of soils in urban areas and the management of their fertility. However, the use of conventional methodological approaches and procedures faces some problems at the current stage of urban soil science. Thus, search for additional investigative techniques is of current importance, and their adaptation to the study of urbostratozems and urbistratified soils can give more objective results [3].

To study urban soils, we used computer X-ray tomography, a method for the nondestructive analysis of the internal structure of solid objects, which is widely applied to different fields of science and industry. Image brightness (gray gradations) in the X-ray shadow projection reflects the attenuation of X-ray radiation due to the diffusion and absorption of the signal passed through the sample. The attenuation depends on the density and effective atomic number of the substance under study [4]. Computer processing of tomographic projections makes it possible to create a 3D digital copy of internal structure of the object under study and to calculate the morphometric parameters for each visible X-ray contrast phase. Computer tomography is suitable for studying the internal structure of most natural and artificial solid bodies (hard rocks, soil particles [5], composite materials, metal parts, electronic components, etc. [6]). Exceptions are objects with high contents of lead, heavy metals from the lower part of the periodic table, or platinum-group metals. Tomographic study can be performed at different resolution levels, from hundreds of nanometers to fractions of millimeter, depending on the instrument performance.

## 2 Material and Methods

### 2.1 Description of the Study Area and Soil Sampling Sites

Objects of this study include natural and anthropo- and technogenically transformed soils of Rostov agglomeration.

The Rostov agglomeration is one of the largest agglomerations (the population is about 2 million) in southern Russia, which is located in the southeastern region of Rostov oblast and has pronounced monocentric indices. The first level of Rostov agglomeration, so-called Great Rostov, consists of the nucleus (city of Rostov-on-Don) and adjacent cities and rural settlements (Bataisk, Aksai, Chaltyr') located at 10–12 km from the metropolis.

Physical properties of soils were characterized using a series of humus-accumulative A horizons sampled from 20 soil profiles, which were subdivided, depending on the land use pattern and, hence, the transformation of their morphological indices, into the following groups:

**First Group.** Surface humus-accumulative horizons of soils with natural structure, which are not significantly affected by urbanization processes. These are calcareous ordinary chernozems (A–B–BC–Cca) (Calcic Chernozems according to WRB [7]) on upland areas in the park-recreational zone of the city and fallows areas within or adjacent to the city limits.

**Second Group.** Buried humus-accumulative horizons of anthropogenically transformed soils covered by asphaltic and/or other impermeable layers. Shielded urbostratozems (Asf-UR-[A-B-BC-Cca]) (Ekranic Technosols over Calcic Chernozem according to WRB [7]) and shielded urbistratified chernozems (Asf-UR-[A-B-BC-Cca]) (Novic Chernozems (Ekranic)). Under the asphalt layer, shielded urban soils retain full-profile chernozems and their characteristic genetic humus-accumulative horizons. This soil type is confined to new residential regions in the peripheral part of the city, although it also can occur in residential quarters of the agglomeration center.

**Third Group.** The humus-accumulative horizon of deep calcareous ordinary chernozem on loess-like loam from the northern Azov region (migration-segregation chernozem according to the 2004 Classification of Russian soils [20]; Calcic Chernozem according to WRB [7]) was used as a conventional reference material. The profile was established in the Persianovskaya Steppe Reserve, at 52 km to the northeast of Rostov-on-Don. The reserve represents a unique massif of preserved virgin vegetation and soil cover in the Azov upland steppe.

## 2.2 Analytical Methods

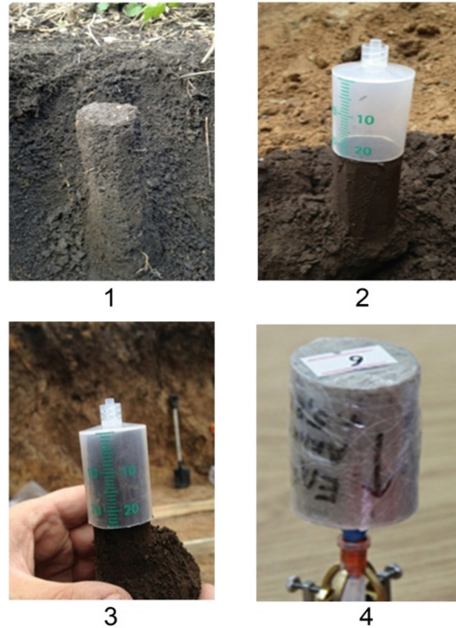
The structure of humus-accumulative horizons of urban soils was studied by computer X-ray microtomography. Studies were performed on a SkyScan 1172G X-ray microtomograph with a peak energy of 10 keV and a spatial resolution of 16  $\mu\text{m}$  in the Dokuchaev Soil Science Institute. The selected resolution makes it possible to confidently detect collector pores coarser than 32  $\mu\text{m}$  involved in the filtration of liquid water and solid-phase particles of analogous sizes.

Tomographic study requires a special approach to the selection of soil samples. It was decided to study soil structure in micromonoliths at the natural water content corresponding to the sampling moment. The micromonolith prepared to analysis is a hermetically sealed plastic cylinder 3 cm in diameter filled with soil of undisturbed structure (Fig. 1, panel 4). During the sampling procedure, the soil sample is adjusted to the cylinder size, which retains undisturbed the internal structure of soil [3, 8]. The sealing of sample with a sticky type prevents the shrinkage and closure of pores, which are inevitable at soil drying (Fig. 1).

Processing of tomographic data (shadow projections) and preparation of tomographic sections (reconstruction) were performed using Bruker nRecon software [9]. During the reconstruction, radiation intensity on the initial X-ray patterns is converted to CT density, the resolution of which depends on the used computer system [10].

Tomographic sections were processed and analyzed using the following software:

- Data Viewer for the preparation and scanning of tomographic sections under the required angle;



**Fig. 1.** Soil sampling for tomographic study.

- CTvox for the reconstruction of a structural fragment of sample with all revealed X-ray contrast phases [11];
- CTvol for the reconstruction of separate 3D objects and structures of pore space; and
- CTan for the mathematical processing and calculation of 3D morphological indices of internal structure for X-ray contrast phases. The software provides results in  $\text{mm}^3$  or percentage of total sample volume. The morphometric parameters include the volume of the studied sample components (pores, aggregates), their surface areas, the sample porosity (total, open, and closed), the content of particles and structural units in the sample, and the content of contacts between linked particles or structural units [12]. The total porosity of sample is determined as the total volume of all pores visible on tomographic images under the given resolution. The open porosity consists of pores traversing the boundaries of the preset virtual cylinder within the sample; the closed porosity consists of pores contained within this virtual cylinder [13].

### 3 Results

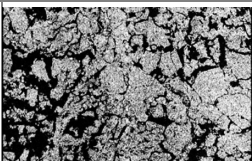
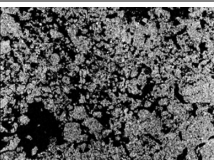
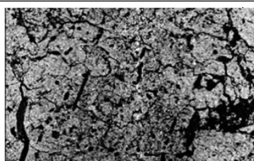
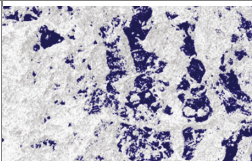
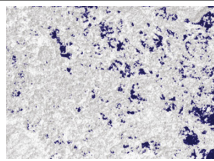
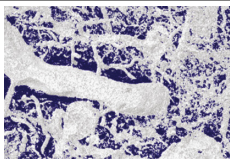
The morphometric parameters determined in tomographic studies (porosity, pore space connectivity, the number of objects, etc.) are actual only for the resolution used. Some authors [14, 15] showed that the total tomographic porosity of separate chernozem aggregates exceeded 70% under a resolution lower than  $1 \mu\text{m}$ . In our case,



interaggregate porosity (packing pores of structural units, channel pores, and crack pores) becomes the main object of calculation under a resolution of 16  $\mu\text{m}$ . Interaggregate porosity looks like a small closed volume within the soil aggregate and composes only a small portion of the total tomographically-determined volume of pore space. From the obtained data, the total porosity for virgin and forest-park chernozems is 23–28%, and their closed (mainly interaggregate) porosity is 1.3–2%.

Similar imaging conditions allow assessing the scale and details of structural changes in urban soils against virgin chernozem. 3D morphometric data for each object of study, as well as fragments of the vertical tomographic section of sample and the 3D structural model of its pore space, are given in Tables 1 and 2. Scanning and analysis were performed using identical scanning and reconstruction settings.

**Table 1.** 3D morphological parameters of humus-accumulative A horizons of Calcic Chernozem (virgin soil and forest-park).

	Calcic Chernozem, forest-park, Rostov-on-Don	Calcic Chernozem, forest-park, Rostov-on-Don	Calcic Chernozem, virgin, settlement of Persianovskii
Vertical tomographic section (black pores)			
3D model of pore space fragment			
Solid phase volume, $\text{mm}^3$	1322.55	1327.78	1406.02
Solid-phase object surface area, $\text{mm}^2$	22223.96	27137.24	28605.61
Number of solid-phase objects in $1 \text{ mm}^3$	287.58	233.15	221.95
Total number of solid-phase objects	525202	425803	405349
Number of solid-phase contacts in $1 \text{ mm}^3$	460.63	571.56	678.77

(continued)

**Table 1.** (continued)

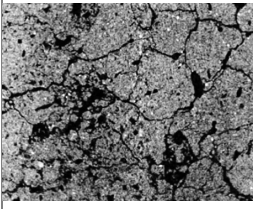
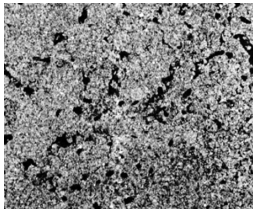
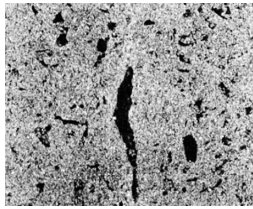
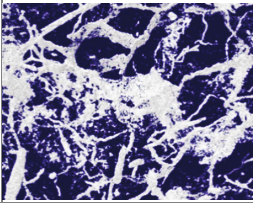
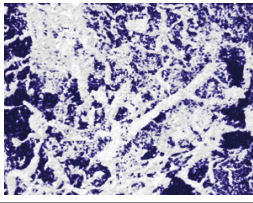
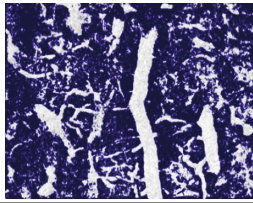
	Calcic Chernozem, forest-park, Rostov-on-Don	Calcic Chernozem, forest-park, Rostov-on-Don	Calcic Chernozem, virgin, settlement of Persianovskii
Total number of solid-phase contacts	841252	1043829	1239631
Number of pores in 1 mm <sup>3</sup>	1227.13	1302.90	1544.39
Number of closed pores in 1 mm <sup>3</sup>	489.79	965.95	1492.52
Total porosity, %	27.58	27.3	23.01
Open porosity, %	26.60	26.09	21.46
Closed porosity, %	1.35	1.64	1.97
Closed pore surface area, mm <sup>2</sup>	4459.58	5191.39	6612.08
Pore space connectivity, %	97.17	96.71	94.72

3D tomographic model of pore space is a good index of soil structural state. It is free from some disadvantages of the planar (2D) analysis of pores and aggregates in thin sections or isolated tomographic sections. The tomographic study easily distinguishes channel pores from bubble pores [16, 17]. In our study, the pore system under a resolution of 16  $\mu\text{m}$  represents a coupled system in which liquid and gas flows move. A very high pore space connectivity (usually >95%) is noted in soils of natural texture. This parameter increases from 94.72 to 97.15% in the series virgin chernozem–chernozem of the forest-park zone, which is primarily related to the higher biogenesity of the latter soil. In the upper horizons of fallow chernozem, connectivity slightly decreases (to 88.69%), which largely agrees with the parameter value for buried humus-accumulative horizon of shielded urbistratified chernozem (Novic Chernozem (Ekranic)): 87.29%. However, pore space connectivity in shielded urbostratozem (Ekranic Technosol over Calcic Chernozem) with strongly deformed structure varies significantly, its filtration properties are disturbed, and connectivity significantly decreases compared to the natural state, as confirmed by our studies.

## 4 Discussion

The obtained results indicate that the humus-accumulative horizons of urban soils, regardless of their anthropo- and technogenic transformation, retain some similar indices, including the presence of spherical macropores, empty or filled with fragmental

**Table 2.** 3D morphometric parameters of surface and buried humus-accumulative A horizons of urban soils.

	Calcic Chernozem, virgin, Botanic garden, Rostov-on-Don	Novic Chernozem (Ekranic), residential zone, Rostov-on-Don	Ekranic Technosol over Calcic Chernozem, residential zone, Rostov-on-Don
Vertical tomographic section (black pores)			
3D model of pore space fragment			
Solid phase volume, mm <sup>3</sup>	1570.76	1501.94	1679.79
Solid-phase object surface area, mm <sup>2</sup>	20932.36	32754.83	17226.98
Number of solid-phase objects in 1 mm <sup>3</sup>	150.03	134.88	96.66
Total number of solid-phase objects	273996	246322	176521
Number of solid-phase contacts in 1 mm <sup>3</sup>	424.01	671.62	310.20
Total number of solid-phase contacts	774361	1226569	566526
Number of pores in 1 mm <sup>3</sup>	1832.05	2199.50	1949.63
Number of closed pores in 1 mm <sup>3</sup>	1303.40	1359.37	1465.78
Total porosity, %	13.99	17.76	8.02
Open porosity, %	12.23	15.19	5.08
Closed porosity, %	2.00	3.03	3.10
Closed pore surface area, mm <sup>2</sup>	7719.96	11335.75	10461.97
Pore space connectivity, %	88.69	87.29	58.61

material, as well as elongated, predominantly vertical, root holes. The diameter of tomographically visible macropores increases in the series of urbostratozem–urbis-tratified chernozem to fallow chernozem to virgin chernozem to forest-park chernozem. Therefore, the parameters of virgin and forest-park soils are close to those of the reference soil. The structure on the tomographic section is seen as undisturbed. Small differences can be due to the features of mesorelief, vegetation, and moisture in the moment of sampling. The humus horizon of virgin chernozem is characterized by multiordinal aggregation with aggregates of 0.02 to 1–1.5 cm in size, as well as a network of fine crack-like pores of random orientation penetrating the entire sample. Crack-like pores reach 0.4 mm in width (diameter). The upper horizons of forest-park chernozems are closest to those of virgin chernozem from suburbs. This is confirmed by the multiordinal aggregation of material and the vast network of branched crack-like pores of random orientation with openings of 0.6 to 1. mm. The aggregate diameter varies from 0.5 to 5 mm (Table 1).

The tomographic imaging data most clearly demonstrate the individuality of buried humus-accumulative horizons of anthropo- and technogenic transformed soils, which differ from other soils by the low degree of aggregation and integrity of material. According to Prokof'eva et al. [18], almost all soils sealed under asphalt are compacted or strongly compacted. This is confirmed by the significantly worse 3D morphometric parameters of anthropogenically transformed soils than those of natural soils (Table 2). Before overlapping the surface horizons of chernozems in city undergo intensive anthropogenic impact. As a result the A horizons structure of Calcic Chernozem, which will become the basis for the formation of Ekranic Technosol were seriously disturbed. Clear signs of overcompaction are observed, as well as lower porosity than in forest-park and virgin chernozems. The pore space is fragmented and mainly consists of root holes, including those of relic roots. Pore space connectivity is significantly lower than in natural soils. This indicates poor draining properties of this soil and disturbance of its ecological functions, which is due to the burying urbic horizons more than 40 cm thick. Almost no granular structure is present, or there are its compacted rests (smaller solid-phase surface area, smaller number of aggregates in the same volume, closed porosity double that of virgin chernozem); therefore, water and gas transfer occurs only in the rests of root hole network.

The buried humus-accumulative horizon of shielded urbistratified chernozem (Novic Chernozem (Ekranic)), despite its high density (up to 1.8 g/cm<sup>3</sup>), is significantly closer to fallow chernozems (Botanic garden, Rostov-on-Don) than to shielded urbostratozem (Ekranic Technosol over Calcic Chernozem). The disturbance of granular structure is appreciably lower; the pore space consists of numerous pores, including aggregate packings; connectivity reaches 87%, which is insignificantly lower than the analogous parameter of virgin chernozem. However, there are distinct differences from fallow and virgin chernozems: increased closed porosity, numerous fine closed pores, and the largest solid-phase surface area. All this can indicate a significant content of sand in the sample or repeated input of sand from outside [19].

From the results of study, fallow chernozems have an extremely diverse structure. The parameters of deep calcareous ordinary chernozem are close to those of undisturbed virgin and forest-park soils, but differences are visible on the sections. The natural structure is partially preserved; a part of volume is occupied by compacted

structures with low porosity but high fracture density. Humus-accumulative horizons on virgin areas are characterized by abundant uniordinal aggregates and their agglomerates separated by fine crack-like pores. Coarse biogenic voids of different shape up to 1 cm in diameter are also common in the soil (Table 2).

Change in the 3D parameters of humus-accumulative horizons should be considered separately for each studied urban soil:

- **Porosity parameters** (total porosity, open porosity, pore space connectivity) decrease in the buried A horizons of anthropogenically transformed soils (Technosols), while closed porosity can increase due to the degradation of channel-pore network and the separation of pore space segments.
- **Surface area** (pore–solid phase interface) changes less significantly when going from the natural to the anthropogenically transformed soil. The amount of inter-aggregate pores decreases and a tendency of soil cracking appears under overcompaction.
- **The number of pores**, especially closed pores, in buried horizons of anthropogenically transformed soils is 2 times higher than in forest-park chernozem and 1.5 times higher than in the humus-accumulative horizon of virgin chernozem. However, the pores are significantly smaller.
- **Solid-phase parameters** (the number of grains, microaggregates, and other particles) also significantly vary between natural and anthropogenically transformed soils and depend on changes in particle size distribution. Under compaction, the aggregated structure disappears, and coarser dense soil particles separated by resting interaggregate pores and cracks remain.
- **The number of objects and contacts** between them in urbostratozem (Ekranic Technosol over Calcic Chernozem) decrease in 2–3 times compared to virgin soil. However, these parameters can increase significantly at the addition of coarse sand to the soil.

From the obtained data, the minimum values of total and open porosity (8.02 and 3.10%, respectively) are typical for the buried humus-accumulative horizons of shielded urbostratozem and shielded urbistratified chernozem. The surface A horizon of virgin chernozem and the buried A horizon of urbistratified chernozem have close values of total and open porosity, which proves the high self-remediation capacity of the entire chernozem type. The maximum parameter values (total visible porosity of 27.58% and open visible porosity of 26.60%) were recorded for the A chernozem of calcareous ordinary chernozem in the forest-park zone of the city. However, in this soil characterized by increased content of organic matter (7–8%), the porosity values are also lower than the total porosity determined by conventional physical methods, because the tomograph determines only visible porosity.

## 5 Conclusions

Tomographic analysis data clearly demonstrate that the A horizon in the forest-park zone is characterized by high aggregation and the presence of aggregates of different diameter (from 0.2 to 5 mm), loose texture, and high tomographically distinguishable

total (27.58%) and open (26.60%) porosity. The buried humus-accumulative horizons of anthropogenically transformed soils are characterized by unpronounced aggregation and integrity. As a result, they have the minimum values of tomographically distinguishable total and open porosity (8.02 and 3.10%, respectively). The diameter of tomographically distinguishable macropores increases in the series: urbostratozem–urbistratified chernozem–fallow chernozem–virgin chernozem–forest-park chernozem.

The surface A horizon of virgin chernozem and the buried A horizon of urbistratified chernozem have close values of 3D morphometric parameters, which proves the high self-remediation capacity of the entire chernozem type.

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# Hydrophysical Properties of Substrates Used for Technosols' Construction in Moscow Megapolis

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**Abstract.** Constructed Technosols are widely spread in cities and perform important functions, including water purification, transfer and storage. The performance of these functions is affected by hydrophysical properties of materials and substrates implemented for Technosols' construction. In this research, water retention curves of the four different substrates used for soil construction in Moscow megapolis were measured by the equilibrium centrifuging approach. The pore size distribution and soil hydrological constants were analyzed based on the water retention curves. The highest water holding capacity was shown for the valley peat. Typical Chernozem was characterized with largest amount of thin pores. Considering all the analyzed hydrophysical properties and climatic conditions, different combinations of loamy-sandy Retisols with sub-layers of valley peat will likely increase water holding capacity and create the best conditions for sustainable development of urban greenery in Moscow megapolis.

**Keywords:** SUITMAs · Soil functions · Soil constructions  
Water retention curve

## 1 Introduction

Urban soils (hereinafter referred as Soils of Urban, Industrial, Mining and Military Areas, SUITMAs) are very diverse and vary from close to natural soils of urban forests and parks to completely artificial soil constructions [6]. Artificial soil constructions (constructed Technosols) are typical basis for turf grasses, roadside lawns, green roofs and infrastructure and can cover up to 40% of non-sealed city areas [5, 8]. Constructed Technosols are responsible for important functions and ecosystem services, including carbon sequestration, climate mitigation, water purification and storage [10, 11]. Water storage is likely the most important function of constructed Technosols to support greenery, therefore information on soil hydrophysical properties is important to create sustainable soil conditions for urban green infrastructure.



From all SUITMAs, constructed Technosols are the most affected by human and likely the most heterogeneous [15]. Depth and sequence of layers in soil construction as well as characteristics of mineral and organic substrates used for Technosols' constructing are the main factors, influencing hydrophysical properties of constructed Technosols [12]. Some physical properties, e.g. aggregates' stability [1], porosity and water infiltration [18], water and temperature regimes [15, 16] were studied for constructed Technosols of different genesis and management. However, information on integral parameters evaluating hydrophysical properties of different substrates used for Technosols' constructing is lacking, but necessary to support decisions in soil engineering and management.

Water retention curve (WRC) defines the relation between soil water potential and water content and is widely accepted as an integral soil hydrophysical parameter. The WRC can be used to characterize water availability and to derive information on pore size distribution [2, 9]. In this research we examined WRC shapes and derived hydrophysical properties of four contrast substrates used for Technosols' construction in Moscow megapolis.

## 2 Materials and Methods

### 2.1 Research Area Experiment Set-up

Moscow (55 N; 37 E) is the largest city of Russia and the one of the largest urbanized areas in Europe. Traditionally, Moscow was an economical and industrial center of Russia, however recent urban planning prioritizes development of green infrastructure to enhance environmental quality in the megapolis [14, 17]. Landscaping and greening activities coincide with input and translocation of tones of soil and artificial substrates and increase the amount and role of constructed Technosols in Moscow city. For the research, four different substrates used for Technosols' constructing in Moscow were used: valley peat (VP), topsoil layer of the reference loamy-sandy Retisol (LSR), topsoil layers of a Typical Chernozem (TCh) and bank sand (BS). The VP, LSR and BS substrates were collected in the Moscow region, whereas TCh was sampled from 0–30 cm layer of cropland in Kursk region (55 N; 36 E), 500 km to the south-west from Moscow.

### 2.2 Water Retention Curve Measurement and Modelling

The WRCs were estimated based on the equilibrium centrifuging approach [7, 14]. The investigated substrates were air-dried, sieved to 2 mm fraction and placed into 4 ml plastic vials for centrifuge Eppendorf 5804R with an angular rotor. Afterwards, substrates were water saturated during 24 h, weighted and placed into the centrifuge. At the centrifuge the vials with saturated substrates were sequentially rotated at the speeds of 200, 300, 400, 500, 1000, 2000, 3000, 4000 and 5000 rpm during 90 min at each speed. After rotation at each speed, the vials were weighted to estimate soil moisture. The obtained results on soil moisture (%) were plotted in relation to matric potential

(kPa) at the logarithmic scale to get an experimental WRC. The experimental WRCs for each substrate were approximated by van Genuchten Eq. (1)

$$\theta(\psi) = \theta_r + (\theta_s - \theta_r) / [1 + (\alpha|\psi|)^n]^{1-1/n} \tag{1}$$

where  $\theta$  is the volumetric water content ( $\text{m}^3\text{m}^{-3}$ ),  $\psi$  is the matric potential (kPa),  $\theta_s$  is the saturated volumetric water content ( $\text{m}^3\text{m}^{-3}$ ),  $\theta_r$  is the residual volumetric water content ( $\text{m}^3\text{m}^{-3}$ ),  $\alpha$  is related to the inverse of the air entry suction ( $\text{m}^{-1}$ ), and  $n$  is a shape parameter.

The model fit was examined in statistical software Sigma Plot 11.0 and characterized by the determination coefficients  $R^2$  and  $R^2_{\text{adj}}$  and  $\theta_r$ ,  $\theta$ ,  $\alpha$  and  $n$  parameters of van Genuchten equation were estimated. The estimated parameters were used to analyze pore size distribution and to estimate the main soil hydrological constants: water saturated capacity (WSC), field capacity (FC), maximum molecular capacity (MMC), wilting point (WP) and maximal adsorption capacity (MAC) by Voronin’s approach, using computer algorithms for searching for the points of intersection with the WRC developed earlier [15].

### 3 Results and Discussions

#### 3.1 Water Retention Curves of the Substrates Used for Technosols’ Construction

The analyses for all the substrates showed the classical sigmoid shape of WRCs most often observed in literature [2, 15]. For all the substrates, the experimental WRCs perfectly fitted van Genuchten model with the best fit shown for Typical Chernozems (see Table 1 for model parameters). The obtained model fit is comparable to the previous results obtained by equilibrium centrifuging approach [7, 14] and higher than those obtained by conventional approaches [3].

**Table 1.** Approximation parameters of the experimental WRCs for the substrates by van Genuchten model

	BS	TCh	LSR	VP
$R^2$	0.9971	0.9999	0.9998	0.9966
$R^2_{\text{adj}}$	0.9953	0.9999	0.9996	0.9945
$\theta_r, \%$	1.4821	15.1397	5.8682	46.2141
$\alpha, \text{J}^{-1}\text{kg}$	0.2193	0.1380	0.3149	0.3957
$n$	3.6315	1.5928	2.0475	1.6571
$\theta_s, \%$	22.7304	56.6970	39.4092	135.8128

The WRCs obtained for the investigated substrates were significantly different in inflexion, as well as in saturated and residual water contents. Both saturated and residual water contents increased in a row  $\text{BS} < \text{LSR} < \text{TCh} < \text{VP}$  (Fig. 1), which

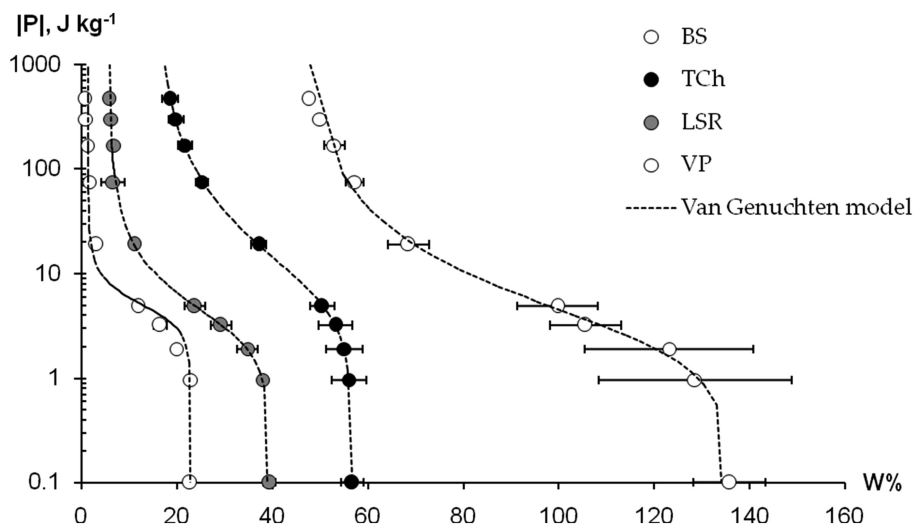


Fig. 1. The WRC for the studied substrates

corresponds with the previous comparative research of WRCs of soils with different texture and organic matter content [2, 13, 14].

### 3.2 Hydrological Constants and Pore Size Distribution of the Substrates Used for Technosols' Construction

The obtained WSCs were used to estimate hydrological constants of the investigated substrates. The highest water capacity was shown for VP judging by all the observed constants. The FC, MMW, MAC and WP for the VP were from 2 to 4 times higher than for any substrate. The values of the hydrological constants obtained for the TCh were less than for the VP, but significantly higher than for LSR and BS (Tables 2 and 3). The maximal water content available for plants can be estimated as the difference between WSC (or FC for homogeneous substrates) and WP. The highest maximal volume of available moisture (WSC-WP) was obtained for VP, however, when considering only the FC, VP contains 2–3 times less available water than TCh (Table 3).

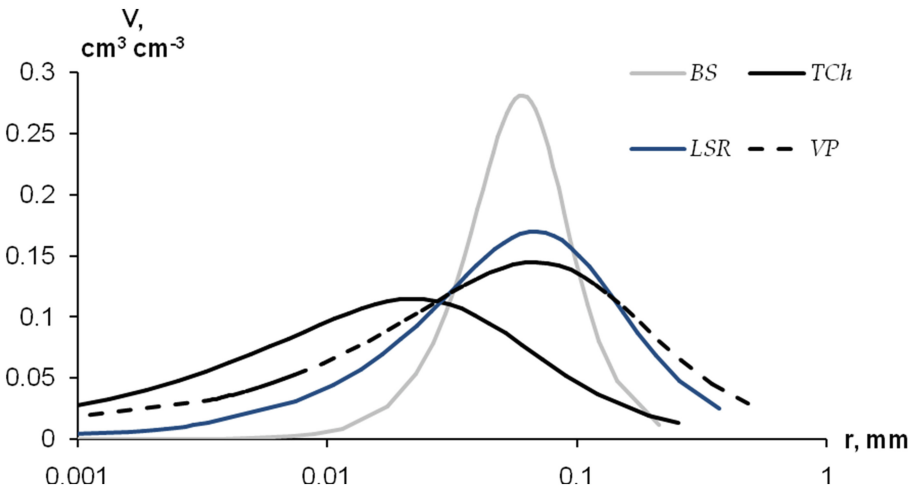
Table 2. Hydrological constants (% per mass) of the investigated substrates

Hydrological constant	BS	TCh	LSR	VP
FC	2.3	32.1	10.9	57.9
MMW	2.1	24.9	9.3	49.2
WP	1.5	16.9	5.9	47.6
MAC	1.5	15.4	5.9	46.2
WSC-WP	21.2	39.8	33.5	88.3
FC-WP	0.8	15.2	5.0	10.3

**Table 3.** Hydrological constants (% per volume) of the investigated substrates

Hydrological constant	BS	TCh	LSR	VP
FC	3.8	34.0	14.2	33.3
MMW	3.5	26.4	12.0	28.4
WP	2.5	17.9	7.7	27.4
MAC	2.5	16.3	7.6	26.6
WSC-WP	35.1	42.1	43.4	50.9
FC-WP	1.4	16.1	6.5	5.9

Comparison of the pore size distribution curves highlighted the difference between the investigated substrates. The TCh curve was clearly shifted to the left compared to other substrates (Fig. 2). This indicates the largest volume of the thin pores obtained for the TCh, which is likely explained by its well developed structure.



**Fig. 2.** Pore size distribution in the studied substrates

### 4 Conclusions

Constructed Technosols are artificially engineered SUITMAS, which functions are mainly driven by human. The obtained information on soil hydrophysical properties of the four contrast substrates implemented for the Technosols’ construction in Moscow is critical evaluate and project the capacity of soil constructions to transfer and store water and to construct Technosols for sustainable development of urban greenery. In our study, the highest water holding capacity was shown for valley peat, however, the Chernozem and loamy-sandy Retisols substrates could contain more water available for plants. The best hydro-structural properties were shown for the Typical Chernozem, where the pore volume was the largest and the distribution of the pore size was the

most equal. However, Chernozems are not sustainable to temperate climate of Moscow and their prosperous qualities would likely reduce after several years of exploitation. Considering climatic conditions, different combinations of loamy-sandy Retisols with sub-layers of valley peat will likely increase water holding capacity and create the best conditions for sustainable development of urban greenery in Moscow megapolis.

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# Current Issues in Legal Regulation of Urban Soil Management

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**Abstract.** This article analyzes the issue of using legally regulated quality standards for urban soil as criteria for assessing the health of this part of nature. The authors explore the legal implications of assessing the condition of this environmental component using impact limits (maximum permissible emissions and discharges of substances or microorganisms) rather than quality standards. The purpose of this publication is to find gaps and inconsistencies in Russian law regulating soil quality.

**Keywords:** Soil · Ecological functions of soils  
Environmental quality standards · Negative impact on the environment  
Damage compensation

## 1 Introduction

The environmental functions of urban soil stem from its ability to regulate the composition of surface air by reducing the effect of industrial and other pollutants, allowing it to serve as a universal physical, chemical and biological filter. “Surface strata heat and moisture dynamics depend on soil. At the same time, soil is an indicator of the stable functioning of the ecosystem and its components” [1]. Urban soil is an important factor in creating ecological and sanitary conditions in cities, playing an important role in providing a healthy environment for urban populations.

A significant amount of urban soil is covered by asphalt, buildings, and other structures due to the construction of roads and housing, as well as industrial activities. Contact with excessive amounts of pollutants reduces the ability of soil on the remaining territory to renew itself, support natural ecological communities, and fulfill its environmental functions. Besides the construction industry, vehicular transport and contaminated soil in industrial sites and their buffer zones also have a significant negative impact on soil.

Therefore, protecting the quality of the environment, including the condition of land and soil, is cited as a priority in Russia [2]. Ensuring environmental sustainability,

in order to provide the public with the full spectrum of ecosystem services, is an integral part of urban planning in Russian cities.

## 2 Ecological Standardization of Soil

Russia's federal law On Environmental Protection establishes norms for environmental protection by setting standards for environmental quality and permissible impacts on the environment. It provides technical parameters and other regulatory documents. These standards are used to regulate the environmental impact of economic and other activities and to prevent negative impacts on the environment (Clause 19 of [3]).

According to the provisions of the law, adherence to these quality standards should ensure a sustainable environment in which natural ecosystems, as well as the genetic pool of plants, animals, and other organisms, are preserved (Article 1, 21 of [3]).

However, there are no Russian legal standards or instructive-methodological guidelines establishing environmental quality standards for urban soils that can be used as criteria in assessing the proper condition of this environmental component and the environment as a whole.

Thus, it would appear the very accurate statement made by V. Petrov more than twenty years ago, that "in the modern sense, environmental quality standards are evaluative standards – used to determine environmental quality and standards for permissible impact – that limit the level of negative impact on the corresponding part of the environment [4]," has not been applied in practice.

At first glance, the environmental regulations would seem to be quite reasonable – they present environmental quality standards as "an ideal" set of physical, chemical, biological and other environmental parameters that will ensure that ecological systems are sustainable and natural objects preserved [3].

Sustainable environmental and ecological conditions can only be maintained when environmental quality standards limit the amount of impact on environmental components and all natural resource users adhere to these standards.

However, due to an absence of established environmental quality standards and ambiguous interpretations of the above-described federal law On Environmental Protection, state regulators have substituted ecological standards for maintaining environmental quality with standards that limit negative (permissible) impact, including widely applied hygienic standards. Hygienic standards are designed exclusively for ensuring human safety, and not for sustaining natural communities (ecosystems), which are often more vulnerable.

However, in regulating sanitary-epidemiological (hygienic) conditions, the biggest emphasis falls on assessing the effects of environmental pollution on public health caused by consuming agricultural products and drinking water, as well as breathing polluted air. In the legislation of the Russian Federation, environmental risks are not taken into account when making management decisions concerning urban soil.

Soil degradation is defined as "a set of processes leading to changes in the functions of soil as a component of the natural environment. This entails the quantitative and qualitative deterioration of its properties and regimes, as well as the reduction in the natural and economic value of land [5]." It is essential to note that the characteristics of



this qualitative and quantitative deterioration appear in the legal regulations of the Russian Federation only in a fragmented manner. In particular, various relevant agencies of the Russian Federation have made attempts to specify criteria for land degradation in methodological regulations, mainly for agricultural lands [1, 5–11], using evaluations of danger levels that cannot be objectively measured (e.g. high, medium, low, etc.). Criteria for urban land do not exist.

“Land reclamation” is defined in terms of the goals of the reclamation: “the restoration of the productivity and economic value of damaged land and the improvement of the state of the environment [12].” A number of standards regulating the technological aspects of its implementation were also adopted.

However, none of these legal standards or methodological guidelines, separately or as a whole, establish criteria for determining basic soil quality parameters, nor do they include approaches for determining the degree of purification necessary to restore territories and objects to functional (intended) use, taking into account geographical and climatic factors and the type of land use permitted.

Thus, it is regrettably necessary to state that ecological standards for soil quality are either absent in the environmental laws of the Russian Federation or have been replaced by sanitary-epidemiological (hygienic) standards in a piecemeal fashion. This situation makes it impossible to establish a systematic approach that would obligate land users and landowners in inhabited areas to maintain land in proper condition. Consequently, it is not possible to create a legal basis for claims demanding fulfillment of obligations or for the reasonable application of penalties for non-compliance, including compensation for environmental damage.

At least two obstacles complicate the ecological standardization of soil under different land uses. First, every type of land use changes the natural properties of the soil. Second, every type of use has its own statutory rules for the treatment of land resources that are reflected in the economic, social, ecological, and medical standards for allowable soil conditions. These often have a technical character.

Thus, in the process of establishing standards for soils of different classifications, a complicated multidimensional problem is encountered that is often decided without proper scientific substantiation in the rapidly developing practice of natural resource management. As a result, the current vagueness does not permit the precise calculation. Accordingly, of deviations of soil properties from acceptable ecological norms for a particular soil type and land use. to properly assess the appropriateness of their economic use is not possible and clear decisions cannot be taken on the necessity of carrying out reclamation work, etc.

This problem can only be solved by creating a unified set of scientifically sound standards for ecological soil quality on lands designated for various economic use, to be adopted by all of the government’s environmental protection and nature-resource agencies. To do this, it would be advisable to begin by establishing general limits for “impact” parameters permissible for soils of all known categories of land.

Soil’s ability to maintain stability under pressures caused by a particular human land use, i.e. its ability to sustain its core natural-resource properties, can serve as the main criterion for determining lower limits for soil quality and permissible impacts on it [13].

Accordingly, in a general outline, we have determined unified limits for soil parameters for all land categories. In establishing general limits, individual limits for

ecological norms can be allocated for every category of land taking into consideration the specifics of their economic use. The system of parameters applied in determining the acceptable range of values for the ecological state of urban soils and human impacts on them for territories with different functional uses is presented in Tables 1 and 2 [13, 14].

**Table 1.** System of parameters used for the determination of the range of allowable values of the ecological state of urban soils and the human impact on them for territories with different functional uses.

Parameter	Allowable levels of soil quality and loads on the soil	Types of specialized use of functional zones			
		Natural	Residential	Communal	Industrial/Transport infrastructure
Particle size composition	Optimum	Light, medium loam			Sandy loam, light loam
Thickness of the humus layer, cm	Minimum	10	10	10	10
	Background	10	15–20	15–20	10–20
	Maximum	Not limited			
Concentration of Corg in the layer of 0–20 cm, %	Minimum	1	1	1	1
	Background	3	3	3	2
	Maximum	Not limited	30	30	30
Density in the layer of 0–20 cm, g/cm <sup>3</sup>	Minimum	0.9	0.9	0.9	0.9
	Background	1.1	1.2	1.2	1.2
	Maximum	1.3	1.3	1.3	1.3
Density in the layer of 20–50 cm, g/cm <sup>3</sup>	Minimum	1.1	1.1	1.1	1.1
	Background	1.3	1.3	1.3	1.3
	Maximum	1.4	1.4	1.4	1.5
Density in the layer of 50–100 cm, g/cm <sup>3</sup>	Minimum	1.1	1.2	1.2	1.2
	Background	1.4	1.3	1.3	1.4
	Maximum	1.5	1.4	1.4	1.5
pH	Minimum	4.0	5.0	5.0	4.5
	Background	5.5	7	7	7.5
	Maximum	8.0	8.0	8.0	8.5
Concentration of mineral nitrogen in the layer of 0–20 cm, mg/kg	Minimum	5	5	5	5
	Background	10	10	10	5
	Maximum	60	60	60	60
Concentration of mobile phosphorus in the layer of 0–20 cm, mg/kg (MAC 200 mg/kg of soil)	Minimum	20	40	40	40
	Background	40	90	90	90
	Maximum	400	400	400	400

(continued)

**Table 1.** (continued)

Parameter	Allowable levels of soil quality and loads on the soil	Types of specialized use of functional zones			
		Natural	Residential	Communal	Industrial/Transport infrastructure
Concentration of soluble potassium in the layer of 0–20 cm, mg/kg	Minimum	10	60	60	40
	Background	20	100	100	60
	Maximum	350	350	350	350
Sum of easily soluble salts, %	Minimum	–	–	–	–
	Background	<0.04	0.04	0.04	0.08
	Maximum	0.08	0.08	0.08	0.15
Electrical conductivity of the pore solution, dS/m	Minimum	–	–	–	–
	Background	<1.5	2	2	2
	Maximum	4	4	4	4
Soil respiration (biological activity), mg of C-CO <sub>2</sub> /kg * h	Minimum	1.7	1.7	1.7	0.4–0.8
	Background	3.5	3.5	3.5	3.5
	Maximum	3.5	3.5	3.5	1.7–3.5
Summary index of contamination Z <sub>s</sub>	Optimum	–	<16	<16	16
Concentration of 3, 4benz(a)pyrene, mg/kg	Optimum		<0.02		<0.04
Concentration of oil products, mg/kg	Optimum		<300		<1000
Concentration of opportunistic microorganisms, index	Optimum	<10			
Concentration of pathogenic microorganisms, viable helminth eggs and larvae	Optimum	Absent			

In addition, it is necessary to create a legal mechanism to integrate the information obtained during the survey on soil quality within land plots into the government real estate cadaster. This will make it possible to enter the obligations included in the law on soil surveys in contractual documentation regarding real estate structures. Establishing such a procedure will simplify the identification of the party responsible for bearing the cost of compensation if the need arises.

Article 1 of the federal law On Environmental Protection [3] defines harm to the environment as a negative change in the environment as a result of its pollution, which entails the degradation of natural ecosystems and depletion of natural resources.

**Table 2.** System of parameters used for the determination of the range of allowable values of the ecological state of urban soils and the anthropogenic impact on them for territories with different functional uses.

Element	Soil group	Allowable levels of the soil quality and the load on the soil					
		Minimum	Background	Maximal			
				Types of specialized use of functional zones			
				Natural	Residential	Communal	Industrial/Territories of transport infrastructure
<i>Total content of heavy metals, mg/kg</i>							
Copper	A	8	30	132	132	132	264
	B	4	15	66	66	66	132
	C	2	8	33	33	33	66
Zinc	A	30	50	220	220	220	440
	B	20	30	110	110	110	220
	C	10	20	55	55	55	110
Cobalt	A	8	10	40	40	40	80
	B	5	8	30	30	30	60
	C	3	5	20	20	20	40
Nickel	A	12	40	80	80	80	160
	B	10	30	40	40	40	80
	C	5	15	20	20	20	40
Lead	A	8	26	130	130	130	260
	B	5	20	65	65	65	130
	C	2	12	32	32	32	64
Arsenic	A	3.5	4.5	10	10	10	20
	B	1.2	2.5	5	5	5	10
	C	0.5	1.5	2	2	2	4
Cadmium	A	–	0.3	2.0	2.0	2.0	4.0
	B	–	n/d	1.0	1.0	1.0	2.0
	C	–	n/d	0.5	0.5	0.5	1.0
Manganese	A, B, C	250	1260	1000	1000	1000	1000
Mercury	A, B, C	–	0.1	2.1	2.1	2.1	2.1
<i>Concentrations of the mobile forms of heavy metals, mg/kg</i>							
Cobalt	A, B, C	0.3	2.0	<5	<5	<5	<10
Manganese	A, B, C	25	80	<700	<700	<700	<1400
Copper	A, B, C	0.5	4.0	<3	<3	<3	<6
Nickel	A, B, C	-/-	1.5	<4	<4	<4	<8
Lead	A, B, C	-/-	1.2	<6	<6	<6	<12
Fluorine	A, B, C	-/-	2.0	<2.8	<2.8	<2.8	<5.6
Chrome (III)	A, B, C	-/-	5.0	<6	<6	<6	<12
Zinc	A, B, C	5/0	8.0	<23	<23	<23	<46

Note: A - loamy soils, pH 5.5; B - loamy soils, pH < 5.5; C - sandy and sandy loamy soils.

A sequence of events linked by cause and effect follows from a literal interpretation of this definition: (1) actual pollution, (2) the resulting negative change in the environment, (3) its manifestation as degraded natural ecosystems and depleted natural resources.

Therefore, in analyzing the first two of the three consecutive events (pollution – negative environmental change), stipulated in the law as determinants of the presence or absence of environmental harm, it appears that at least two must be present:

(1) activities entailing the pollution of the environment, and (2) consequences manifesting as a negative change in its qualitative state.

Consequently, the current absence of a system of standards for soil quality makes it impossible to assess the consequences of land contamination objectively, and, thereby, to establish a causal relationship between this event and possible negative changes in the quality of the soil on land plots. Therefore, on discovering contaminated soil, it is impossible to establish as a proven fact that a concrete economic entity brought harm to the environment because, for example, exceeding hygienic soil standards may or may not result in damage to the environment, depending on natural and climatic conditions.

This conclusion well illustrates the proven ability to establish quality standards for different soil types and subtypes characterized as sharing the same stability under external pressures, as well as various sets of climatic and terrain conditions, taking into account their land categories and zoning in territorial planning documents.

This approach was successfully implemented in preparing standards for permissible residual oil content in soils for a number of constituent territories of the Russian Federation [15, 16] (in Table 3), which were developed in accordance with the provisions of the Order of the Ministry of Natural Resources and Environment of the Russian Federation [7].

**Table 3.** Allowable residual content of oil in soils of different land categories, g/kg

Land category	Komi Republic		Khanty - Mansi Autonomous Okrug		Republic of Tatarstan
	Soil group				
	Organic	Organomineral	Organic	Organomineral	Organomineral
Forest land	30	10	60 (100)	2–15	–
Agricultural land					
Hayfields and pastures	30	10	–	1–5	2.9
Cropland	5	1	–	1–5	2.9
Industrial land	80	30	–	5	–
Water conservation land	5	1	1	0.1	–
Specially protected natural territories	5	1	–	–	–

Note: Dashes denote the absence of developed norms for the particular land category.

According to [7], the standards are intended for evaluating land reclamation work and represent values for oil and its transformation products in the content of soils. Under these, the possibility of oil flowing into neighboring environments or adjacent territories is eliminated and land plots can be brought into commercial use based on their intended purpose with possible restrictions (non-environmental) on their mode of use. They can also be used in introducing conservation regimes to ensure the achievement of sanitary-hygiene standards for the content of oil and its transformation products in soil, as well as compliance with other standards established by current legislation for the self-restoration of land, without additional resource-intensive activities.

The provisions of [7] provide the list of factors that determine the versatility of regulatory standards: zonal-climatic features that influence the composition of soil cover and the speed of transformation of petroleum constituents; terrain-lithologic-geomorphological conditions, including the granulometric composition and structure of the soil profile; the categories and types of land use, and the chemical composition of oil and its transformation products.

At the same time, the methodological issue of establishing as fact that real harm has been done to the environment still requires definition. In the current Civil Code of the Russian Federation, the main characteristic for determining legal responsibility for inflicting harm is contained in Sect. 1 of Article 1064 [17], according to which the inflicted harm should be compensated for in full by the legally responsible party. Likewise, Article 77 of [3] establishes an obligation to compensate for damage caused to the environment in full.

According to Article 1082 of the Civil Code of the Russian Federation [17], forms of redress for harm can be compensation in kind or restitution for inflicted damages. Article 78 of [3] stipulates that damage to the environment can be compensated by obligating the responsible party to restore the damaged environmental conditions in accordance with a recovery plan at their own expense.

The ideal calculation for compensation for damages in kind (be they environmental, social, or economic, according to the terminology of the Constitutional Court of the Russian Federation [18]) in environmental protection legislation should have been rendered by the “spoiled – return to previous state” formula. A return to the “previous state” would preclude the need for the additional stipulation of any “or” in the form of reparation for damages.

However, it seems unlikely that restored soil areas will possess the same environmental qualities (degree of buffering, ability to absorb pollutants, etc.) and, therefore, maintain (support) the ecological balance of all the environmental components surrounding it, as it did in its previous state. Moreover, a long time will be needed after soil cover restoration for the development of bio habitats, which play a fundamental role in fulfilling ecological functions.

Therefore, strictly speaking, civil laws allowing for compensation in kind for damage inflicted on the environment are hardly applicable, as restoration to the “previous state” is impossible in principle, and no one is capable of putting in the necessary quantity and quality of work.

In the sphere of soil protection, it is more appropriate to emphasize monetary compensation for harm already incurred and future damages (in the form of loss of

ecosystem services), which is established in current civil law as an alternative to redress “in kind.” The Supreme Court of the Russian Federation also emphasizes that “in determining environmental damage in monetary terms, not only the cost of restoring the natural environment should be taken into account, but also ecological damage that is impossible or difficult to repair [19].”

In addition, the Constitutional Court of the Russian Federation noted in the case of land recultivation that “the restoration of the state of the environment is to be carried out after the elimination of the consequences of environmental pollution and is not one procedure”; “carrying out only one recultivation does not constitute full compensation for environmental damage, and is only a means to remove obstacles to restoring the ecological system” [19].

However, the methods for determining compensation for real damage inflicted on the environment, as stipulated by civil law provisions laid out in environmental legislation, are quite contradictory. In one Article of [3], priority is put on determining the amount of environmental damage based on approved rates and methods, and, in another, on the actual cost of restoring the state of the damaged environment [3].

Inconsistent enforcement practices have evolved due to these internal contradictions.

On the one hand, the Supreme Court of the Russian Federation clearly specifies the necessity of applying “approved rates and methods when calculating the amount of harm (damage) inflicted on the environment when deciding the size of compensation in monetary terms [20].”

On the other hand, the Constitutional Court of the Russian Federation supports the application of rates and methods citing the fact that “the peculiarities of environmental damage, primarily non-obvious causal relationships between negative environmental impacts and the harm inflicted, should determine the difficulty or impossibility of compensation in kind and, because of this, the calculation of the harm caused [21].”

Although the Ministry of Natural Resources and Environment of the Russian Federation has approved a “methodology for calculating the amount of damage caused to soil as an object of environmental protection [22],” the rates listed in this methodology are parameters whose values are not correlated with the size of the inflicted damage due to the absence of, as noted earlier, quality standards for determining the regulatory status of the health of the affected environment.

The Constitutional Court of the Russian Federation specifies that “the method for calculating the amount of harm inflicted to objects under environmental protection, including water, as a consequence of violating relevant legislation, in any case, cannot be arbitrary and should be based on quantitative limits for negative environmental impacts [23].”

Due to its use of unsubstantiated values, the amount of damages calculated by the Ministry of Natural Resources’ methodology [22] can be higher or lower than the real damage inflicted on nature. If the extent of damage is understated, the principle of full compensation for harm is violated. If the amount is overstated, business entities are unreasonably punished.

Despite the above-noted positions taken by the higher Russian courts, in view of the objective lack of a legal framework providing regulatory tools, these very “quantifiable limits for negative impacts on the environment” that the Constitutional Court of

the Russian Federation talks about continue to be supplanted by a second level of regulation. As we have seen above, these standards, which include permissible emissions and discharges of substances and microorganisms, as well as maximum allowable concentrations of pollutants, cannot qualitatively assess the condition of environmental components or the environment as a whole.

In such a situation, business entities are repeatedly compelled to bear the cost of so-called “restorations” of damaged environmental components in the form of compensation in kind or empirically calculated monetary restitution.

In addition, it should be recognized that the above-described instruments for determining the amount of monetary compensation for environmental damage do not take into consideration the “opportunity cost” of ecological losses that are difficult to replace, as required by civil law.

Thus, a violation of maximum permissible contamination should not be automatically defined as an infliction of damage on the environment in all cases, as it may not entail damage to environmental quality, and therefore, will not lead to an infringement of the environmental, social or economic interests of the state or society.

In this case, forcing the offender to bear the senseless costs of returning the object to its “previous state” is unjustified and unfair. The amount and type of work employed to restore the ecological functions of urban soil should be determined by the planned use of the land plot, albeit with an objectively stated “lowered bar” for its environmental value. In this case, the guilty party should bear the costs of compensation for the social consequences of the loss of ecosystem services due to pollution of urban soils.

### 3 Conclusion

In order to ensure sustainable development in urban areas, it seems appropriate when preserving soil quality that environmental management decisions be primarily guided by a categorized system of soil quality standards whose parameters objectively establish norms for acceptable soil exposure to different economic activities.

Making management decisions using such soil quality standards will help to achieve ecological and economic balance, particularly when the environmental impacts on this environmental component are insignificant or unidentified.

In situations when environmental damage has been inflicted and the consequent deterioration in quality has been established, it is necessary to understand to what extent the environmental component can be restored to its “previous state.” In the absence of a sound basis to conclude that there are real prospects for recovery, reducing the status of the natural object in question should be considered (e.g. putting the land into a lower environmental category, etc.). In this case, forcing the offender to bear the irrational costs of returning the object to its “previous state” is unjustified and unfair. The amount and type of work employed to restore the ecological functions of urban soils should be determined by the planned use of the land plot, albeit with an objectively stated “lowered bar” for its environmental value.



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23. Decision of the Supreme Court of the Russian Federation dated 03.06.2015 No. 310-ES15-1168 with regard to case No. A54-503/2014. Legal Reference System "Consultant Plus"



# Sustainable Development of Forest Ecosystems in Urbanized Territories as a Way of Wildfire Control in Russia

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**Abstract.** Human effect on natural ecosystems is known as increasing at the last decades. This results in changes in ecosystems functioning and causes the monitoring works became more and more urgent. One of the principal factors which effects on terrestrial and adjacent aquatic ecosystems is wildfires. Wildfires results in declining of abandoned, unaffected lands in nature. For example, wildfires of 2010 were so catastrophic that have occupied more than 8 mln ha of productive lands. The results of the studies of soil and vegetation changes after wildfires in two different natural zones (forest-steppe and tundra) have been reviewed.

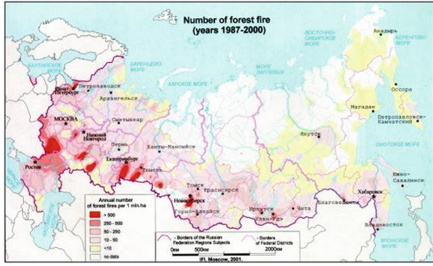
**Keywords:** Wildfires · Forest ecosystem · Reforestation · Soils  
Urbanized territory

## 1 Introduction

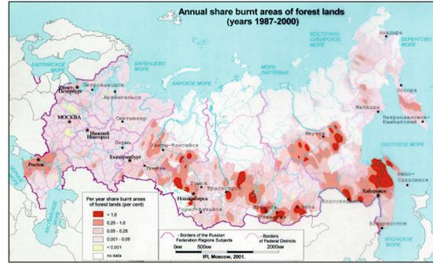
Wildfires are the most dangerous exogenous violation of natural ecosystems in Russia. Climatic changes of the last decades significantly increase a threat of forest fires. Weather variability significantly increases, which is expressed in the alternation of showers and long warm and dry periods, sometimes with a heat wave, like in the summer of 2010 at the center of European Russia. Such specifics create a threat of forest fires high, especially of high severity, so-called catastrophic wildfires. These fires result in serious ecosystem degradation, significantly damage the economy and infrastructure and also negatively influence on living conditions and population health in the regions of wildfires distribution.

Wildfires are one of the most serious unsolved problems of Russian forests. The fact that they cause a huge damage is recognized even by a management of the federal agency that is responsible for forestry (Federal Forestry Agency). The forest resources of Russian Federation are under authority of three ministries – Natural Resources, Agricultural Industry and Defense. Therefore, it is these ministries that should pay special attention on forests conditions and fire conditions.

The maximum density and frequency of wildfires is characteristic for densely populated regions of European part of our country (Fig. 1), and the maximum percent



**Fig. 1.** Number of wildfires in different regions of Russia



**Fig. 2.** The share (%) of the burnt forest area

of area affected by fire is be accounted for by multiforest regions of Siberia and Russian Far East with poorly developed infrastructure (Fig. 2) [1].

Abnormally dry and hot 2010 year has provoked numerous forest fires across the European part of Russia: there was 34.8 thousand of wildfires, which have passed 2.0 million ha of forest area, in July and August in Russian Federation. It has become a global environmental disaster as it has completely changed a functioning of forest ecosystems.

The studies of the postfire functioning of forest soils under relatively uniform climatic and geomorphological conditions are of great interest, it is important for understanding the dynamics of forest ecosystem components restoration and predicting the ecosystem state under influence of different fire severity. Therefore, postpyrogenic pedogenesis is interesting and rather outstanding model of restoration of the soil-plant cover after catastrophic natural impacts.

The aim of this work was to study wildfires' effects in different natural zones (on the example of forest-steppe and tundra) at the early stage of the demutational change of the vegetation. The following tasks were set: (1) to investigate the effect of different types of fires on the soil and plant covers, (2) to analyze the results of remediation measures on the postpyrogenic areas, and (3) to study the dynamics in soils after wildfires.

## 2 Materials and Methods

Two types of zonal environments, affected by fires have been selected for this investigation: tundra and forest steppe. Plots situated in surroundings of Pangodi settlement (Yamal region) and Togljatty city (Samara region) were investigated with scenarios of surface and crown fires. Sampling was conducted in few months after the wildfires. All chemical soil parameters were studied on a fine earth of soil according to standard methods. Total carbon and nitrogen contents were determined by using a C-H-N analyzer in the fine earth. The pH values were determined using the standard method in water suspension. The intensity of the soil basal respiration was measured in laboratory

using incubation method. The value of  $V_{\text{basal}}$  was expressed in  $\mu\text{g CO}_2\text{-C}\cdot\text{g}^{-1}\cdot\text{soil (substrate)}\cdot\text{h}^{-1}$ . The content of carbon in microbial biomass ( $C_{\text{mic}}$ ) was determined in the samples by the fumigation method. The content of  $C_{\text{mic}}$  was expressed in  $\text{mg/g soil}$ . The functional activity of soil microbial community was estimated from the microbial metabolic quotient ( $q\text{CO}_2$ ) calculated as the ratio of basal respiration to the microbial biomass:  $q\text{CO}_2 = (\mu\text{g C-CO}_2/\text{h})/\mu\text{g C}_{\text{mic}}$ .

### 3 Results and Discussion

#### 3.1 Forest Fires in Samara Region

Especially complicated situation was in Samara region near Togljatty city. According to Uniform interdepartmental information and statistical system data a sharp increase of number of wildfires is observed in 2010 in comparison with 2009 and 2011 (Table 1). About 1.5 thousand from 8475 ha (20-25%) of city forest vegetation were destroyed by wildfire in July-August near Togljatty city. It became a local environmental disaster as completely changed functioning of forest ecosystems. How it was? Regular surface fires were taking place in June–July of 2010 in the city forests of Togljatty. Separate crown fires were beginning to appear at the end of July in certain places. People are forbidden to be in city forests of Togljatty on 30<sup>th</sup> of July, 2010 according to the resolution of the mayor of Togljatty, and the city situation was became extraordinary. Then the situation begins to develop in a way that there were no light and water in houses on 31<sup>th</sup> of July in Portposelok and mobile communication was not work. Together security service and population coped with wildfires in Togljatty city by 9<sup>th</sup> of August: the open fire sources were not revealed.

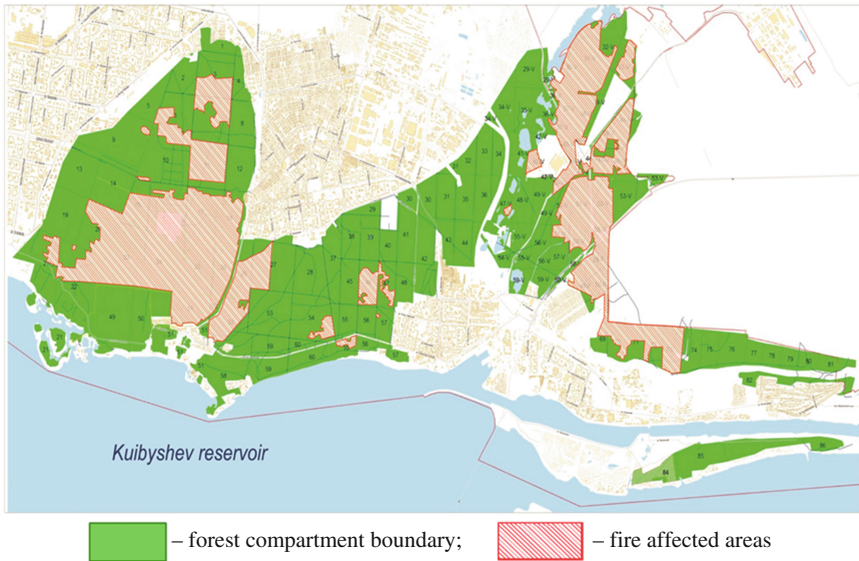
**Table 1.** Number of wildfires in 2009–2014 in Russia according to Uniform interdepartmental information and statistical system data

Region	2009	2010	2011	2012	2013	2014
Russian Federation	23245	34812	21074	20238	10249	17058
Moscow region	548	2332	475	55	28	47.4
Leningrad region	237	265	250	92	143	504
Samara region	511	792	38	39	32	63

According to Federal Forestry Agency a damage from wildfires in Togljatty city of 2010 was 85.5 billion rubles. It exceeds expenses of the federal budget on forestry in more than four times. Probably Federal Forestry Agency data of a wildfires damage are repeatedly underestimated; it takes into account only direct losses of forest resources, but doesn't consider losses of environmental-forming and natural values by forests and especially doesn't consider a damage caused by fire and fume to life and human health.

Wildfires 2010 in Togljatty city resulted in deterioration of ecological situation in the city - a fire has destroyed the whole forest ecosystem. The soil as an integral part of forest communities is influenced by diverse effects of wildfires.

There were 35 wildfires during fire danger period 2010 in forests within the boundaries of Togljatty city. A total area affected by fire was 2087 ha (Fig. 3). According to results of forest pathology survey carried out on 2665.7 ha area, it has been suggested to carry out the following activities: sanitary final harvesting – 1059.6 ha, selective sanitary harvesting – 791.6 ha, wastes cleaning – 470.9 ha [2].



**Fig. 3.** Forest areas of Togljatty

Forest areas in Togljatty city belong to forest-steppe zone, where boreal forests are in contact with south of forest-steppe ecosystems.

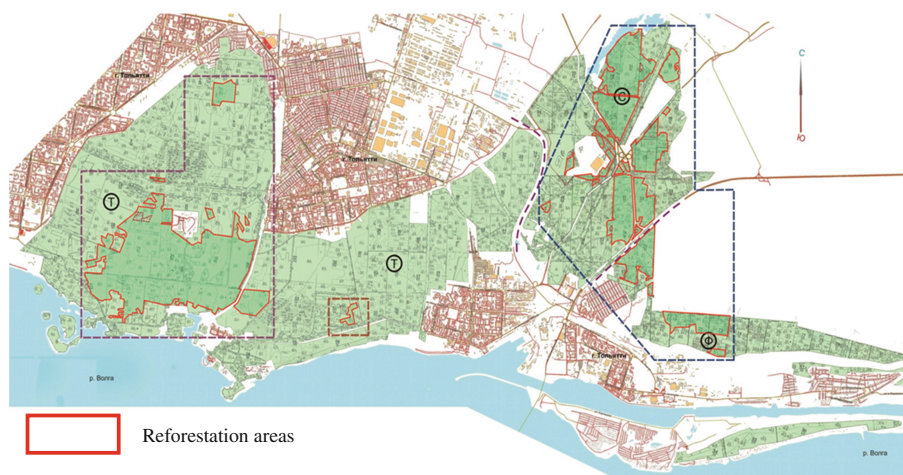
A tree layer survived after surface fires, but the fire damaged trunks in different degrees. Herbaceous and shrub layers have more suffered by wildfires, however, they have not completely burned, but some areas remained unaffected by fire.

A different picture is in forest communities affected by crown fire. Tree layer has completely burned, as well as herbaceous and shrub layers, spontaneous postpyrogenic successions began there.

Cut-down and fell burned trees are laying on a surface in some places, and nobody is going to remove them and use it in some kind of industry.

A reforestation is planned on a damaged territory of city forests in Togljatty city of more than 700 ha. Works of reforestation are conducted by 19 contract organizations on the territory of the Togljatty city forests. In 2010-2011 forest planting was carried out on the 85 ha area. In 2012 spring planting was carried out on the 56 ha area, in autumn – on 295 ha area. 250 ha of city forests were cleared for restoration at the moment [2] (Fig. 4). However, there are huge territories which are not even prepared for planting and still someone burns out debris.





**Fig. 4.** Reforestation areas in Togliatti city

Funds for purchase of transplants, soil preparation, planting and agrotechnical tending are allocated from the Samara region budget [3].

However, natural forests regeneration is preferable since vegetation close to undisturbed ecosystems is formed in this case. These plant communities will be more tolerant to local ecological and climatic conditions, and diversity will be higher, than in case of communities that will be created by human.

Catastrophic wildfires in urban forests of Togliatti city have led to a formation of pyrogenic-transformed soils in 2010, these soils significantly differ from unburned according to morphological characteristics and basic chemical and physical properties.

The first stage of vegetation restoration after wildfires is a distribution of ruderal vegetation. Tree and shrub vegetation begin to develop later due to natural regeneration.

Pyrogenic processes are widespread phenomenon, that has a huge impact on soil formation processes, and that fact makes to pay special attention to the study of natural ecosystems. A significant amount of publications is devoted to wildfires role in the natural dynamics of forest cover, since wildfires are the most powerful environmental factor among other factors that determine forests structure and dynamics and also the ecological state. Meanwhile, a problem of post-fire soil formation occasionally attracts the attention of scientists, and it is necessary to recognize that this is happening less frequently. Fire destroys soils and forests for a moment, but nature is restored for years, decades, centuries. Therefore, the results of postfire functioning of forest soils studies in relatively homogeneous climatic and geological and geomorphological conditions are quite important for an environmental characterization of forest ecosystems. It is important for understanding ways of forest ecosystem components recovery dynamics and for prediction of their condition at different pyrogenic impact. Thus, postpyrogenic soil formation is an interesting model for soil and vegetation recovery after catastrophic natural impacts studying. Carrying out a monitoring of postfire areas and predicting what will happen to our soils in future, we will be able to save correctly our forest

resources, to create conditions for sustainable development of forest ecosystems and to carry out measures to prevent the loss of land productivity.

One of the objects of this research are postpyrogenic soils characterized by formation of specific charcoal horizon with increased portion of postfire organic matter near Togliatti city (Samara region, Russia) affected by spontaneous forest fires in 2010. Three plots were studied: after surface forest fire, after crown forest fire and control.

The results of morphological analysis have showed that only the most upper horizons of soil profiles changed after fires. Particularly, surface fires lead to more intensive organic carbon loss than crown fires (2.85% – after surface fires and 2.37% – after crown fires) [4]. Moreover, soils' dehumification has been found after forest fires, which is related to the organic horizons' destruction, root residues' mineralization, and the almost complete absence of fresh plant waste on the postfire areas [4].

Moreover, several changes in soil organic matter structure have been detected [4, 5]. Humus losses and decreases in total carbon stocks and content are observed after fires' effect on forest floor and humic horizon. Furthermore, the content of humic acids, that indicate a degree of organic matter humification, increased in the pyrogenic horizons, especially after surface fires. Fire also lead to formation of humic acids with increased portion of aromatic compounds than in control soils, which indicates the degradation of carboxylic and aliphatic groups of molecules under the burning effect. This good corresponds with decreasing of hydrogen portion if comparing the elemental composition of burned soil with mature ones. Furthermore, results of <sup>13</sup>C NMR spectroscopy showed that there is an intensive increase in aromatic compounds in HA molecules in postpyrogenic soils. There is a pronounced and statistically significant decline of aliphatic chain content in response to exposure to fire. The free radicals content and the degree of molecular stabilization assessed with electron spin resonance showed an essential alteration of the HAs, expressed in the increase in the radicals portion, in post-fire soils compared with that found in soils not exposed to fire. The accumulation of aromatic compounds indicates only apparent stabilization of HAs due to the loss of periphery alkylic carbon species, which was confirmed by destabilization of the molecules as illustrated by the increase of free radicals [9].

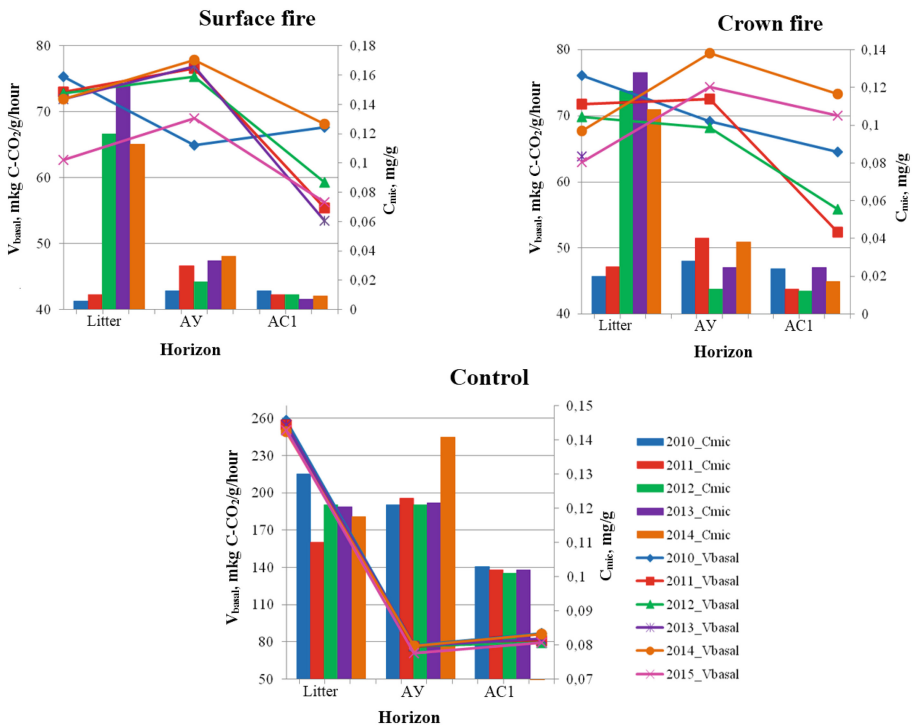
Physical soil properties have also been changed after forest fires. A determination of a soils' contact angle showed an increase of an upper horizons' hydrophobicity as a result of wildfires, especially as a result of crown fires. The studied postpyrogenic soils are sandy loams according to particle size distribution results. Two methods of particle size distribution were compared with the aim to reveal the real grain sizes and clay content in soils. These were laser diffraction and classical sediment method. It was substituted that the method of sedimentry supports higher values of the clay fraction content due to underestimation of density and influence of soil organic matter. The particles of SOM, especially the part that forms after wildfires - black carbon components, compose clay fraction, but actually they are not the part of it. This effect is called pseudofractions in sedimentometry. Considering various landscape positions, it can be noted that maximum of silt fraction content is at accumulative positions, and its minimum is characteristic for slope positions [4].

Moreover, the maximum of polycyclic aromatic hydrocarbons resulting from the wildfires as well as clay fraction is characteristic for accumulative geochemical positions. The surface forest fires result in more intensive PAHs accumulation in



comparison with crown forest fire. Higher PAHs values were determined in accumulative geochemical positions. The incomplete wood combustion results in 2-nuclear naphthalene and 3-nuclear phenantrene accumulation [4].

Fires caused significant changes in the soil biological activity (Fig. 5). The lowest soil basal respiration intensity was recorded at the post-pyrogenic plots both after surface and crown fires: it decreased in litter by 3.4 times in comparison with the control. The decrease in basal respiration after the fire was observed not only in the uppermost horizons but also in the lower layers. The carbon of soil microbial biomass ( $C_{mic}$ ) in the upper horizons (0–20 cm), as well as basal respiration, is highly sensitive to pyrogenic impacts. Microbial metabolic quotient ( $qCO_2$ ) was used for a microbial community functional activity assessment after pyrogenic impact [5]. The  $qCO_2$  values are calculated as a relation of the respiration intensity to microbial biomass unit [6, 7, 10] ( $qCO_2 = (\mu\text{g C-CO}_2/\text{h})/\mu\text{g C}_{mic}$ ). Obtained data showed that basal respiration intensity of soil microbial community decreases in a row: control → crown fire → surface fire. It testifies that microbial communities in the solum have lack of available nutrients and substrates which are released during a mineralization of organic matter. Three years later after the fires the values of metabolic quotient decrease and become close to control variant.



**Fig. 5.** Basal respiration ( $V_{basal}$ ),  $\mu\text{g CO}_2\text{-C}\cdot\text{g}^{-1}$  soil (substrate) $\cdot\text{h}^{-1}$  (lines), and soil microbial biomass ( $C_{mic}$ ), mg/g (columns). Togljjatty city (values of  $V_{basal}$  are on the left Y-axis; values of  $C_{mic}$  are on the right Y-axis)

A parameter  $C_{\text{disturbed}}$  characterize how violent disturbance has soil microbiota been subjected to. It defines as a ratio of  $q\text{CO}_2$  between disturbed and undisturbed soil ( $C_{\text{disturbed}} = q\text{CO}_2_{\text{disturbed}}/q\text{CO}_2_{\text{undisturbed}}$ ) (Table 2) and is called soil microbiota disturbance degree. Values greater than 1, as well as significantly less than 1, testify to disturbance of soil microbial complex resistance [8, 10].

**Table 2.** Soil microbiota disturbance degree

Soil horizon, depth, cm	$C_{\text{disturbed}} = q\text{CO}_2_{\text{disturbed}}/q\text{CO}_2_{\text{undisturbed}}$				
	2010	2011	2012	2013	2014
Surface fire					
Litter, 0–5	6.54	3.16	0.29	0.22	0.30
AYpir, 5–14	4.45	4.10	6.34	3.28	4.51
AC1, 14–27	2.74	6.98			4.22
Crown fire					
Litter, 0–5	1.92	1.24	0.28	0.23	0.30
AYpir, 5–10	2.14	2.91	8.19	3.70	4.47
AC1, 10–15	1.38	5.08			3.29

The greatest value of soil microbiota disturbance ( $C_{\text{disturbed}} = 5.92\text{--}7.56$ ) was observed in upper soil horizon after surface forest fire (2010). Soil microbiota disturbance degree in soils affected by crown forest fire was significantly lower compared to surface fire ( $C_{\text{disturbed}} = 1.93\text{--}3.72$ ). This characteristic decreases in time and is close to 1 in a litter in 5 years after fires whereas in the solum it still differs from 1 ( $C_{\text{disturbed}} = 1.87\text{--}2.28$ ) [8].

For this reason, fires lead to reorganization of soil microbial community, which is expressed in a change of its functional state determined by microbial metabolic quotient. A “stabilization” of postpyrogenic soil microbial community functioning was noted after the fires (2–3 years).

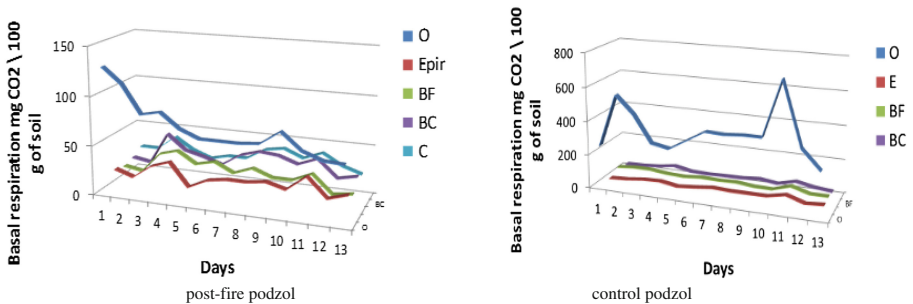
## 4 Wildfires in Yamal Region

Wildfires has been affecting not only on traditionally dangerous fire regions, but also the tundra. Wildfires in tundra – are the natural catastrophic events leading to the release of huge amounts of carbon dioxide to the atmosphere.

Forest fires were reported during summer time period (2016) in the southeast area of the Yamal-Nenets region, Nadym city. The affected territory was approximately 15 ha, and included the areas surrounding the Pangodi settlement (i.e., location of the compressor Pangodinkaya station, which is a key part of the Siberian gas pipeline system). The reason of the fire occurrence was the abnormal high temperatures established since the beginning of the July (27–33°C). According to long-term monitoring data, wildfires in the permafrost zone of the North-west Siberia occurs more frequently over the last decade.

The content of SOM in upper soil horizons significantly decreases compare to control plot (from 38.3 in control to 26.6% in postfire case). The same picture was observed for soil organic carbon stocks in upper organic (O, 0–3 cm) and subsequent eluvial horizons (E, 3–10(20) cm) – declining from 20.28 and 0.89 kg/m<sup>2</sup> in control plot to 2.69 and 0.28 kg/m<sup>2</sup> in postfire soil. Furthermore, an increase of N total content as well as an increase of calculated nitrogen stocks was observed after wildfires (the maximal level of N total content was 0.94% in the ash). Nutrients release from organic residues and plant material to the upper horizons of soil due to high temperatures effect. So, this is a reason of significant increase of nitrogen content in postfire soils. Lower values of C/N ratio in post-fire soil show enrichment of SOM with nitrogen, incoming from the mineralization of organic horizons.

Basal respiration intensity of upper horizons soil affected by the fire showed the continual decrease with time, suggesting the suppression of biological activity of soils (Fig. 6).



**Fig. 6.** Basal soil respiration, mg CO<sub>2</sub>-C·100 g<sup>-1</sup> soil (substrate)·h<sup>-1</sup>. Yamal region, Nadym City

Substantial increase of the total content of Polycyclic aromatic hydrocarbons was found in topsoil layer affected by the fire, with a domination of such compounds as phenanthrene, benzo(a)anthracene and even benzo(a)pyrene.

## 5 Conclusions

Significant changes in a soil profile were observed after wildfires. Humus losses are the most intensive processes that happen when forest floor and sod (humic) horizon have burnt. Some time later the intensification of surface erosion process is observed. Moreover, destroying of organic matter because of the fire can lead to low molecular organic fraction illuviation in middle part of soil profile. Ash accumulation on soil surface leads to increasing of pH values or soil neutralization. The significant decline of soil microbial biomass and basal respiration rate in upper horizons was observed in case of postfire soils. Thus, as a result of fires there is a depression of microbial community. Thus, soil-forming processes are essentially influenced by forest fires, and,

therefore, this problem demands an assessment and careful researches. A problem of wildfires fight is difficult, comprehensive and very actual. Unfortunately, government is unable yet to cope with the situation arising annually during the fire-dangerous period. A decision of this problem requires involvement and cooperation of specialists in various disciplines such as ecologists, foresters, economists, firefighters, specialists in preserving a biodiversity and health protection, etc.

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# Design and Construction of Facsimile Yellow Kandosols at Barangaroo, Sydney

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**Abstract.** A re-design of redundant port facilities within Sydney's CBD involved a restoration of endemic Sydney Harbour soil and vegetation edaphology. Analysis of natural benchmark Hawkesbury sandstone soils showed P and Ca to be the main limiting elements in this ecosystem.

Research was conducted into the amounts of these limiting elements held in the standing biomass in eucalypt woodland on sandstone. This work provided estimates for mimicking the "ash-bed" effect in this fire-prone forest type where P and Ca is returned to the soil following bushfire. The work showed that an ash-bed effect would be best approximated by the addition of 10% by volume of a mixed garden waste compost commercially available in Sydney.

Trial work was conducted using 5%, 10% and 30% of compost with and without acidification using sulphate of iron. No nutrition other than small amounts of urea N were provided. *Banksia marginata* and *B. spinulosa*, P sensitive species, grew best and did not show elevated P or P induced Fe deficiency at 10% compost and showed elevated foliar P levels at 30% compost. Where acidification was used *Eucalyptus haemastoma* showed Mn toxicity at the lowest pH regardless of compost level. A strong correlation between soil pH and foliar Mn was established in this species.

The work informed the development of tender specifications for a constructed Kandosol that included 5% compost for the most sensitive heathland species, 10% for Eucalypt woodland species and 20% for turf and park tree areas. Plant losses were less than 1% in the project and no plant losses could be attributed to nutritional factors.

**Keywords:** Barangaroo · Anthrosol · Manganese toxicity  
Phosphorus sensitivity

## 1 Introduction

Until 2008, Millers Point was a working port and shipping facility at Sydney Cove. The NSW State Government via NSW Port Authority decided to redevelop the concrete foreshore into a mixed residential/commercial space with parkland.

Named 'Barangaroo', a feature of the new site would be 6 ha of headland park containing naturalistic parkland, walking trails, lookouts, and rock pools. The concept evolved into a revegetation using 84 plants species indigenous to the Sydney region at the time of European settlement.

The geology supporting Sydney's unique flora is Hawkesbury Sandstone, a coarse quartzitic sandstone deposited in the mid-Triassic. Limited research on Sydney Sandstone soils indicated very low soil fertility and early attempts to farm in Farm Cove failed to yield adequate crops [1]. To successfully grow endemic species, specific soil profiles catering to their needs had to be constructed. The plants would be growing in a fully re-constructed soil made from on-site resources such as crushed sandstone.

In the Australian Soil Classification (ASC), the term 'Anthroposol' relates to natural soil profiles that have been modified by human activity [2]. The ASC has no definition for urban landscape soils that are deliberately manufactured. The USDA Keys to Taxonomy describes only 'Anthropic Eipedon' referring to surficial human affected layers [3]. Stroganova [4] would describe the soil as a 'Constructozem', a term that describes manufactured soils. In this paper, the growing media will be referred to as an Anthroposol.

## 2 Aim and Methodology

The overarching aim of this project was to develop soil specifications for Barangaroo Headland Park, using site source crushed sandstone as a base.

This project required a series of consecutive steps.

### 2.1 Define Site Soil Types to Support Vegetation

Seven concept 'Landscape Units' were initially described as shown in Table 1. For tender purposes, these were simplified into three soil types to accommodate the seven vegetation types (Table 2).

**Table 1.** Initial concept vegetation community edaphology

Landscape Unit	General appearance	Edaphic position	Concept Soil Type
1. Ridge-top Woodland	Dry sclerophyll open eucalypt woodland. Sparse understorey with floral display. Scribbly Gum dominant with <i>Angophora costata</i>	Exposed north and west upper slope positions	Shallow yellow Kandosol exposed rock, low fertility
2. Heath and Scrub	Dense prickly tall shrub with floral display	All locations but generally full sun	Shallow poorly drained yellow earth
3. Open Dry Forest	Dry open woodland with mostly single trunk trees but with lower branching, not straight trunked. Rough and smooth barked trees with medium-dense understorey. <i>Angophora</i> and <i>Bloodwood</i> dominant	Exposed north, west mid-slope and upper SW slope positions	Yellow earth, low to moderate fertility

(continued)

**Table 1.** (continued)

Landscape Unit	General appearance	Edaphic position	Concept Soil Type
4. Tall Moist Forest	Single straight trunk tall trees rough and smooth bark with dense green understorey. Blackbutt or Blue gum Sydney Peppermint dominant	Lower north and west slope mid-SW slope and upper south slope	Deep yellow earth to 800 mm, moderate fertility
5. Damp Gully Forest	Moist gully, tall form smooth-bark trees with lush green understorey	Mid and lower south and SW and SE slopes	Deep yellow Kandosol 800–1500 mm, moderate fertility
6. Waterfront Promenade	Waterfront flats, all aspects. Umbrageous trees in turf and paved pathways, little or no understorey, waterfront species. Eg <i>F. rubiginosa</i>	Lower soil “bench” encircling the entire headland with promontories	Trees in Alluvial soil to 1500, turf in shallow Yellow Earth
7. Headland Park	Headland plateaux and northern slope. Umbrageous trees in turf and paved pathways. Display beds of indigenous plants including cultivars. Edged with crowd control and display plants	Plateaux and slope facing generally north and west	Trees and garden beds in Deep Yellow Earth 800 to 1500 mm, turf in shallow Yellow Earth to 400

**Table 2.** The three soil types for tender.

Soil type	Plant species
Type A. Headland and Foreshore Turf and Park Trees	<i>Ficus macrophylla</i> in turf with <i>Angophora costata</i> and <i>E. haemastoma</i> beds
Type B. Ridge top Woodland, Heath and Scrub	Open Eucalypt woodland with understorey, heath and scrub
Type C. Open Dry Forest, Tall Open Forest, Tall Moist Forest, Damp Gully Forest	Tall closed canopy Eucalypt woodland, lush gully forest with palms and ferns
Type D. Subsoil	All areas

## 2.2 Benchmarking Native Soils in Hawkesbury Sandstone (at Mangrove Mountain, NSW)

The aim of the benchmarking study was to understand soil fertility requirements of the different vegetation communities in Tables 1 and 2, with particular focus on P and Ca. Previous commercial work by the author on sandstone soils in mine sites showed P and Ca to be the most limiting elements in the geology and soils.

Mangrove Mountain is located North of Sydney, in the Central Coast region of NSW. The sandstone geology hosts vegetation very similar to that chosen for Barangaroo headland park. Soil samples were collected along a catena from the top of the exposed north-facing headland down into a footslope position with closed canopy tall Eucalypt forest. Both the A and B horizons were sampled. Sodium, potassium, calcium, magnesium, iron, manganese, iron, zinc copper and phosphate were analysed using a Mehlich 3 extract. Total P was analysed via oxidising acid digestion.

### 2.3 Pre- and Post-Bushfire Analysis at Somersby, NSW

As Australia's flora regenerates after fire, the author hypothesised that soil nutrient levels would not fully represent the vegetation community fertility requirements. The aim of this analysis was to develop an 'ash-bed' model of nutrients returned to the soil after burning, and adjust the benchmarking conducted at Mangrove Mountain.

Somersby is located on NSW's Central Coast, approximately 15 km south-east of Mangrove Mountain. The site was to be subjected to a controlled burn, allowing for pre-and post burn soil nutrient analysis. The Somersby site carried tall open eucalypt woodland composed of *Angophora coastata*, *Eucalyptus piperata*, *E. haemastoma* and *E. gummifera*. Samples of soil, leaf litter and biomass were sampled prior to the burn including foliage, wood, bark and twigs. Laboratory methods were the same as the Mangrove Mountain analysis.

### 2.4 Pot Trial 1

The aim of Trial 1 was to establish a benchmark for soil fertility for the P sensitive species. Two extremes of compost - 10% and 30% by volume – were used with the expectation that the 30% Anthrosols would induce P toxicity. Plant species included Silver Banksia (*Banksia marginata*), Hill Banksia (*Banksia spinulosa* var. *collina*), Forest Red Gum (*Eucalyptus tereticornis*), Scribbly Gum (*Eucalyptus haemastoma*), and Sweet-scented Wattle (*Acacia suaveolens*). These species covered a range of known Phosphorus sensitivities.

The trial was not conducted using a statistically valid degree of replication. It was intended to explore the general growth and health of a range of species in preliminary soil designs that used crushed sandstone and recycled green waste compost.

Four tubestock specimens of each species were planted into media prepared according to the four soil treatments in Table 6. Plants were initially watered and fed on an 'as needed' basis with a solution containing two grams per litre of urea. No other fertiliser was applied. After 8 weeks plant height, above, and below ground mass was measured and foliage composited within species and treatment for foliar analysis. Soil was also composited within treatment for analysis.

### 2.5 Pot Trial 2

The aims of Trial 2 were to:

- (a) Determine whether the Fe and Mn deficiency and elevated P problems seen in Trial 1 could be resolved by acidifying with a common soil acidifying agent - iron sulfate ( $\text{FeSO}_4$ ). Trial 2 used a 5% and 10% compost rate, two  $\text{FeSO}_4$  additions ( $1.5 \text{ kg/m}^3$  and  $2.0 \text{ kg/m}^3$ ), and used the two most P-sensitive species from Trial 1 - *E. haemastoma* and *A. suaveolens*. Each treatment had 5 replicates.
- (b) Determine ideal P nutrition for the lowest nutrient vegetation communities – *Angophora scribbly gum*.

For laboratory analysis, soil was composited within replicates but kept separate between species,  $\text{FeSO}_4$  and compost rates.



## 2.6 Develop a Concept Soil Profile and Soil Specifications for the Different Vegetation Types

Based on the successive benchmarking analysis and pot trials, topsoil and subsoil specifications were developed for the different vegetation types.

## 3 Results

### 3.1 Benchmarking at Mangrove Mountain

Table 3 provides key data from the hilltop and footslope samples. Plant available Ca and P levels were very low. Total P was very low and consistent with levels of P seen in samples of crushed sandstone (around 20 mg/kg) previously tested for this project.

**Table 3.** Mangrove Mountain natural sandstone soils.

	Hilltop A horizon (0–75 mm)	Hilltop B horizon (100–400 mm)	Footslope A (0–200 mm)	Footslope B (800–1000 mm)
Organic Carbon %	1.2	0.7	2.7	0.4
EC dS/m	0.28	0.19	0.28	0.29
Na % CEC	0.7	1.3	0.5	1.7
K % CEC	1.8	1.2	1	0.7
<b>Ca % CEC</b>	<b>2</b>	<b>0</b>	<b>0.5</b>	<b>0</b>
Mg % CEC	10.9	21.9	6	14.5
Al % CEC	13.9	15.7	16.9	20.3
Fe mg/kg	330	159	644	0
Mn mg/kg	1.5	0.6	1.5	0
Zn mg/kg	0.65	0.65	0.65	0
Cu mg/kg	0.64	0.64	0.64	0
<b>PO<sub>4</sub> mg/kg</b>	<b>2.5</b>	<b>0.4</b>	<b>0.2</b>	<b>0</b>
Total P mg/kg	30.9	18.3	38.9	18.3

### 3.2 Pre- and Post Bushfire Analysis at Somersby

Fire altered the nutrient status of the soil (Table 4). pH, Ca, P, and K increased. Exchangeable hydrogen and aluminium decreased.

As Australia's flora regenerates after fire, the author hypothesised that limiting nutrients such as Ca and P were likely to be in the standing biomass (leaves, branches) rather than in the soil, and would be released to the soil after bushfire. Pre bushfire analysis of standing biomass are given in Table 5.

**Table 4.** Kandosol A horizon at Somersby pre- and post bushfire.

Analyte	Pre-bushfire	Post bushfire
pH H <sub>2</sub> O 1:5	5.1	5.4
pH CaCl <sub>2</sub> 1:5	4.0	4.7
Ca %	8.5	27.7
K %	5.1	5.4
Exchangeable Al %	10.9	1.8
Exchangeable H %	62.7	46.5
Total P mg/kg	46	90
Total Ca mg/kg	336	756
PO <sub>4</sub> mg/kg	3.8	14.4
Ca mg/kg	151	588
K mg/kg	176	224
Fe mg/kg	457	322
Mn mg/kg	5.5	13

**Table 5.** Nutrient content of standing biomass in eucalypt woodland, pre-burn.

	Total P (mg/kg)	Total Ca (mg/kg)
Litter	80	2045
Top 200 mm	45	335
Sub 400 mm	25	150
<i>E. haemastoma</i>		
Foliage	325	7005
Twigs	200	10850
Bark	105	15070
Wood	36	670
<i>E. gumifera</i>		
Foliage	320	2975
Twigs	235	6005
Bark	90	2700
Wood	30	270
<i>A. coastata</i>		
Foliage	505	3415
Twigs	605	9140
Bark	140	15690
Wood	60	2455

**Table 6.** Trial 1 soil mixes.

% by volume	Treatment 1a	Treatment 1b	Treatment 2a	Treatment 2b
Washed 5 mm Quartz sand	35	35	45	45
<10 mm crushed sandstone	35	35	45	45
Green waste compost	30	30	10	10

### 3.3 Pot Trial 1

There was no significant difference in plant height or mass between treatment. The greenwaste compost raised the pH of the soil such that Fe and Mn deficiency was induced in *Banksia*. This caused slight chlorosis in the younger foliage. Symptoms were more pronounced in the 30% than the 10% compost Anthroposols.

*Acacia suaveolens* showed slight reddening of leaf tips and margins at 10% compost, and significant reddening at 30% compost. Compared to foliar analysis on a natural stand of *A. suaveolens* (Table 7), total P levels were elevated, and Fe and Mn deficient.

**Table 7.** Data from foliar analysis

	pH (H <sub>2</sub> O)	Total P (%)	Fe (mg/kg)	Mn (mg/kg)	P:Fe ratio	Symptoms of P toxicity/Fe and Mn deficiency
<i>Acacia suaveolens</i> 30%	7.3	0.15	47	45	31.9	Yes
<i>Acacia suaveolens</i> 10%	7.2	0.13	84	52	15.5	
<i>Acacia suaveolens</i> natural stand	–	0.05	104	389	4.8	–
<i>Banksia marginata</i> 30%	7.4	0.18	124	346	14.5	No
<i>Banksia marginata</i> 10%	7.3	0.06	162	345	3.7	
<i>Banksia spinulosa</i> 30%	7.4	0.31	103	292	30.1	Mild
<i>Banksia spinulosa</i> 10%	7.4	0.07	122	158	5.7	
<i>Eucalyptus haemastoma</i> 30%	7.4	0.59	25	281	236.0	Yes
<i>Eucalyptus haemastoma</i> 10%	7.1	0.25	28	240	89.3	
<i>Eucalyptus tereticornis</i> 30%	7.5	0.12	33	206	36.4	Yes
<i>Eucalyptus tereticornis</i> 10%	7.4	0.13	37	280	35.1	

*Banksia marginata* and *B. spinulosa*, P sensitive species, showed increasing foliar P levels with increasing compost rate. Neither showed elevated P or P induced Fe deficiency at 10% compost. Both showed elevated foliar P levels at 30% compost and slight yellowing. *Banksia marginata* took up less P than *Banksia spinulosa*. Additionally, *B. spinulosa* showed more yellowing than *B. marginata* at 30% compost.

Phosphorus levels in *E. haemastoma* were high and responsive to added compost. In *E. tereticornis* there was no P response to added compost.

### 3.4 Trial 2

#### Soil Analysis

The 5% compost rate showed lower pH, exchangeable Ca, total Ca and total P at both FeSO<sub>4</sub> addition rates (Table 8). Since compost is the only source of P, Ca, K and organic matter this is not unexpected. Extractable Mn was not overly different between the two compost rates but since the extractant used (Mehlich 3) is strongly acidic this does not reflect availability at soil pH.

**Table 8.** Selected soil analysis.

	A*	E**	A	E	A	E	A	E
<i>Compost (%)</i>	5%				10%			
<i>FeSO<sub>4</sub> (kg/m<sup>3</sup>)</i>	1.5		2		1.5		2	
pH (H <sub>2</sub> O)	5.68	5.58	5.78	5.64	6.09	5.91	6.32	6.08
pH (CaCl <sub>2</sub> )	4.72	4.65	4.82	4.72	5.28	5.05	5.33	5.21
Ca (% CEC)	36.8	40.5	64.5	39.2	56.7	44.3	58.3	55.8
PO <sub>4</sub> (mg/kg)	12	7	15	14	19	18	22	29
Fe (mg/kg)	385	288	370	345	277	287	337	392
Mn (mg/kg)	21	17	18	17	18	17	17	21
Ca (mg/kg)	269	257	421	361	497	425	537	437

\* *Acacia suaveolens*

\*\* *Eucalyptus haemastoma*

#### Foliar Analysis

Plants generally grew well with *A. suaveolens* showing the best growth and good foliage colour, and an absence of any of the reddening seen in the first trial.

Some *E. haemastoma* showed reddening and chlorosis seemingly at random across treatments. Foliar analysis (Table 9) showed the reddening was most likely due to Mn toxicity. The foliar Mn level at both 5% treatments were much higher than those seen in a wild specimen growing along Mona Vale Rd, St Ives NSW in sandstone geology.

Mn uptake increased in *E. haemastoma* when pH in CaCl<sub>2</sub> dropped below 5.0. A pH in CaCl<sub>2</sub> of 5.0–5.2 corresponds to a foliar level of around 600–800 mgMn/kg. This does not occur for the *A. suaveolens*. A strong correlation ( $R^2 = 0.9907$ ) between soil pH and foliar Mn was established in *E. haemastoma* [5].

**Table 9.** Comparison of trial *E. haemastoma* and wild-grown species.

	10% compost Trial 1 (0 g FeSO <sub>4</sub> )	Second Trial				Mona Vale Rd.
		5%, 1.5 kg	5%, 2.0 kg	10%, 1.5 kg	10%, 2.0 kg	
N (%)	0.55	1.7	1.9	1.6	1.6	1.1
P (%)	0.25	0.10	0.12	0.13	0.11	0.04
Ca (%)	0.68	0.5	0.6	0.6	0.5	0.8
Fe (mg/kg)	28	34	30	44	40	30
Mn (mg/kg)	240	1250	1137	772	619	291
P/Fe (mg/kg)	89	89	236	35	36	10

## 4 Discussion

### 4.1 Phosphorus Toxicity

Several species in the mid and upper slope communities were known or suspected of being sensitive to P. Work by Handreck [6, 7] suggests that at least one of the species chosen, *Banksia marginata* was likely to be moderately sensitive to P. While the P sensitivity of *B. spinulosa* was not specifically studied in Handreck's experiments, other narrow leaf Banksias such as *B. ericifolia* and *B. hookeriana* were known to be quite sensitive. Although Eucalypts and Acacias are not generally considered P sensitive, many are known to have low P requirements [8].

Plants that have evolved in very low P environments sometimes react adversely when grown in soils containing higher P levels. Physiologically these plants have cannot exclude excess P because their roots form proteoid roots—special structures to enhance the uptake of P. Elevated P in plant tissue has deleterious effects, often when iron (Fe) reserves are immobilised by the formation of iron phosphate (FePO<sub>4</sub>). Consequently, the first symptoms of P toxicity are iron deficiency (yellowing or chlorosis of leaf tissue), which can lead to death of the leaves and eventually the whole plant. The condition can be exacerbated by high soil pH that reduces iron uptake from the soil. P toxicity can sometimes be alleviated by applying iron to the plant or soil [7].

### 4.2 Benchmarking at Mangrove Mountain and Somersby

Although some of the selected species are adapted to low nutrient environments, the nutrient content of the Mangrove Mountain soil seemed too low to support the vegetation. Previous commercial work showed natives starving on crushed sandstone profiles with levels of P around 25 mg/kg. Soil nutrient levels at Mangrove Mountain were consistent with deficiency in Australian native vegetation.

As some of Australia's flora regenerates after fire, limiting nutrients such as Ca and P were likely to be in the organic matter, litter and standing biomass (leaves, branches) rather than in the soil and would be released to the soil after bushfire [9, 10].

Using some assumptions on total standing mass per hectare of 200 t/ha, based on the forestry work of Attiwill [11], the standing biomass was estimated to contain around 46 kg/ha of P and 796 kg/ha of Ca. If these nutrients were returned to the top 200 mm of soil, levels were calculated to rise to around 63 mg/kg of P and 645 mg/kg of Ca in soil.

The post-fire analysis at Somersby confirmed soil nutrients, specifically Total P, PO<sub>4</sub> and Ca, increased after fire. The fire was a low intensity burn and did not return all the standing biomass to the soil. If this were to occur the P, K, Ca and pH level would likely be higher. The post-fire results suggest that the Eucalyptus woodland could develop or re-grow after fire at soil levels of 60–70 mg/kgP, and Ca levels of around 700–900 mg/kg.

Based on the nutritional analysis of commercial greenwaste compost, 10% compost by volume in crushed sandstone would mimic a P and Ca fertility level immediately following fire (the ‘ash-bed effect’) similar to those calculated from biomass analysis and seen in the post fire soil analysis. These estimates were assessed using the two pot trials.

### 4.3 Trial 1

Trial 1 performed as expected, with 30% compost inducing P toxicity in some species. The trial also helped tease out varying degrees of P toxicity. *B. spinulosa* showed more yellowing than *B. marginata* at 30% compost, suggesting that *B. spinulosa* is more P sensitive than *B. marginata*. *E. tereticornis* did not show P toxicity indicating it is not sensitive to excessive P.

Phosphorus levels in *E. haemastoma* were high and responsive to added compost. The very high P/Fe ratio at the 30% compost rate suggests *Eucalyptus haemastoma* may be prone to P induced Fe deficiency.

*Banksia marginata* took up less P than *Banksia spinulosa*. Additionally, *B. spinulosa* showed more yellowing than *B. marginata* at 30% compost. This suggests that *B. spinulosa* is more P sensitive than *B. marginata*.

The scoping work on Mangrove Mountain and Somersby suggested 10% compost should have been acceptable for *A. suaveolens*. However, elevated foliar P and Fe deficiency show pH was likely limiting solubility and availability of Fe and increasing P availability. This suggested that to obtain optimal nutrition from green waste compost, pH must be controlled at least for some species. This was the subject of trial 2.

### 4.4 Trial 2

In Trial 1, all Eucalyptus plants showed iron deficiency symptoms at foliar Fe levels of 25–28 mg/kg. In the 5% compost treatment in Trial 2 for *E. haemastoma*, Fe levels are not markedly increased at 30–34 mg/kg (Table 9). Leaf reddening is attributed to Mn toxicity or Mn induced Fe deficiency due to an antagonism between Mn and Fe [12].

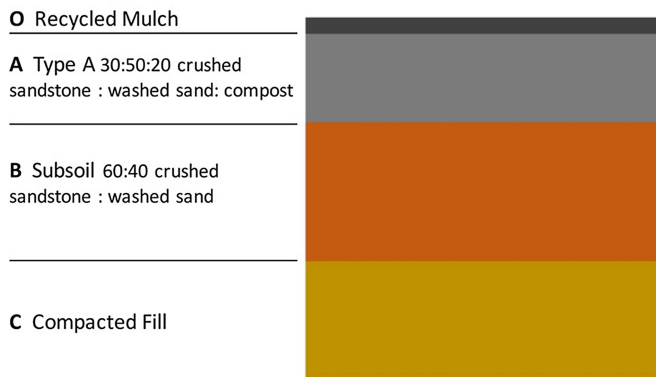
Mn uptake increased in *E. haemastoma* when pH in CaCl<sub>2</sub> dropped below 5.0. A pH in CaCl<sub>2</sub> of 5.0–5.2 corresponds to a foliar level of around 600–800 mg/kg. This did not occur for the *A. suaveolens*, which was better at picking up iron and less prone to taking up excessive Mn at acidic pH.

Trial 2 confirmed:

- That 5% green waste compost provided adequate P nutrition for the ‘Ridge top Woodland Heath & scrub plus Angophora and Scribbly Gum beds’, the lowest nutrient vegetation community being installed.
- That the symptoms of Fe deficiency/P toxicity evident in Trial 1 can be prevented by adding  $\text{FeSO}_4$  to acidify the soil, improve iron and reduce P availability.
- To avoid excessive Mn accumulation in species such as *E. haemastoma* and *E. gummifera*, a target pH in  $\text{CaCl}_2$  of 5.0 would be appropriate to prevent Mn toxicity while allowing adequate iron availability [13].

## 5 Final Specifications

Based on the scoping studies and trials, tender specifications were finalised. Four soil areas were designated. Soil types A, B and C are topsoils (A horizon). Soil type D is the subsoil (B horizon) that was used throughout. Figure 1 illustrates the concept Barangaroo Anthrosol, while Table 10 presents the soil specification for topsoil chemical properties.



**Fig. 1.** Barangaroo Anthrosol with Type A topsoil.

Suggested physical components and fertiliser/ameliorant additions required to achieve these levels in topsoil are given in Table 11 below. The exact ratios varied with the source and type of inputs. All formulations were checked and validated as compliant before installation.

**Table 10.** Topsoil chemical properties specifications for Tender.

Property	Unit	Acceptable range
pH 1:5 in water Types B and C	pH units	5.6–6.3
pH 1:5 in CaCl <sub>2</sub> Types B and C	pH units	5.0–6.0
Electrical conductivity 1:5 in water	dS/m	<0.5
pH 1:5 in water Type A	pH units	5.8–6.5
pH 1:5 in CaCl <sub>2</sub> Type A	pH units	5.2–6.2
Total phosphorus		
Type A	mg/kg	90–150
Type B	mg/kg	50–80
Type C	mg/kg	60–90
Organic matter		
Type A and Type C	% w/w	2–5
Type B	% w/w	1–3
Cation exchange properties		
Exchangeable Sodium (Na)	% of CEC	<10
Exchangeable Potassium (K)	% of CEC	2–8
Exchangeable Calcium (Ca)	% of CEC	45–65
Exchangeable Magnesium (Mg)	% of CEC	25–35
Exchangeable Aluminium (Al)	% of CEC	<5
Mehlich 3 Extractable Iron (Fe)	mg/kg	100–300
Mehlich 3 Extractable Manganese (Mn)	mg/kg	10–25
Mehlich 3 Extractable Zinc (Zn)	mg/kg	5–20
Mehlich 3 Extractable Copper (Cu)	mg/kg	1–5
Mehlich 3 Extractable Boron (B)	mg/kg	0.5–5
Nitrate-N (NO <sub>3</sub> )	mg/kg	>5

**Table 11.** Suggested topsoil type formulations for tender.

Soil type	Crushed -15 mm sandstone (%v/v)	Washed -3 mm sand (%v/v)	Green Waste Derived Compost (% v/v)	Fertilisers/Ameliorants
Type A. Headland and Foreshore Turf and Park Trees, <i>Angophora costata</i> and <i>E. haemastoma</i> beds	30	50	20	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> 1.5 kg/m <sup>3</sup> IBDU or Methylene Urea 0.5 kg/m <sup>3</sup>
Type B. Ridge top Woodland Heath and Scrub including headland park <i>Angophora costata</i> and <i>E. haemastoma</i> beds	47.5	47.5	5	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> 1.5 kg/m <sup>3</sup> IBDU or Methylene Urea 0.3 kg/m <sup>3</sup>
Type C. Open Dry Forest, Tall Open Forest, Tall Moist Forest, Damp Gully Forest	40	50	10	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> 2.0 kg/m <sup>3</sup> IBDU or Methylene Urea 0.5 kg/m <sup>3</sup>
Type D. Subsoil, all areas	60	40	0	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> 0.5 kg/m <sup>3</sup>



## 6 Project Conclusion

5% compost was used for the most sensitive heathland species, 10% for Eucalypt woodland species and 20% for turf and park tree areas. Iron sulphate was added at the specified rates. Plant losses were less than 1% in the project and no plant losses could be attributed to nutritional factors. The only fertilisers applied post establishment were some nitrogen (as no Methylene Urea was added initially) and some potassium to replace that lost due to heavy rainfall during planting.

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# Managing Urban Soils for Food Security and Adaptation to Climate Change

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**Abstract.** The 21<sup>st</sup> century is the era of rapid global urbanization. Urbanization can have severe ecological consequences because of the perturbation of the cycles of water (H<sub>2</sub>O), carbon (C), nitrogen (N) and other elements, and contamination/pollution of soil and the environment. Drastic reduction in the forest vegetation cover and soil compaction, truncation, mixing and perturbation aggravate disruption of soil functions and the attendant ecosystem disservices. Most soils of urban ecosystems are severely depleted of their soil organic carbon (SOC) reserves, and the total magnitude of the terrestrial C pool (soil plus vegetation) is drastically reduced. There are also shortages of fresh supply of vegetables, fruits and other food commodities in densely populated urban centers. These problems may be aggravated by climate change, increase in frequency and intensity of extreme events, and increase in risks of contamination of soil and eutrophication of water resources. Urban ecosystems are also a major source of greenhouse gases through consumption of energy-based services (e.g., transport, heating, cooling, infrastructure development and management). Despite numerous challenges in restoration and sustainable management of soil, water, vegetation and other natural resources, judicious management of urban soils and landscapes also provides opportunities of sequestering C in soil and vegetation, improving the environment, recycling nutrients in biowaste and gray/black water to grow food and biofuel feedstock, and developing industries focused on production of food and energy, purification of water, and production of amendments.

## 1 Introduction

This is the era of urbanization, and it is an anthropogenic phenomenon (Fig. 1). The rate of urbanization is especially rapid in Asia and Africa, the continents in which the urban population will double between 2000 and 2030. The percent of global population living in cities was 2 in 1800, 14 in 1900, 30 in 1950, 50 in 2008, and is projected to be 61 in 2030, 66 in 2050, 76 in 2075 and 84 in 2100 (Fig. 2). As much as 54.5% of the world population lived in cities or urban settlements in 2016 and 60% will be urbanized by 2030. Globally, the rate of growth of urban population (%/yr) was 1.33 between 1950–1955, 0.83 between 1995–2000, 1.04 between 2000–2005, and is projected to be 0.70 between 2020–2025, 0.62 between 2025–2030 and 0.48 between 2045 and 2050 [1–3]. There were 512 cities globally in 2016 with at least 1 million inhabitants.

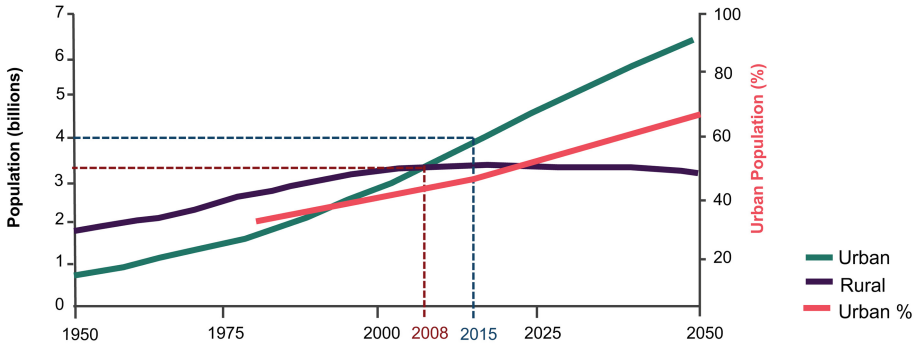


Fig. 1. Trends in global rural and urban population (Adapted from U.N., 2014) [2].

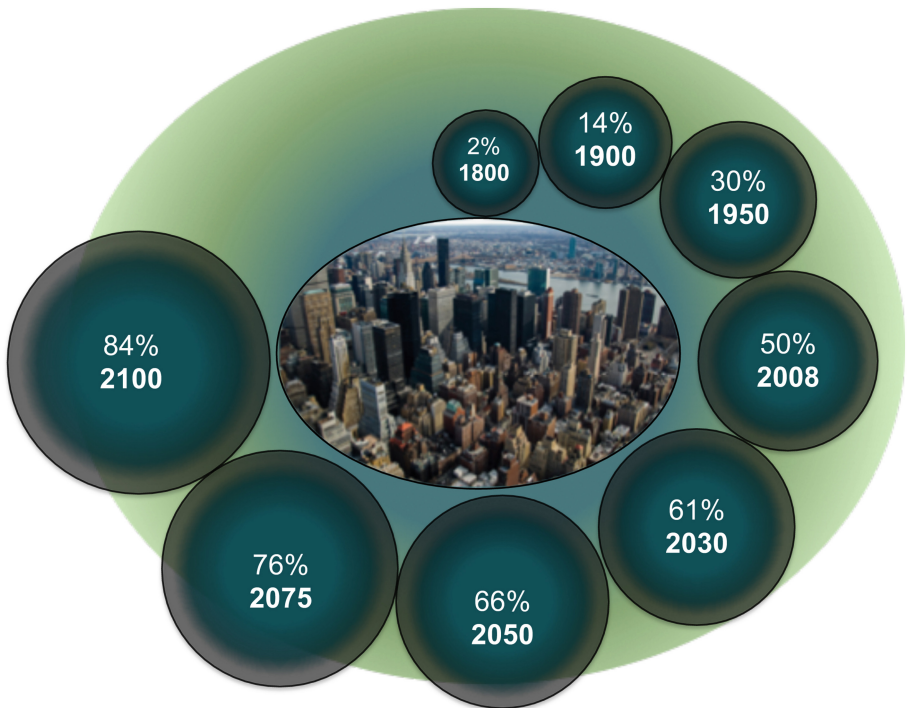
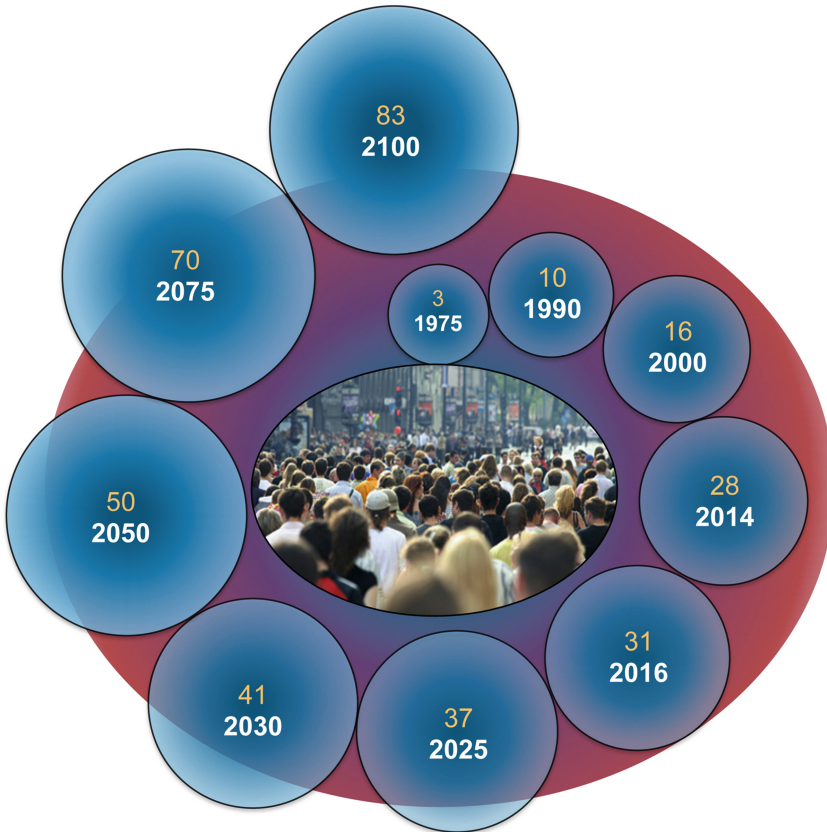


Fig. 2. Global urban population from 1800 to 2100 as percent of the total population (Adapted from U.N., 2014) [2].

The number of megacities, with population of 10 million, was 31 in 2016 and will be 41 in 2030 (Table 1). Globally, the number of megacities was 3 in 1975, 10 in 1990, 16 in 2000, 28 in 2014, 31 in 2015, and is projected to be 37 in 2025, 41 in 2030, 50 in 2050 and 83 in 2100 (Fig. 3). World cities with population of >40 million by 2100 are listed in Table 2. Several cities in Africa will have population of >70 million each.

**Table 1.** Global cities and their population (Added from U.N. 2014a) [2].

Population (10 <sup>6</sup> )	Global number		Population (10 <sup>6</sup> )	
	2016	2030	2016	2030
≥ 10	31	41	500	730
5–10	45	63	308	434
1–5	436	558	861	1128
0.5–1	551	731	380	509
<0.5	–	1985	–	2257
Rural	–	3371	–	3367



**Fig. 3.** Growth in number of mega cities in the world between 1975 and 2100 (U.N., 2014; PRB, 2017; Hoonweg and Pope 2014) [2, 71, 72].

Of the 19 cities with population >40 million 8 will be in Africa and 9 in Asia, and none in Europe, Americas or the Pacific (Table 2). Since 1950s, the urbanization has been especially rapid in China, Asia and Africa (U.N. 2014) [1–3].

**Table 2.** Number of megacities in the world and their projected population by 2100 (U.N., 2014a) [2].

City	Population (10 <sup>6</sup> )
Lagos	88.3
Kinshasa	83.5
Dar Es Salaam	73.7
Mumbai	67.2
Delhi	57.3
Khartoum	56.6
Niamey	56.1
Dhaka	54.2
Kolkata	52.4
Kabul	50.3
Karachi	49.1
Nairobi	46.7
Lilongwe	41.4
Blantyre city	40.9
Cairo	40.5
Kampala	40.1
Manila	40.0

In addition to population, it is the land area under cities which impacts the environment (i.e., micro-climate, hydrology, soil health, air quality, and the heat island effect). In general, urban growth occurs on prime agricultural land. Hooke et al. [4] estimated that all human activities have transformed >50% of earth's land surface, and human appropriate 20–40% of earth's NPP. Urbanization competes with agriculture for basic resources (e.g., land, water, energy). Among concerns about urbanization are the competition for natural resources with agriculture and the impact on the environment. Therefore, the objective of this article is to describe the ecological impacts of urbanization, identify the strategies to minimize the environmental footprint of urban growth, describe the impact of urbanization on soil quality, and deliberate management of urban soils for carbon (C) sequestration and advance food security.

## 2 Urban Expansion on Croplands

Estimates of the global urban land area vary widely between 1–3% of the world's land area (Tables 3 and 4), because of the different definitions of urban land [5]. Urbanization implies that an increasing share of a nation's population is living in urban areas because of factors other than the natural increase and primarily due to the net rural to urban migration and immigration from other nations [6]. The net effect is the change in population density. The term urbanization can also be used for the expansion of urban land uses. Thus, a city can be defined as an aggregation having a certain population [7]. There are several types of cities: compact, dispersed, fragmented and extensive [8].

**Table 3.** Estimates of land area under urban use.

Percent of cropland loss	Percent of the world total land area	Reference
1.8–2.4 by 2030	–	Ben d’Amour et al. (2016)
–	3.5 (or 350 Mha)	Cox (2010)
–	3	Liu et al. (2014)
–	0.5	Schneider et al. (2009)

**Table 4.** Estimates of global land area under urban development (Calculated from Hooke and Martin-Duque 2012) [4].

Year	Land area (Mha)
1800	6.35
1900	9.53
1925	15.81
1975	31.75
2000	44.45
2025	69.85
2050	95.25

To minimize confusion, Liu et al. [5] proposed a hierarchical framework for defining the urban land. It comprises of 3 spatially-nested definitions: (i) **urban area** delineated by administrative boundaries, (ii) **build up area** dominated by artificial surfaces, and (iii) **impervious surface area**, which is devoid of life. Expansion of urban centers occurs mostly on croplands. While, it is difficult to assess the exact land area under urban use, there have been some estimates of the global land area (Tables 3 and 4).

By combining spatially explicit projections of future urban expansion, Bren d’Amour et al. [9] estimated that urban expansion will result in 1.8–2.4% loss of cropland area (27 to 36 M ha) by 2030. Bren d’Amour and colleagues reported that about 80% of the future global cropland loss by urbanization would occur in Asia and Africa where most of the cropland lost is more than twice as productive as the national average croplands. Globally, urban expansion will occur on land that is 1.77 times more productive than the global average [9]. In South Asia, rapid urbanization also causes the removal of top 1-m of soil for brickmaking, adversely affecting the quality of soil and of the agricultural produce [10]. The GRUMP (Gridded Population of the World and the Global Rural-Urban Mapping Project) has estimated the land area under urban centers at 350 M ha, which is considered to be too high [11]. Using the hierarchical framework, Liu et al. [5] estimated the global urban land at ~3% of the earth’s total land area, the buildup area at 0.65%, and the global impervious area at 0.45%. Schneider et al. [12] estimated that total urban land footprint is ~0.5% of the world total land area, with 0.17% in Africa, 0.67% in North America, 0.47% in South America, and 0.53% in Asia. Biello [13] estimated that by 2030, urban land area (suburbs, slums and city centers) may grow by more than a million km<sup>2</sup> (tripling the current urban land area) by 2030. Seto et al. [14] reported a worldwide increase in urban land area of 5.8 M ha (58,000 km<sup>2</sup>) from 1970 to 2000, with the highest

expansion in India, China and Africa, and the largest change in total urban extent in North America. Seto and colleagues estimated that by 2030, the global land cover will increase between 43 M ha and 1,257 M ha (12,568,000 km<sup>2</sup>) with a more probable expansion of 153 M ha. With a large variation in available estimates of the land area under urban ecosystem, there is a strong need for standardization of the methodology.

There are several factors affecting the spread of urbanization. Highway construction and access to roads etc. is one of the factors. For example, between 1945 and 2007, the U.S. lost 19.3% of its agricultural land due to construction of 68,000 km of interstate highway system. Mothorpe et al. [15] estimated that each additional km of interstate highway reduces agricultural land by 116 ha (1 mile reduces agricultural land by 468 acres). Highway construction also impacts soil quality [15]. Vegetation cover and population density are among other factors affecting urbanization. There exists an inverse correlation between percent “forest land cover” and “population, housing and road densities” [6]. Global average urban population density is estimated at 4,200 persons/km<sup>2</sup>. However, the average urban population density varies among continents (persons/km<sup>2</sup>), and it is 6,500 for Africa, 6,300 for Asia, 3,100 for Europe, 1,600 for North America, 1,500 for Oceania, and 5,400 for South America [16]. Similar to the need for standardizing the definition of urban centers and the methods to assess the land area, there is also a need to identify the factors affecting urban encroachment and its impacts on the environment.

### 3 Environmental Impacts of Urban Ecosystems

Intensification of urbanization has numerous adverse environmental consequences, both on-site and off-site (Fig. 4). Important among these are air pollution, noise, reduced space for recreation, water contamination, and loss of wildlife and biodiversity. A serious environmental hazard is caused by the use of road salt, which has been used in the U.S. since 1940s as a de-icing agent [17]. Heavy metal contamination of soil of urban centers is a major issue, and soil contamination by heavy metals can be aggravated by irrigation with sewage water [18–20]. Because of severe adverse impacts on soil quality, heavy metals can strongly impact human health [21, 22]. Urbanization adversely impacts hydrology and its biogeochemistry. In addition to changes in the

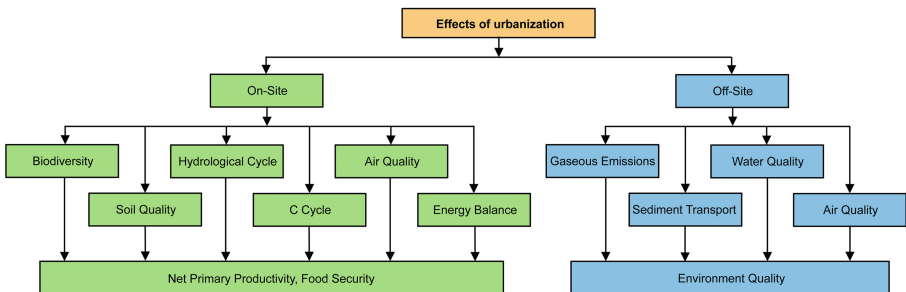


Fig. 4. On-site and off-site effects of urbanization



**Table 5.** Impacts of urbanization on soil contamination and other properties.

Country	Impacts of urbanization on soil health and ecosystem services	Reference
China	Trace metal contamination	Liu L et al. (2016), Hu et al. (2004)
USA	Heavy metal contamination	Mielke et al. (1999)
Portugal	Organic pollutants (e.g., PAH, PCB)	Cachada et al. (2012)
China	Adverse impact on soil quality	VanMetre et al. (2000)
USA	Coal-tar seal coated pavement emitting PAH and benzo-pyrene indust	Schneider et al. (2012)
USA	Ecosystem services and disservices	Diawara et al. (2006)
Japan	Changes in hydrological cycle	Kondoh and Nishiyarna (2000)
China	Alteration in hydrology of Yangtze river	Xu et al. (2010)
Mexico	Changes in water quality and quantity and other ecosystem services	Jujnovsky et al. (2010)

water (and energy) balance, it also perturbs the geochemical characteristics of the watershed [23–26]. Regional atmospheric deposition can also impact the urban fringe ecosystems. Water quality is drastically altered which disrupts the delivery of essential ecosystem services (ESs) [27, 28], and creates numerous disservices (Table 5). Intense urbanization is also affecting China’s water security, which is a serious threat to socioeconomic development and its sustainability [29].

Along with disruption of the hydrological cycle, urbanization and change in land cover also have a strong adverse impact on the C cycle which has numerous sociological implications [30, 31]. Alterations in microclimate by urbanization is characterized by the so-called “heat island” effect [32–35].

#### 4 Afforestation to Minimize Adverse Environmental Effects of Urbanization

Urban ecosystems are characterized by complex interactions among social, economic, institutional and environmental variables [36]. While urban agriculture is important to advancing food security, soil quality may not be suited to public health because of contamination with heavy metals and other pollutants [37]. Thus, alternative urban patterns must be identified which can generate differential ecological consequences and minimize or alleviate the adverse effects of urbanization. For example, negative effects of urbanization can be minimized through creation of green space and forest restoration [38, 39].

Urban woodlands can reduce the effects of particulate pollution [40]. Properly managed urban forests can provide and deliver numerous ESs (Table 6). Similarly, wastewater can be treated and reused for irrigation. The treatment of wastewater is



**Table 6.** Ecosystem services delivered by urban forestry ecosystems.

Component		Reference
Urban forestry	Non-monetary value of urban forests ecosystem services goods	Dobbs et al. (2011)
Domestic gardens	Green infrastructure, environmental impact, temperature moderation (GHG emission, wildlife loss, misuse of fertilizers, introduction of alien plants)	Cameron et al. (2012)
Urban gardens	Proper management of urban gardens is important to reduce health risks of heavy metals	Szolnoki and Farsang (2013)

PAH = Polyacrylic hydrocarbons

essential to minimize the health hazard. Understanding properties and dynamics of urban soils is essential to identifying strategies for their sustainable management [41].

Soil health-induced risks on public health must be appropriately assessed and adequate measures taken to alleviate these risks. Geostatistical techniques can be used to map risks to human health [42]. Important among options of managing urban soils include decontamination of heavy metals, buildup of SOC concentration and stock, alleviation of soil compaction, and improvements in soil fertility. Establishing perennial vegetation cover has positive impacts on soil health. Afforestation of urban lots can deliver numerous ecosystem services (Table 6), and alleviate disservices. Use of compost and organic amendments are also among important options for improving soil health [43]. Amendments can be used on an urban soil to improve its health and reduce the adverse impacts of heavy metals. In urban lots of Cleveland, OH, USA, Obrycki et al. [44] reported that mixing compost and sediment with soil was a useful option to dilute concentration of Pb and improve soil aggregation. Mixing compost also reduced benzo(a)pyrene content.

## 5 Urbanization and Food Security

Urbanization is declining the ratio of food producers to food consumers. There were 6.7 rural dwellers to each urban dweller in 1900, and there will be 1.5 urban dwellers for each rural dweller by 2025 [6]. Until 1980s, as many as 75–80% of the population in Africa and Asia lived in rural environments and practiced subsistence farming. During 2000s, about 50% of Africans and Asians live in cities, and the urban population is growing at the rate of 3.5 to 4.5%/yr [45]. Food security challenges of rapidly growing urban population are different, and necessitate integrated food systems: production and post-production system than on-farm to household consumers—production, storage, processing, distribution, and household management. A high efficiency is required at every step. Integrated food systems can reduce losses and improve efficiency [45].

Rapid urbanization has demonstrable effects on food security. Measurable effects on urban food security have been reported in Tanzania, China and South Asia [25, 46–49]. Urbanization also impacts food security through encroachment upon prime agricultural lands such as in Costa Rica, China, Alberta, Canada, California and elsewhere in the U.S. [1, 50–53]. Rapid urbanization in densely populated countries of Asia and Africa

increases risks of food insecurity to the vulnerable population. In addition to the loss of cultivated land to urban encroachment in China, there are also other issues. Food insecurity is driven by the loss of cultivable land, environmental degradation, and new dietary demands on food production, which is also linked to nutritional issues in developing countries [54, 55]. Demographic transition is a major driver of change in farm size with less land available per family until off-farm job opportunities are available [56].

In Africa, small landholders in rural areas close to urban areas may benefit from the growing markets for the high value products. In such scenarios, food security may be a more serious issue for marginal areas untouched by urbanization [57].

Because urban encroachment is a threat to the prime agricultural land, there is a strong need for farmland protection policies developing an urban sprawl index and identifying methods of sustaining agricultural production in peri-urban areas, and by promoting vertical farming [48, 58–60].

## 6 Managing Health of Urban Soils

The term soil quality is not synonymous with soil health. Soil quality is related to soil functions or what it does. In comparison, soil health presents the soil as a finite and dynamic living resource. Soil health is directly related to health of plants and those who consume plant products directly or indirectly (e.g., animals, people, and ecosystems). Soil quality and soil health are difficult to measure directly. Nonetheless, some of the important things that cannot be measured must be managed (Edward Demming, an American Business Consultant). In the context of soil quality and health, the question is not what is in the soil that can be measured, but what it does and that which can be quantified. What it does is called “soil functionality” or “soil quality”. Both soil health and soil quality are measured indirectly by using certain indicators [10].

Because drastic perturbation of urban landscape strongly impacts soil health, soil analysis can be used as a diagnostic tool of environmental quality that can affect health of plants, animal and people. Urban soils, contaminated with heavy metals (Zn, Pb, Cd) have strong effects on human health, especially of children. Observations regarding the adverse effects of heavy metal contamination in urban soils have been reported from around the world (Table 4). Contamination by heavy metals can also be caused by use of contaminated compost which can alter the SOC content [61]. In addition to contamination by heavy metals, some urban soils are also polluted with organic compounds (e.g., PAHs and PCBs), which are associated with heavy metals concentration in urban soils including that of Cu, Zn, Pb, Hg etc. [62]. In China, concentration of heavy metals in soils has been reported to be in the order of Cd > Hg > Cu > Zn > Pb > Ni > Cr with moderate contamination from Hg and Cd [33]. Some examples of urban agriculture on the quality of vegetables are shown in Table 7. Using a good quality compost, to improve SOC content, can improve the quality of vegetables [44].

Whereas urban agriculture offers a framework for local self-reliance with regards to production of fresh vegetables (lettuce, tomatoes, beans, cucumber etc.), the risks of soil contamination must be minimized and scientifically addressed [63]. Thus, it is important to identify the parameters/ indicators of soil health. Some plants (e.g., lettuce) can be an important indicator of soil health (Table 7) [63].

**Table 7.** Impacts of urban soils on quality of vegetables produced.

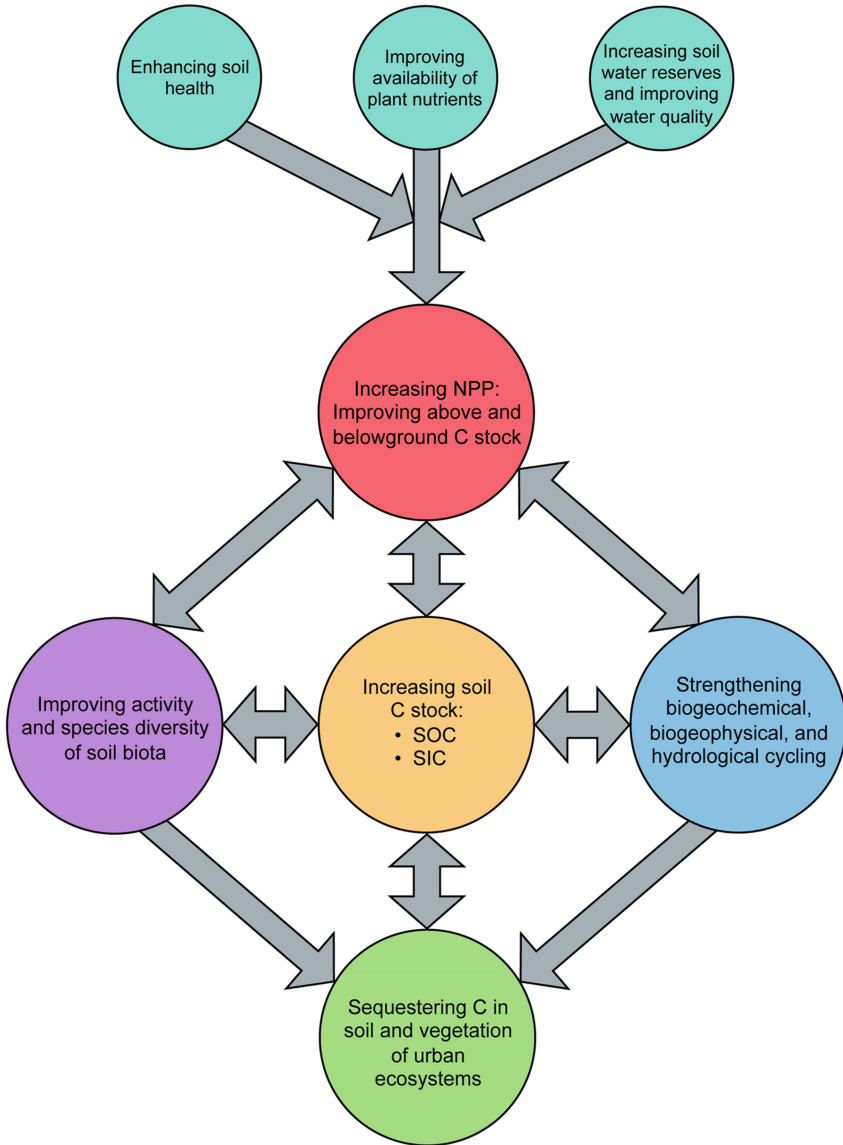
Crop	Country/Region	Treatment	Impact	Reference
Green beans, lettuce carrots	–	Compost at 0, 9, 25%	High concentration of Cd, Pb	Murray et al. (2011)
Lettuce	Ohio, USA	Vacant lots	Lettuce growth and quality	Knight et al. (2013)
Tomatoes	Ohio, USA	Market gardens	No difference in yield among type of garden	Reeves et al. (2014)
Vegetables	Ohio, USA	Urban agriculture	Composting reduced the concentration of heavy metals	Obrycki et al. (2017)

## 7 Potential of C Sequestration in Soil and Vegetation of Urban Ecosystems

Drastic perturbation by urbanization strongly disrupts the C cycle along with those of water (H<sub>2</sub>O), nitrogen (N), phosphorus (P), and sulfur (S). Concentration and stock of C and N are severely depleted, and the water cycle is affected by increase in surface runoff and evaporation and decrease in soil water storage and deep seepage to recharge the groundwater (Fig. 4). Therefore, the net primary productivity (NPP) of urban ecosystems is drastically reduced. The problem is exacerbated by contamination of soil along with pollution and depletion of water resources. Thus, systems of improved management of soil, plant nutrients, vegetation cover and water resources can reverse the degradation trends, improve NPP, enhance water resources and increase the C stock in soil, vegetation and the ecosystem on the whole (Fig. 5). The strategy is to create a positive ecosystem (soil + vegetation) C budget by improving soil health, establishing rapidly growing plants (shrubs, trees, grasses, and seasonals), enhancing availability of plant nutrients (N, P, K, Ca, Mg, S, Zn, Fe, B, Mo) and water. There are a wide range of opportunities of terrestrial C sequestration in diverse components of urban ecosystem including roof gardens, wetlands, urban forestry, home lawns, recreational facilities and urban agriculture (Fig. 6).

The green water supply (plant available water capacity in the rootzone of 0–30 cm depth) must be increased while the losses of blue water by runoff and evaporation must be decreased. The gray/black water (sewer water) can be reused for irrigation of urban and peri-urban agriculture provided that it has been adequately treated to remove not only pathogens and parasites but also heavy metals and organic pollutants.

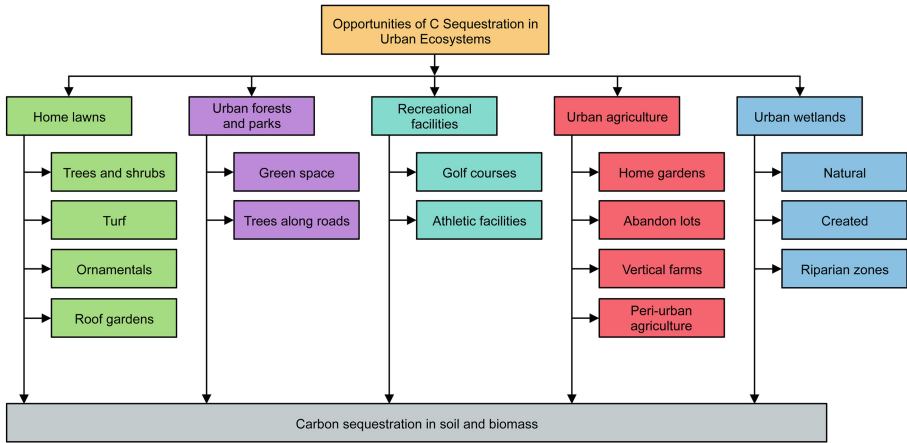
There is a large technical potential of C sequestration in urban ecosystems. Opportunities of C sequestration (soil and vegetation) exist in home lawns, roof gardens and green roofs, urban forests, recreational facilities, urban agriculture, and urban wetland [64, 65]. There are several reports regarding the technical potential of urban ecosystems for C sequestration in soil and vegetation including the green roofs and urban agriculture [66–69]. Emerging opportunities of C sequestration in urban



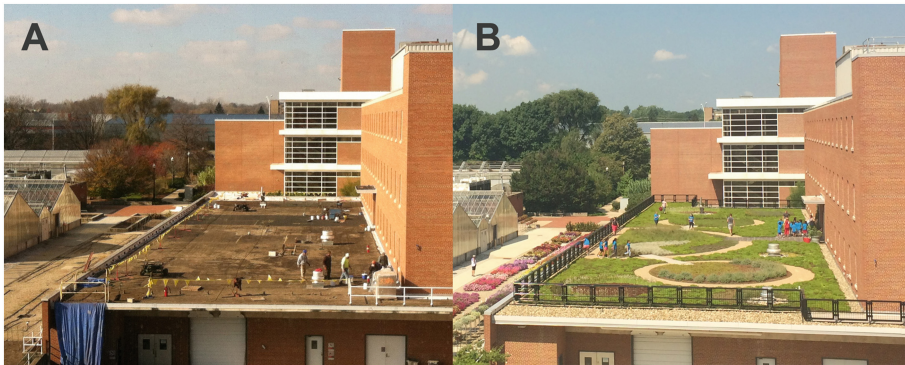
**Fig. 5.** Reversing ecological degradation trends in urban ecosystems and sequestering carbon in soil and biota.

ecosystems include those in roof gardens (Photos 1, 2, 3, 4), and urban agriculture in conventional and vertical farms [60, 70].

In addition to improving the overall environment, C sequestration in urban ecosystems has numerous co-benefits: adaptation and mitigation of climate change;



**Fig. 6.** A wide range of opportunities of terrestrial carbon sequestration in urban ecosystems (soil and vegetation, wetlands).



**Photo 1.** (A) A roof garden under construction in the Department of Horticulture and Crop Sciences at The Ohio State University, Columbus, OH, USA. (B) Completed roof garden at OSU, used as a teaching facility.

improvement of soil air and water quality; increase in biodiversity; decrease in energy use for heating and cooling of homestead; and increase in availability of fresh produce. Improved management of urban ecosystems can advance the Sustainable Development Goals (SDGs) of the United Nations [16].





**Photo 2.** Vegetation of a roof garden at the Technical University of Dresden, Germany.



**Photo 3.** A roof garden at the Technical University of Dresden, Germany.



**Photo 4. a,b,c** Urban garden in a hotel compound in Washington, D.C.

## 8 Conclusions

The 21<sup>st</sup> century is the era of rapid urbanization. By 2100, as much as 84% of the total world population will live in urban centers. Urbanization encroaches upon prime agricultural lands, and the loss of agroecosystems is especially severe in Asia and Africa. Urbanization has strong impacts on quality of soil, water, vegetation and air through drastic perturbation of biogeophysical, biogeochemical and hydrological cycles. There is a drastic disturbance of carbon cycle. Adoption of improved management of soil, plant nutrients and water resources can reverse the degradation trends in urban ecosystems. Therefore, there exists a large potential of C sequestration in both the terrestrial (soil, vegetation) and aquatic (wetlands and riparian lands) ecosystems. In addition, urban agriculture (both conventional and modern) can advance food security of densely populated cities. Improving urban ecosystems is also in accord with advancing the SDGs of the U.N.

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