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How do properties and heavy metal levels change in soils fertilized with regulated doses of urban sewage sludge in the framework of a real agronomic treatment program?

Giuseppe Protano[1] • Fabio Baroni[1] • Luigi Antonello Di Lella[1] • Ambra Mazzoni[2] • Francesco Nannoni[1] • Andrea Papale[2]

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Abstract

Purpose This field study was performed to assess the variation in chemical and agronomic properties and total and extractable concentrations of heavy metals in soils fertilized with regulated doses of urban sewage sludge (USS) for 6 consecutive years in the framework of an agronomic treatment program.

Materials and methods Chemical and agronomical properties, total contents and extractable concentrations of Cd, Cr, Cu, Hg, Ni, Pb and Zn were determined in agricultural soils treated with USS for 6 consecutive years, agricultural soils cultivated using mineral fertilizers and uncultivated soils representative of the local geochemical background.

Results and discussion USS application caused a decrease in pH and an increase in extractable concentrations of Cr, Cu, Pb and Zn. No organic carbon, total nitrogen and total phosphorus enrichment trend was observed in the treated soils due to biodegradation of the organic compounds supplied by USS. The decomposition of USS organic matter was presumably the main process responsible for the pH decrease in the USS-fertilized soils. There was no heavy metal accumulation in treated soils, and total heavy metal contents were below the corresponding maximum threshold concentrations set by European and Italian legislation. Increased availability of Cr, Cu, Pb and Zn was found in treated soils due to an increase in their extractable concentrations in the treatment period.

Conclusions The results of this study suggest that the environmental risks related to the accumulation and availability of heavy metals in agricultural soils fertilized with USS are limited when treatment observes recommended doses in agronomic treatment programs.

Keywords Agronomic properties · Agronomic treatment · Availability · Heavy metals · Soil · Urban sewage sludge

1 Introduction

The management of urban sewage sludge (USS) is currently a major worldwide economic and environmental issue as continuous population growth and water consumption coupled with rapid, large-scale urbanization in industrialized and developing countries are increasing the production of organic waste from municipal wastewater treatment (Kelessidis and Stasinakis 2012; Urbaniak et al. 2017). Among the methods of USS managing, such as landfilling, incineration for energy production, anaerobic digestion, pyrolysis or gasification for biogas generation and use of industrial processes (Fytili and Zabaniotou 2008; Kacprzak et al. 2017), USS are used in agriculture as soil amendment and fertilizer to increase soil stability and fertility and plant productivity (Lloret et al. 2016; Bai et al. 2017). Recycling USS as a source of soil organic matter and plant nutrients is a cost-effective, beneficial and sustainable agricultural practice when USS is properly treated to achieve chemical stabilization, biological maturation and sanitization. Application of USS to agricultural soils is an economically attractive alternative to landfill

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✉ Giuseppe Protano
giuseppe.protano@unisi.it

[1] Department of Environmental, Earth and Physical Sciences, University of Siena, Via del Laterino 8, 53100 Siena, Italy

[2] Aquaser s.r.l., ACEA Group, Piazzale Ostiense 2, 00154 Roma, Italy

disposal and use of mineral fertilizers (Zoghlami et al. 2016; Melo et al. 2018). Furthermore, it is effective since it may improve soil physical (e.g. porosity, aggregate stability and water holding capacity), agronomical (e.g. organic carbon and nitrogen storage, nutrient content) and microbiological (e.g. microbial activity and biomass) properties, ameliorating soil fertility, plant nutrition and crop yield (Mantovi et al. 2005; Singh and Agrawal 2008; Roig et al. 2012; Poulsen et al. 2013; Latare et al. 2014; Mattana et al. 2014; Scotti et al. 2015; Tontti et al. 2017). These results are largely due to physicochemical properties and compositional features of USS, such as high organic matter and macro- and micronutrient content (Herzel et al. 2015; Rigby et al. 2015).

However, the recycling of USS in agriculture may involve risks for the environment and human health mainly related to toxic elements and substances in sewage sludge that may accumulate in soil and become available to crops, entering the food chain (McBride 2003; Singh and Agrawal 2008; Aparicio et al. 2009; Passuello et al. 2010; Smith 2009; Goss et al. 2013; Sharma et al. 2017). Indeed, even when properly treated and stabilized before application to soil, USS contains heavy metals (e.g. Cd, Cr, Cu, Hg, Ni, Pb and Zn), organic contaminants [e.g. polycyclic aromatic hydrocarbon (PAHs), polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), organochlorine pesticides], pharmaceuticals, detergents, salts and pathogenic microorganisms (Dai et al. 2006; Sànchez-Brunete et al. 2008; Sidhu and Toze 2009; Clarke and Smith 2011), the concentrations of which vary in relation to the composition of wastewater and how wastewater and USS are treated.

Addition of USS to agricultural soils poses special concerns about the transfer of toxic and potentially toxic heavy metals to soil and plants. Soils treated with USS may accumulate heavy metals such as Cd, Cr, Cu, Hg, Ni, Pb and Zn, depending mainly on the chemical composition and stabilization of USS, doses and time of application, soil properties and element behaviour in soil (Roig et al. 2012; Zoghlami et al. 2016; Iglesias et al. 2018; Yang et al. 2018). In these soils, heavy metals may be mobilized due to decomposition of the readily degradable organic compounds of applied USS and release from the inorganic soil components (Merrington et al. 2003; Sànchez-Martin et al. 2007), and taken up by cultivated plants (Sekhar et al. 2002; Lavado 2006; Singh and Agrawal 2007, 2010; Jamali et al. 2009; Latare et al. 2014).

Limits to the total concentrations of Cd, Cr, Cu, Hg, Ni, Pb and Zn in USS to be used on agricultural soils, and in treated soils themselves, were set by the European Community in European Directive 86/278/EC and in Italy with Legislative Decree 99/92 currently in the process of amendment. Conversely, no guidelines or legislation consider the chemical fractionation of heavy metals in soils treated with USS, despite the fact that the extractable fraction defines their mobility and environmental availability and rules their soil-to-plant transfer (Chen et al. 1996; Ahumada et al. 2004; Shrivastava and Banerjee 2004).

Several short-term experimental field, greenhouse and laboratory studies have been conducted on soils treated with high doses of USS exceeding national statutory thresholds (e.g. 5 and 15 t/ha of USS dry matter in 3 years according to the German and Italian legislations, respectively; 6 t/ha per year in Portugal), to assess how addition of USS influences soil chemical properties and heavy metal accumulation and availability (Wei and Liu 2005; Sànchez-Martin et al. 2007; Fernández et al. 2009; Singh and Agrawal 2010; Latare et al. 2014; Zoghlami et al. 2016). The long-term evolution of soil geochemistry resulting from USS application has been investigated in field experiments using high USS loads (Roig et al. 2012; Iglesias et al. 2018; Yang et al. 2018) and recommended doses (Mantovi et al. 2005). Conversely, there have been few studies focused on changes of soil geochemical features due to prolonged and regulated agronomic treatments with USS under real agricultural conditions (Gaskin et al. 2003).

We performed a field study to determine the cumulative effects on the properties and levels of heavy metals in soils treated with USS for 6 consecutive years in the framework of an agronomic treatment plan of a farm in southern Tuscany (Italy). Chemical and agronomical properties, total contents and extractable concentrations of Cd, Cr, Cu, Hg, Ni, Pb and Zn were determined in agricultural soils treated with a single annual addition of USS for 6 consecutive years, agricultural soils cultivated using mineral fertilizers and uncultivated soils representative of the geochemical background of local soils.

As novelty, this study focused on soils subjected to a medium-term USS treatment under a real agronomic program using regulated doses. Other remarkable features were as follows: (i) a large area of agricultural land (about 50 ha) was involved; (ii) the chemical/agronomical properties and heavy metal levels of USS-fertilized soils were compared to those of mineral fertilized soils and uncultivated soils; and (iii) the soils were analysed every year for the 6 years of treatment.

The results of this study are a contribution to the discussion of the scientific community regarding the sustainable use of USS in agriculture, and in particular to understand how applying USS to soil in regulated doses under real agricultural conditions affects its chemical and agronomical properties and total heavy metal content and availability.

2 Materials and methods

2.1 Study area

The study concerned cultivated land belonging to a farm in southern Tuscany (Italy). Morphology is flat and altitude about 280-m a.s.l. Climate is temperate with mean annual precipitation of 926 mm and average temperature 14.1 °C. Wheat, maize and rapeseed are the main crops.

Geology is characterized by Pleistocene volcano-sedimentary deposits and volcanites belonging to the Vulsini Volcanic Complex of the Roman Magmatic Province. The volcano-sedimentary deposits consist of marls, silts and sands with elements of volcanic rocks and diatomites, formed in a marshy setting. These deposits represent the most widespread lithology in the study area. The volcanites are pyroclastic deposits (Sovana, Sorano and Farnese formations) related to the magmatic activity of the Latera eruptive centre (0.3–0.1 Ma; Palladino and Simei 2005).

In the study area, soils of 15 agricultural plots were fertilized for 6 consecutive years with USS resulting from treatments of municipal wastewaters in 50 plants located in Tuscany and Lazio (Italy). The USS was stabilized through aerobic biological digestion aimed to reduce volatile solids and pathogenic organisms and eliminate unpleasant odours.

The annual average dose of USS added to agricultural soils varied from 3.89 t/ha (in 2012) to 6.16 t/ha (in 2016). In agreement with the Italian legislation (Lgs D. 99/92) that establishes amounts up to 15 t/ha in 3 years, the doses were 12.45 t/ha in the period 2011–2013 and 14.51 t/ha in 2014–2016. The USS was loaded into a tractor hopper, distributed uniformly in the field and then mixed to soil by ploughing up to 40-cm deep.

2.2 Soil sampling

The sampling activity concerned the following soil types: (i) agricultural soils subject to a single annual application of USS for 6 consecutive years (from 2011 to 2016); (ii) agricultural soils cultivated using mineral fertilizers; and (iii) uncultivated soils representative of the geochemical background of soils in the study area.

The sampling surveys were performed annually in late spring–early summer from 2011 to 2016, about 8 months after USS application in late summer–early autumn. A total of 111 soil samples were collected in (i) 15 plots (0.9–5.8 ha) subject to USS treatment for 6 consecutive years ($n = 90$); (ii) 9 plots (0.1–3 ha) cultivated with mineral fertilizers ($n = 9$); and (iii) 12 uncultivated sites close to the abovementioned agricultural plots. All soils formed from the same parent rocks consisting of volcano-sedimentary and volcanic lithologies of the Vulsini Volcanic Complex.

Topsoil samples (0–40-cm deep) were collected in agricultural plots and uncultivated sites. In the agricultural plots, the soil sample was a composite sample consisting of 5 subsamples per ha. Depending on the shape of the plot, soil subsamples were taken along X-, Y- or W-shaped lines. In the uncultivated sites, the soil sample was a composite sample formed by 3 subsamples collected within a circle of 2-m radius.

2.3 Laboratory treatment

Soil samples were air-dried in the laboratory at room temperature, sieved manually to 2 mm and homogenized by quartering and mechanical pulverization.

To determine total heavy metal contents (Cd, Cr, Cu, Hg, Ni, Pb and Zn), soil samples were solubilized by adding a mixture of HF, HNO_3 and H_2O_2 (ultrapure reagents) to about 250 mg of powdered sample (US EPA 1996).

A selective chemical extraction technique using acid acetic was applied to remove the extractable fraction of heavy metals from the soil samples, namely, step A of the sequential extraction scheme proposed by the Community Bureau of Reference (Rauret et al. 1999).

2.4 Determination of chemical and agronomic properties

Soil pH was measured in a 1:1 (w/v) soil/water mixture by method III.1 of the Italian Legislative Decree 248/99. The method of Hendershot and Duquette (1986) was used to determine effective cation exchange capacity (CEC), and the procedure of Walkley and Black (1934) to measure organic carbon (C_{org}) content. Total nitrogen content (N_{tot}) was measured using method XIV.1 of the Italian Legislative Decree 248/99. The total phosphorus content was determined by X-ray fluorescence spectroscopy (XRFS) with a Philips MagiX PRO spectrometer.

2.5 Determination of heavy metal total content and extractable concentrations

The total contents and extractable concentrations of Cd, Cr, Cu, Hg, Ni, Pb and Zn were determined in soil samples by inductively coupled plasma-mass spectrometry (ICP-MS) using Perkin Elmer Elan 6100 and NexION 350 spectrometers. Analytical accuracy was assessed by analysing the following standard reference materials: SRM 2709 (San Joaquin Soil) and SRM 2710 (Montana Soil) of NIST (National Institute of Standards and Technology) for heavy metal total contents and SMR 701 (Sediment) of BCR (Community Bureau of Reference) for their extractable concentrations. Analytical precision was estimated as repeatability of the analytical measures ($n = 5$) expressed as percent relative standard deviation (% RSD).

2.6 Statistical analysis

Statistical indices (min and max values, mean, median, 25th and 75th percentiles, standard deviation) were calculated for the chemical features of the USS applied, as well as for the chemical and agronomical properties and heavy metal total contents and extractable concentrations of the agricultural and uncultivated soil samples. Values greater than [Q_3 + IQR] and less than [Q_1-IQR] were considered to be outliers, where Q_3 and Q_1 were the 75th and 25th percentile of the analytical dataset, respectively, and IQR was the interquartile distance (Q_3-Q_1).

Normal distribution and homoscedasticity of datasets were evaluated by the Shapiro-Wilk W-test and Fischer F-test, respectively. Statistical differences were checked by the student *T*-test for normally distributed data and the Mann-Whitney U-test for non-normally distributed data. The statistical differences ($p < 0.05$) were established by comparing soils treated for 6 consecutive years with USS with (i) soils after the first USS addition; (ii) soils treated with mineral fertilizers; and (iii) uncultivated background soils.

3 Results and discussion

3.1 Urban sewage sludge

Table 1 summarizes the chemical features of the USS used to fertilize the soils of the 15 agricultural plots selected in the study area for 6 consecutive years. The chemical characterization is based on the analysis of 168 samples of USS.

The chemical features of the USS complied with the requirements of the European and Italian legislation regulating their use in agriculture. In fact, the contents of organic carbon (C_{org} = 26.8–61%), total nitrogen (N_{tot} = 1.5–28.8%) and total phosphorous (P_{tot} = 0.41–13.8%) were variable but constantly above the corresponding minimum threshold concentrations (20% for C_{org}, 1.5% for N_{tot}, 0.4% for P_{tot}) for USS application to agricultural soils, defined by Italian Lgs. D. 99/92. Likewise, the levels of heavy metals in USS were below the corresponding maximum threshold concentrations for USS suitable for use in agriculture (Table 1). The concentrations of Cd, Cr, Cu, Hg, Ni, Pb and Zn in USS varied by 1 to 2 orders of magnitude and decreased as follows (median, in mg/kg): Zn (796) > Cu (322) > > Pb (68.6) > Cr (40.3) > Ni (28.8) > > Hg (1.0) ≈ Cd (0.8).

In order to establish potential soil contaminants among the heavy metals analysed, the concentrations of Cd, Cr, Cu, Hg, Ni, Pb and Zn in USS were compared with the corresponding concentrations in agricultural soils cultivated using mineral fertilizers. For this purpose, an index, the ratio of heavy metal concentration in the USS sample to its median concentration in mineral fertilized soils, was calculated. The highest values of this index were found for Cu (median 12.3), Zn (9.9) and Hg (5.5). Cd, Cr, Ni and Pb had lower values equal to 1.9, 1.3, 1.2 and 1, respectively. Therefore Cu, Zn and Hg can be considered potential soil contaminants due to their significantly higher concentrations in USS than in the agricultural soils of the study area.

3.2 Soils

3.2.1 Chemical and agronomic properties

As shown in Fig. 1, soils fertilized for 6 consecutive years with USS normally had pH values from 6.1 to 6.7. The subacid to neutral pH of these soils was in line with the geolithological and geochemical characteristics of the parent rocks consisting of volcano-sedimentary deposits and volcanites.

Statistical analysis indicated that the pH of 6-year USS-fertilized soils was significantly lower than that of uncultivated background soils and agricultural soils cultivated with mineral fertilization. Moreover, in the period of USS application (2011–2016), treated soils showed a progressive decrease in pH (Fig. 1). pH values were therefore significantly different in USS-fertilized soils in the 1st and 6th year of treatment.

The decrease in pH in USS-fertilized soils cannot be ascribed directly to USS pH. In fact, USS normally had a neutral to slightly alkaline pH (from 6.6. to 7.8) throughout the period of its application. The levels and trend of pH in USS-fertilized soils presumably depended on the biodegradation of sewage sludge organic compounds. Indeed, decomposition of the sewage sludge organic component is an active process in treated soils (Singh and Agrawal 2008; Alvarenga et al. 2017) as it partly consists of less stable and easily degradable organic compounds, such as proteins (Carvalho et al. 2015). Conversely, more persistent humic substances, such as humic acids, lignin and cellulose, prevail in organic matter of soils formed in undisturbed settings such as woods and meadows (Senesi and Loffredo 1999). In line with this, the uncultivated background soils had significantly higher organic carbon content than USS-fertilized soils (Fig. 1).

Biodegradation of organic compounds in USS-fertilized soils produces CO_2 that reacts with soil water forming carbonic acid (H_2CO_3). Partial dissociation of H_2CO_3 produces H^+ ions, lowering pH. The decomposition of the organic compounds supplied by USS may also produce weak acids such as citric acid, carboxylic acids and phenolic acids (Stevenson 1994). Reduction in soil pH may also be influenced by mineralization processes involving organic N and S (Kirchmann et al. 1996).

In line with the above, various authors reported a pH decrease in agricultural soils fertilized with USS in short-term field experimental studies using high USS loads (Singh and Agrawal 2010; Alvarenga et al. 2017). Likewise, no significant variation or increase in pH values was found in soils subject to short- and long-term treatments with large amounts of USS (Roig et al. 2012; Latare et al. 2014; Zoghlami et al. 2016). In these cases, soil acidification resulting from biodegradation of sewage sludge organic compounds was probably counterbalanced by the buffer capacity of soil (e.g. carbonate buffer) and/or an increase in salt content. Variations in this

Table 1 Chemical features of the urban sewage sludge added to agricultural soils of the study area[a]

		Min–max	Median	Limits	
				European Directive[b]	*Italian Decree*[c]
Chemical properties					
pH		5.8–8.5	7.1		
C_{org}	*% dw*	26.8–61	38.5		> 20
N_{tot}	*% dw*	1.5–28.8	5.6		> 1.5
P_{tot}	*% dw*	0.41–13.8	1.4		> 0.4
Heavy metals					
Cd	*mg/kg dw*	< 0.1–4.9	0.8	20–40	20
Cr	*mg/kg dw*	3.8–138	40.3		
Cu	*mg/kg dw*	47.3–777	322	1000–1750	1000
Hg	*mg/kg dw*	< 0.05–8.6	1	16–25	10
Ni	*mg/kg dw*	5.2–192	28.8	300–400	300
Pb	*mg/kg dw*	10.7–189	68.6	750–1200	750
Zn	*mg/kg dw*	32.1–2372	796	2500–4000	2500

dw = dry weight

[a] Data provided by Aquaser s.r.l. (ACEA Group)

[b] European Council Directive 86/278/EEC

[c] Italian Decree 99/92

chemical property may also be due to a direct influence of USS pH when it is significantly different from soil pH and organic waste is applied at high doses (Kidd et al. 2007; Singh and Agrawal 2010; Alvarenga et al. 2017).

Cation exchange capacity (CEC) was moderately high to high in 6-year USS-fertilized soils, varying from 11.4 to 35 cmol/kg (Fig. 1). These CEC values were comparable with those in soils cultivated with mineral fertilizers (CEC normally 16 to 36 cmol/kg), but significantly lower than in uncultivated background soils (24.1–54.8 cmol/kg). This difference is mainly due to the higher organic matter content of uncultivated soils. It is well known that soil organic matter consists of compounds (e.g. humic substances) that have the highest CEC values (usually 100–500 cmol/kg) of all main solid soil constituents.

In the period of USS application, the cation exchange capacity of USS-fertilized soils showed a slight decrease (no statistically significant difference was found), in line with the lowering of pH over time (Fig. 1). In fact, as soil pH decreases, cation exchange capacity also decreases due to reduction of available negative surface charges of the main solid soil constituents, such as organic matter and clay minerals.

Data in the literature suggests that a CEC increase mainly occurs in soils treated with high USS loads over short to long periods and is presumably due to a relevant enrichment in organic matter (Walter and Cuevas 1999).

The 6-year USS-fertilized soils had low to medium organic carbon content (C_{org} = 0.58–1.5%; Fig. 1) comparable with that of mineral fertilized soils (0.71–1.3%). Conversely, uncultivated background soils had significantly higher C_{org} contents (1.4–8%), as they formed in woodland areas where natural processes built up a thin O horizon of organic matter (5–10 cm) consisting largely of persistent humic substances.

The 6-year USS-fertilized soils had low levels of organic matter, despite the very high organic carbon content of the USS applied (26.8–61%; Table 1). As previously stated, this finding is presumably related to a prevalence of more easily biodegradable organic compounds in USS, as well as to the removal of crop residues from agricultural soils. Decomposition of organic matter in the USS-fertilized soils could also be enhanced by cultivation methods (e.g. ploughing) resulting in greater soil aeration.

In line with the biodegradation of organic compounds supplied by USS, there was no enrichment of organic matter in USS-fertilized soils during the period of application in the study area. In fact, C_{org} content was rather uniform from 2011 to 2016, being in the range 0.7–1.2% (Fig. 1).

A similar result was found in a field experiment by Melo et al. (2018) who found no increase in organic matter in tropical soils subject to 10 years of urban/industrial sewage sludge application in variable doses (mainly 5 to 20 t/ha per year accumulating 50, 100 and 147.5 t/ha over the entire period). Conversely, short- to long-term field experimental studies using recommended (Mantovi et al. 2005; Urbaniak et al. 2017) or unrealistic amounts of USS (Fernández et al. 2009; Singh and Agrawal 2010; Roig et al. 2012; Latare et al. 2014; Zoghlami et al. 2016; Alvarenga et al. 2017; Bai et al. 2017) showed an enrichment of organic carbon/matter in treated

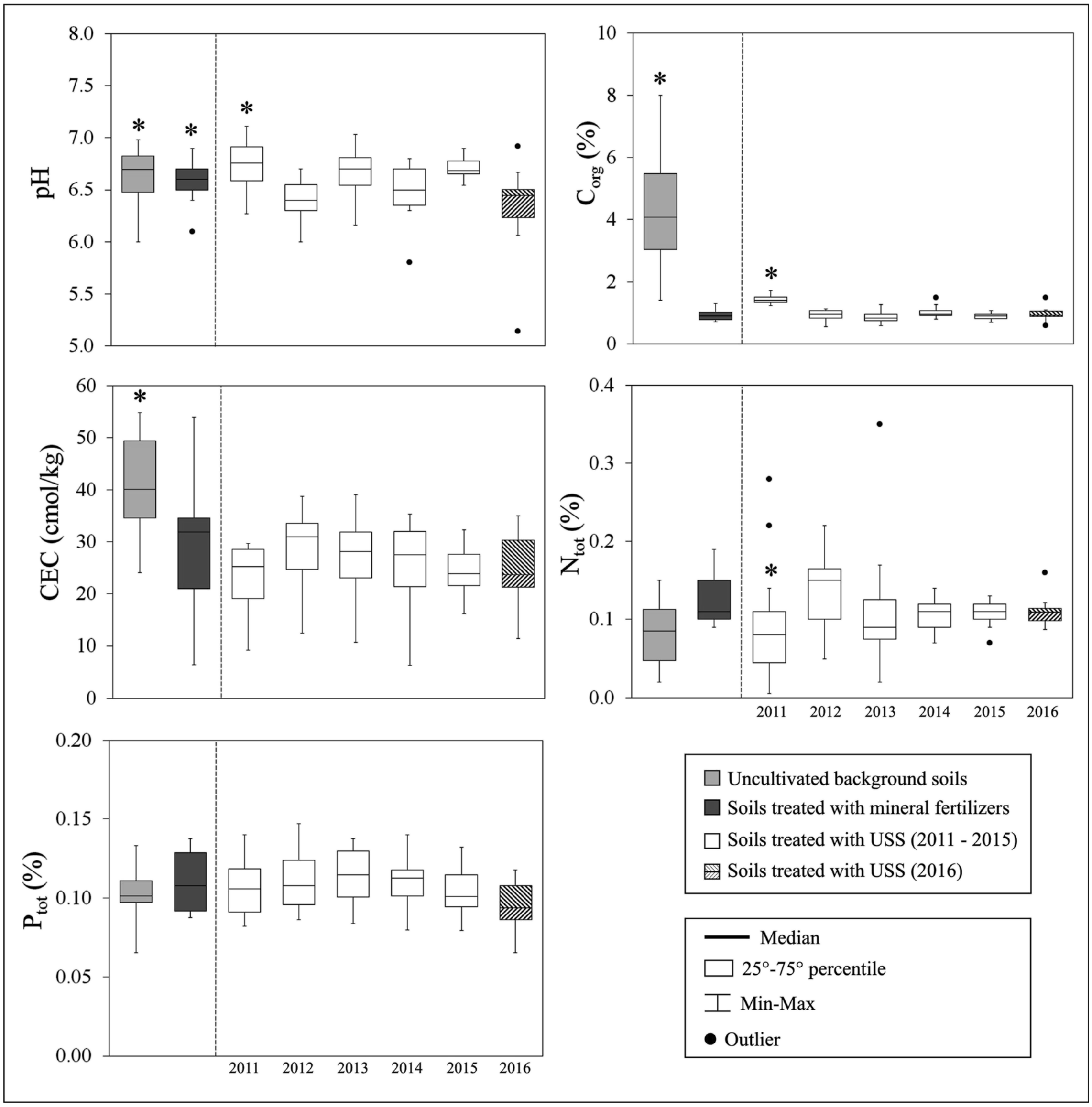

Fig. 1 Chemical and agronomic properties of (i) uncultivated background soils; (ii) soils treated with mineral fertilizers; (iii) soils treated annually with urban sewage sludge (USS) from 2011 to 2015; (iv) soils treated with urban sewage in 2016 (* = statistically significant difference ($p < 0.05$) with respect to soils treated with USS in 2016)

soils, mainly controlled by the nature and chemical features of USS, and the doses, frequency and time span of its application. Among the chemical features of USS, organic carbon content and above all the percentage of stabilized and mature organic compounds play a key role in the accumulation of organic matter in soil (Bastida et al. 2008; Fernández et al. 2009). Sànchez-Martin et al. (2007) showed that in soils treated only once with large amounts of domestic and agricultural-food industrial sewage sludge (40 and 400 t/ha), organic matter content decreased during an incubation time of 18 months, especially in the first 3 months, due to biodegradation of the most labile organic compounds.

The total nitrogen and phosphorous contents (N_{tot} and P_{tot}) in 6-year USS-fertilized soils (0.09–0.16% for N_{tot}; 0.07–0.12% for P_{tot}) were similar to those in the mineral-fertilized soils (0.04–0.19% for N_{tot}; 0.09–0.14% for P_{tot}) and were within the corresponding background in local soils (0.02–0.15% for N_{tot}; 0.07–0.13% for P_{tot}; Fig. 1). As shown for C_{org}, no accumulation trend of N_{tot} and P_{tot} was found in USS-fertilized soils despite their high contents in USS (Table 1). This finding suggests that N and P supplied by USS were largely associated with degradable compounds and therefore available in soil as macronutrients for cultivated plants.

The use of USS in agriculture usually implies an increased N_{tot} and P_{tot} in soil mainly regulated by sewage sludge composition, application doses and time span (Fernández et al. 2009; Singh and Agrawal 2010; Latare et al. 2014; Zoghlami et al. 2016; Bai et al. 2017). Accumulation of N_{tot} and P_{tot} may be partly explained by the application of USS with more stabilized organic compounds containing N and P.

3.2.2 Total heavy metal content

The 6-year USS fertilized soils had total contents of Cd, Cr, Cu, Hg, Ni, Pb and Zn in the following ranges: 0.23–0.4 mg/kg for Cd, 13.4–58.9 mg/kg for Cr, 11–51.3 mg/kg for Cu, 0.09–0.28 mg/kg for Hg, 8.8–38.7 mg/kg for Ni, 46.1–86.5 mg/kg for Pb and 60.5–103 mg/kg for Zn (Fig. 2).

Statistical analysis indicated that the total contents of Cr, Cu, Ni and Zn in these soils were similar to those in soils cultivated using mineral fertilizers and uncultivated background soils, whereas total contents of Cd and Hg were significantly lower (Fig. 2). Only Pb showed a statistically significant increase in total content in 6-year USS-fertilized soils with respect to the local soil geochemical background.

Considering the whole period of application, USS-fertilized soils revealed weak enrichments of Ni and Pb in the first 3 years of USS treatment. In any case, there was no trend of accumulation of the heavy metals in USS-fertilized soils (Fig. 2).

The total contents of Cd, Cu, Hg, Ni, Pb and Zn in USS-fertilized soils were lower than the corresponding maximum threshold concentrations for USS-treated soils established by Italian legislation 99/92: 1 mg/kg for Cd and Hg, 75 mg/kg for Ni, 100 mg/kg for Cu and Pb, 300 mg/kg for Zn (no threshold for Cr). Only Pb content was closer to its maximum threshold concentration (100 mg/kg).

In this regard, the natural variability of Pb (49–73 mg/kg) and Hg (0.17–0.35 mg/kg) in local soils, estimated through their contents in uncultivated background soils, is higher than normal Pb and Hg concentrations in uncontaminated soils, namely, 3–50 mg/kg and 0.02–0.15 mg/kg, respectively (Mihaljevic 1999; Kabata-Pendias 2001; De Vos and Tarvainen 2006). The high natural levels of Pb and Hg in local soils have a geogenic explanation as the study area is part of a wide Pb and Hg geochemical anomaly that involves northern Lazio and southern Tuscany, where Pleistocene volcanites of the Vulsini Volcanic Complex crop out (Di Lella et al. 2003; De Vivo et al. 2009).

In line with other studies, no major enrichment of Cd, Cr, Cu, Hg, Ni, Pb and Zn was found in soils treated with regulated USS doses for long periods (Gaskin et al. 2003; Mantovi et al. 2005) or high amounts for short periods (Alvarenga et al. 2017). Conversely, accumulation of these heavy metals was noticed in soils subject to application of large amounts of USS in prolonged (Roig et al. 2012; Yang et al. 2018) and short-term treatments (Wei and Liu 2005; Sànchez-Martin et al. 2007; Singh and Agrawal 2010; Zoghlami et al. 2016), depending mainly on heavy metal levels in the sewage sludge, and amounts, frequency and time of application. Iglesias et al. (2018) revealed that Cu, Hg, Pb and Zn accumulated in soils amended for 15 consecutive years with USS doses of 13–60 t/ha per year, and Zoghlami et al. (2016) found that the increase in Cd, Cr, Cu and Zn concentrations in soils treated with USS for 2 years at doses of 40, 80 and 120 t/ha per year was significantly proportional to sewage sludge doses and correlated with organic carbon content. Similarly, the levels of Cd, Cr, Cu, Hg, Pb and Zn in soils amended for 16 years with total amounts of USS from 160 to 1280 t/ha were correlated with the number of applications and/or with the doses of sewage sludge (Roig et al. 2012).

These different results mainly depended on the load and fractionation of heavy metals in USS and doses, frequency and time span of their application, as well as soil characteristics such as pH, cation exchange capacity and contents of organic matter, clay minerals and Fe oxyhydroxides that affect soil capacity to accumulate heavy metals released by sewage sludge through sorption and precipitation/coprecipitation reactions.

3.2.3 Extractable heavy metal concentrations

The 6-year USS-fertilized soils had extractable concentrations of the following: (i) Cu significantly higher than soils treated with mineral fertilizers and uncultivated background soils; (ii) Cr and Zn significantly higher than mineral-fertilized soils and comparable with uncultivated background soils; (iii) Cd significantly lower than soils cultivated using mineral fertilizers and comparable with uncultivated background soils; and (iv) Ni and Pb comparable with soils treated with mineral fertilizers and uncultivated background soils (Fig. 3). The extractable concentrations of Hg were below the detection limit (0.01 mg/kg) in all soil samples.

An increase in the extractable concentrations of Cr, Cu, Pb and Zn occurred in USS-fertilized soils in the period of application. This trend was most evident for Cu, available amounts of which increased progressively from 0.11 to 0.43 mg/kg (median). The increase in Pb and Zn extractable concentrations was also progressive but less marked than that of Cu (0.09 to 0.12 mg/kg for Pb_{ext}; 2.21 to 4.12 mg/kg for Zn_{ext}). Extractable Cr progressively increased in the first 3 years of USS treatment (2011–2013), and was rather homogeneous in subsequent years (2014–2016).

Increased availability due to USS application can be considered positively for Cu and Zn as it represents a larger source of micronutrients for cultivated plants, but negatively for Cr and Pb due to their potential toxicity.

Several studies have reported increased availability of essential (e.g. Cu, Zn) and non-essential heavy metals (e.g. Cd, Cr, Ni, Pb) in soils treated with USS doses exceeding the limits imposed by national regulations (Singh and Agrawal 2010; Latare et al. 2014; Alvarenga et al. 2017). According to Iglesias et al. (2018), DTPA extractable concentrations of

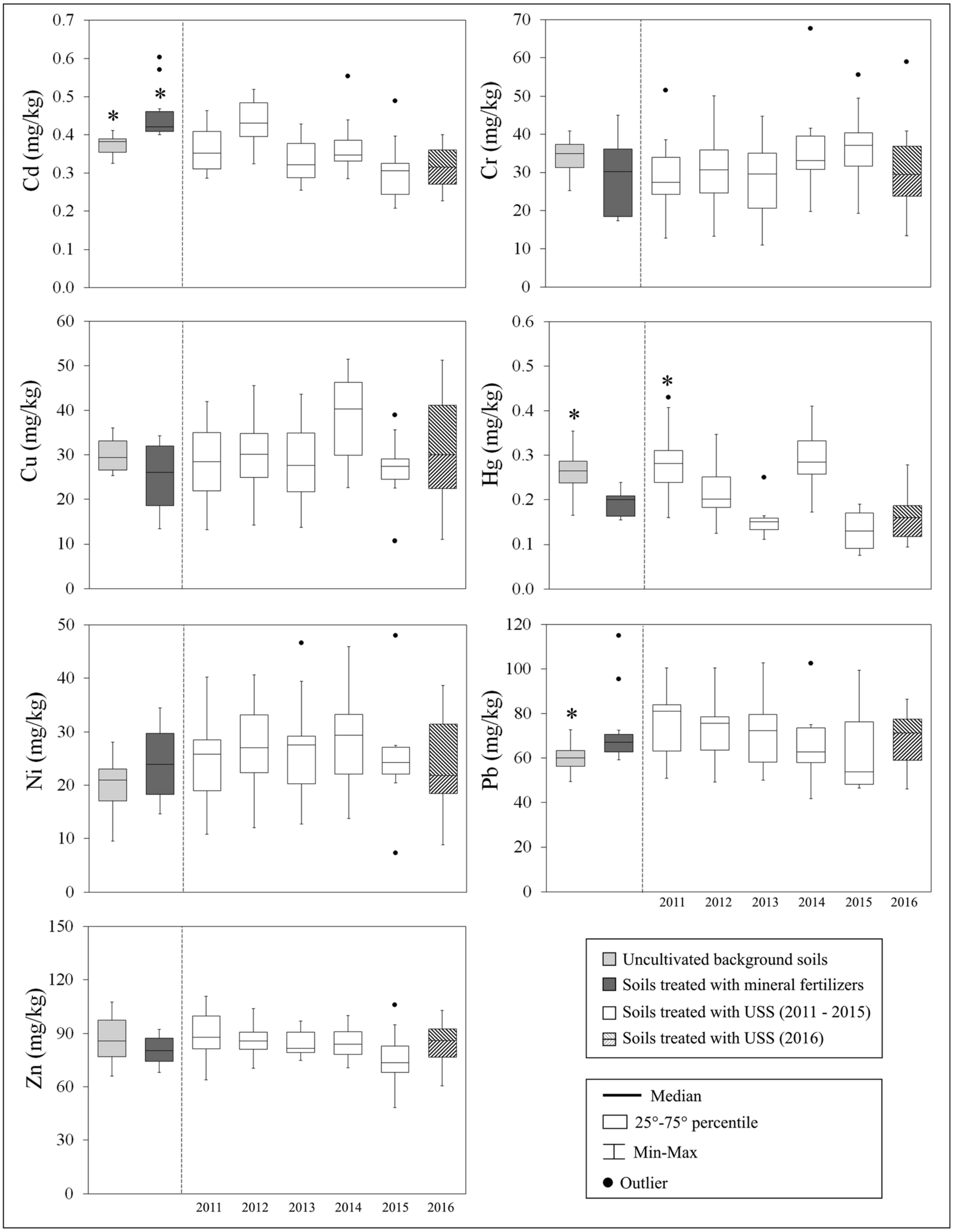

Fig. 2 Total contents of Cd, Cr, Cu, Hg, Ni, Pb and Zn in (i) uncultivated background soils; (ii) soils treated with mineral fertilizers; (iii) soils treated with urban sewage sludge (USS) from 2011 to 2015; (iv) soils treated with urban sewage in 2016 (* = statistically significant difference ($p < 0.05$) with respect to soils treated with USS in 2016)

heavy metals, including Cd, Cu and Zn, were higher in 15-year USS-treated soils (doses of 13 to 60 t/ha per year) than in chemical-fertilized or non-fertilized soils. However, comparison of heavy metal availability results for USS-treated soils is an issue, as extractable amounts vary according to extraction procedure (e.g. use of different reagents such as EDTA, DTPA, acetic acid and salts) and depend on factors such as USS characteristics, soil properties (e.g. pH and CEC) and composition (e.g. content of clay minerals and organic matter), element behaviour in sorption processes

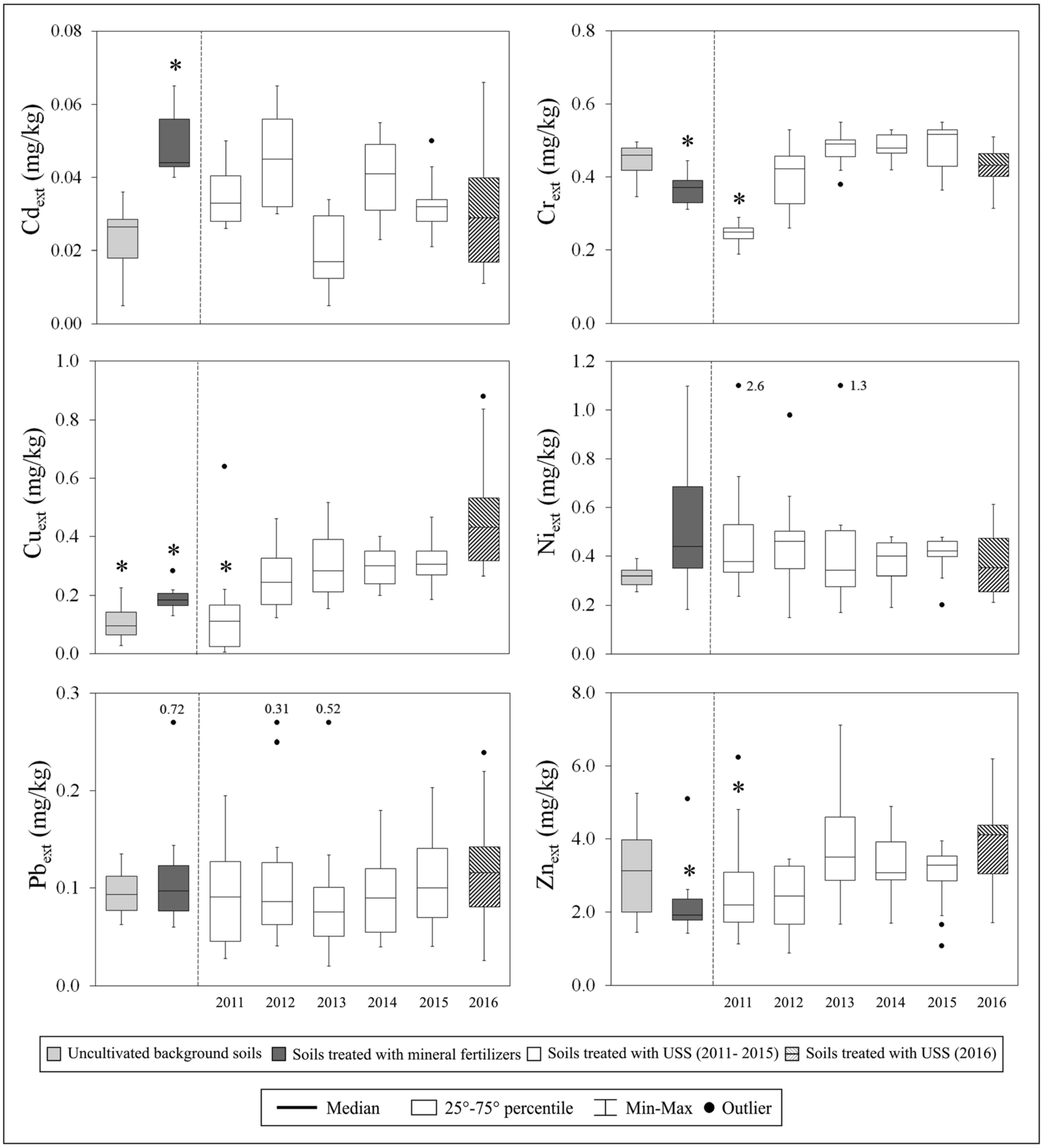

Fig. 3 Extractable concentrations of Cd, Cr, Cu, Ni, Pb and Zn in (i) uncultivated background soils; (ii) soils treated with mineral fertilizers; (iii) soils treated with urban sewage sludge (USS) from 2011 to 2015; (iv) soils treated with urban sewage in 2016 (* = statistically significant difference ($p < 0.05$) with respect to soils treated with USS in 2016)

(e.g. ionic exchange and organic complexation) and root uptake.

On the basis of the mobility factor index (MFI) calculated as the percentage ratio between the extractable concentration of the element and its total content in soil (Kabala and Singh 2001), the order of mobility of the heavy metals analysed in 6-year USS-fertilized soils was (median MFI values) Cd (9.8) > Zn (4.7) > Ni (1.8) > Cu (1.5) ≈ Cr (1.4) > > Pb (0.2). A similar order of mobility was found in soils treated with mineral fertilizers and uncultivated background soils. However, MFIs of Cu and Zn in 6-year USS-fertilized soils were significantly higher than in the other two soil groups. It was not possible to calculate the MFI for Hg as its extractable concentrations in soil samples were always below the analytical detection limit (0.01 mg/kg).

The results of this study agree with the data in the literature suggesting that the extractable aliquots of the heavy metals considered were quite low in USS-treated soils (normally <10%), except for Cd and sometimes Cu, Pb and Zn (Pardo et al. 2011; Iglesias et al. 2018). Kim and McBride (2006) indicated that in sewage sludge-amended soils, Cd and Zn percentages in the extractable fraction with respect to total content were greater than those of Cu, Ni and Pb. High extractable aliquots of Cd and Pb (21.4 and 13%, respectively, in water-soluble, exchangeable and carbonate-bound fractions) and increased mobility were found by Sànchez-Martin et al. (2007) in soils treated with high doses of USS after an incubation period of 18 months.

Urban sewage sludge properties influenced the fractionation and availability of heavy metals in treated soils in the short run, whereas soil characteristics affected their chemical forms in the long run (Zufiaurre et al. 1998).

4 Conclusions

The results of this study showed that application of urban sewage sludge (USS) for 6 consecutive years at regulated doses had a low impact involving only pH and extractable concentrations of certain heavy metals.

Soils treated with USS showed a lowering of pH coupled with a slight decrease in cation exchange capacity (CEC). Despite the very high organic matter content of the applied USS, there was no enrichment of organic carbon, total nitrogen or total phosphorus in USS-fertilized soils due to biodegradation of organic compounds. The decomposition of sewage sludge-related organic matter was presumably the main process responsible for pH decrease in USS-fertilized soils.

Total contents of heavy metals showed no significant changes in USS-fertilized soils, proving to be below the respective maximum threshold concentrations in soils established by European and Italian legislation. Only Pb content approached its concentration limit in soil due to high natural Pb levels in soil of the study area (geochemical anomaly).

An increase in extractable concentrations of Cr, Cu, Pb and Zn was found in USS-fertilized soils. The trend was more evident for Cu, the potentially available amounts of which increased progressively up to fourfold with respect to background level.

The results of this study suggest that the environmental risks related to accumulation and availability of heavy metals in USS-treated agricultural soils are limited when USS is applied to soil in regulated doses in the framework of real agronomic treatment programs.

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