

Chapter 6

Potentially Harmful Elements in Urban Soils

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Abstract Throughout the human history, the anthropic activity inevitably leads to a legacy of increased PHE concentration in the environment. Nowadays the urban environment can be considered the main habitat for humans. Therefore, the acknowledgment and the understanding of the impact of PHEs in urban soils and dusts is imperative in order to develop a plan for the sustainable management of urban areas, which should limit this impact on human and environmental health. A historical background regarding urban soil contamination is presented, along with an overview of the PHEs and PGEs found in urban soils. As humans are daily exposed to PHEs present in air, water and soil, studies are focusing on their long-term effects and on the toxicological impact of PHE (PHEs') combinations, rather than of single elements. The importance of a comprehensive assessment of PHEs in urban soils and dusts, including their bioavailability, is discussed.

Keywords PHE • PGE • Urban geochemistry • Urban pollution • Urban soils • Anthrosols

1 Introduction

Potentially harmful elements (PHEs), in natural condition, can be considered rather immobile in soil. However their continuous release by anthropic activities gives rise to the increase of their concentration level in all the environmental matrices and, in particular, on top soils, as consequence of the presence of organic matter and clay materials. Industrial and urban areas are the most polluted settings, so the

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Table 6.1 Factors affecting natural and anthropic soil formation

Natural soil	Anthropic soil
Parent material	(1) Mixing soil from other areas (2) Mixing material of various origin (3) Removed and/or excavation material
Time	(1) Frequent land use variations (2) Landscape isolation
Climate	(1) Urban areas result warmer than rural or natural (2) Differences in drainage and in rainwater runoff mechanical effect
Morphology	(1) Presence of manmade structures and barriers (2) Presence of water flow barriers
Living organisms	(1) High productivity (2) Presence of exotic species

population is continuously exposed to high levels of PHEs even though their adverse health effects have been recognized their adverse health effects as daily reported in the news (Järup 2003).

Urban soils are particular ecosystems influenced by human activity that alters their pedochemical characters acquired through the natural dynamics of the soil. Human activity, over time, has refined and changed the landscape adapting to its own needs, reworking the original materials, adding new ones: exotic, alien or from technological origin. These soils have thus become accumulation and storage areas for anthropogenic materials released into the environment in such quantities as to change (sometime up to 10–100 times) the natural background. The factors affecting natural and anthropic soil formation and the source of PHE in urban environment are reported in Tables 6.1 and 6.2. Table 6.3 contains some information on the technological substrate present in urban areas and related wastes.

Bockheim (1974) stated that urban soils are material having a non-agricultural man made surface layer more than 50 cm thick that has been produced by mixing, filling or land surface contamination. In such areas soils can be further divided in natural soils, if developed on natural materials, and anthropogenic soils if developed on manmade materials employed to modify urban morphology and for specific activity (Bullock and Gregory 1991; Scheleuß et al. 1998; USDA 2005).

2 History

Studies on urban stratigraphy showed the long-term human influence witnessed, as an example, by Pb variation in wood from nineteenth century to nowadays in old American beech trees, following the industrialization trend and the utilization of leaded and, from 1990, unleaded gasoline (Pierzynski et al. 2005).

Archaeological studies date back evidence of urbanization from 7500 B.C. as for the case of the town of Hacilar, Turkey. From 2500 B.C proof have been reported for Gerico (Palestine) and for the civilizations developed along the course of Nile,

Table 6.2 Sources of potentially harmful pollutants in the urban environment

Sources	Pollutants
Cars (exhaust, fuel, oil,)	Ba, Cd, Pb, Cr, Cu, Pd, Pt, Rh, Zn, V, NO _x , C ₆ H ₆ , PAH, CO, SO ₂ , Pb, Phenols, Hydrocarbons, Halogenated hydrocarbons
Tires	Cr, Cd, Cu, Ni, Zn
Brakes wear	Cu, Zn
Road and urban surface weathering	PAH (asphalt), metals (concrete)
Road and urban surface winter management	Detergents, salts, Cd, Cu, Fe, Ni, Zn
Corrosion of construction materials	Cd, Zn
Domestic heating systems	Co, Mn, Ni, V
Garbage incineration, fire releasing from various materials	Cu, Zn, Ba

Table 6.3 Technological substrates and related wastes commonly present in urban areas

Source	Waste material
Construction and housing	Brick, concrete, mortar, plaster
Road work	Bitumen asphalt, tar asphalt
Ironwork, Steelworks, Foundries, Heavy metal works	Steel and furnace slag, sand of foundry, pumice
Incinerator	Fly and bottom ash
Household	Glass, metal, paper, plastic, ceramic, organic garbage, wood, bulky refuse

Indo, Tigris, Euphrates and Tiber rivers, as the case of Rome that can be considered one of the best sites to study urban soil being continually inhabited from the Bronze Age as testified by archaeological relics in soil profiles (Carandini 2012; Anguillano 2013). More recently studies on the city of Greater Angkor, Cambodia, evidenced that, from 1000 to 1200 B.C., this city represented the most extensive currently known preindustrial urban complex in the world (Simon 2008).

In medieval urban areas garbage deposits containing iron mixed with ceramic and other materials were found. The industrial revolution is witnessed by the increased presence of coal and iron and of the secondary products related to their use and processing. In more recent times the diffusion of the tertiary sector and the introduction of new living standards, continuous and relentless use of land with the increase of anthropic surface extension, results in a serious detriment of natural and agricultural lands. Trends on recent population distribution in the world areas are reported in Table 6.4.

Modern investigation on the geochemistry of urban soils started in the late 1960s. Studies on urban garden evidenced that the levels of some elements such as Cu or Pb, were higher in urban areas than in rural areas, which are strongly influenced by land use. (Purves 1966; Purves and Mackenzie 1969; Thornton et al. 1985; Thornton 1991, Kelly et al. 1996; Ajmone-Marsan and Biasioli 2010).

Table 6.4 Distribution of the population (% of the total) in the world from 1950 to 2011

	Urban	Rural	Urban growth 1972–2001	Annual growth (AG)
Europe	75	25	0.3	Expected AG until 2015: + 0.3 %
Africa	38	62	4.0	+ 3.5 %
Latin America Caribbean	75	25	6.0	AG in 1972: + 58.9 %
North America	77	23	0.1	AG in 1978: 73.8 %
OCEANIA ^a	71.7	28.3	72.7	AG + 1.51 %

^aPeriod 1975–2000

Owing to their origin, urban soils show a high spatial and vertical heterogeneity characterized by abrupt lithological and physical-chemical changes, great porosity, bulk density and texture variability. Notwithstanding these soils are subject to drastic change and degradation, soil properties remain rather similar to those of natural performing ones, some ecological functions such as pollutant absorption and plant growth sustainability. However, in large cities or complex urban environment, the ecological function, such as providing habitat to insects and microorganisms can be greatly reduced. The relation among some soil properties and urban soil contamination is reported in Table 6.5.

While the major inputs of PHEs into soil are atmospheric deposition, application of manure, inorganic fertilizers and sewage sludge, mining and smelting activities, or alluvial deposition, in the urban environment the main sources of trace elements are the emissions from vehicular traffic. Until now, the most studied PHEs were Pb, Cd, Cu, Cr, Fe, Mn, Ni, Pb and Zn. Previous studies have shown that their concentration levels and distribution are related to traffic intensity, to the distance from roads and to roads pattern, local topography and building effects. Pb is, for example, ubiquitous in the urban environment as a result of industrial emissions, and its extensive past use in alkyl-Pb compounds as antiknock additives in gasoline, and Pb-based paints and pipes (Callender and Rice 2000). Until the nineties it was estimated that around 11–15 % of the total refined Pb world consumption was utilized for petrol additives and that the average Pb concentration in petrol was 0.7 g L^{-1} , while in the car exhaust it reached 0.4 g L^{-1} of consumed fuel. Industrial emissions also contributed to the environment release of elements such Cd, Cu, Fe, Cr, Hg, Pb, and Zn.

3 PHEs' Impact on Human Health

Humans are daily exposed to PHEs present in water, air and soil at different concentration levels. Their intake however depends on the chemical characteristics of the PHEs as well as on the population patterns and behaviour. The intake of PHEs can occur either directly via ingestion, inhalation and, to a lesser extent, via dermal contact absorption, or indirectly with the consumption of food grown in contaminated areas (Sharma and Agrawal 2005; Dean 2007). There is a growing

Table 6.5 Influence of some soil properties on soil contamination in the urban environment

Action		Positive effects	Negative effects
<i>Soil sealing</i>	60–65 % of urban areas and 20–30 % of sub-urban areas result sealed	In highly contaminated soils, sealing reduces risk to human health. Soils covered with asphalt limit water percolation	Microclimate alteration: influence of the wind speed, increase temperature and humidity. Soil vegetation and biotopes habitat alteration Water infiltration reduction. Evapotranspiration and runoff alteration; polluted litter accumulation. Alteration of subsoil gaseous circulation
<i>Erosion</i>	Related to construction, building demolition, soil excavation, back-filling and soil handling operation, truncating		Reducing bottom soil protection; degradation of parks, playgrounds and vegetation Increase damages related to heavy rain
<i>Compaction</i>	Differences arise in case of sandy or loamy-clay. Increase of soil density	In case of dry condition loamy and clayey soils result to be resistant to compaction processes	Loamy and clayey soils in case of wet condition evidence high compaction. Aggregates tend to break down, increase of bulk density and sand particles packing. Reduction of vegetation and biological activity, earthworm population habitat restriction, reduction of water infiltration and gas diffusion owing to pore space limitation
<i>Soil pH</i>	Building materials raise the soil pH		Ca release in dry conditions produces top soil cementation and impermeable surface

tendency to promote urban agriculture for the improvement of gardeners' economic and social status, to make more available locally produced food and to improve the social wellbeing of the urban population (Brown and Jameton 2000). However, food production in urban areas implies a through overview and understanding of the presence of PHEs in urban soils. Soil ingestion is generally considered to be the most important exposure route and it is usually associated with eating of dirt in children (pica) and with occupational exposure in adults (Davis and Mirick 2006; ISO/TS 2007). Soil consumption can also occur deliberately (i.e. geophagy), for

example for medical purposes or as part of a regular diet (Abrahams 2005). Geophagists usually consume only certain soils with specific properties, usually with the purpose to compensate a mineral nutrient imbalance, leading thus to a discriminatory intake of soil constituents (Certini and Scalenghe 2007). However, along with the mineral nutrients, PHEs can also be ingested, potentially causing adverse health effects (Abrahams 2012). Several reports have been published concerning this particular topic. For example, the study of Abrahams et al. (2013) on the bioavailability of PHEs in two African geophagical materials, Calabash chalk and Undongo, which are commonly used in Nigeria and among the emigrants in different parts of the world, showed that the consumption of these clay soil material does not substantially contribute to PHEs' intake, nor to a better Fe uptake, one of the primary reasons for the geophagy. Conversely, Al-Rmali et al. (2010) showed that a type of clay, sikor, commonly consumed by Bangladeshi women in Bangladesh and in the United Kingdom, especially during pregnancy, may be an important source of As, Cd and Pb intake. The average daily consumption of sikor would thus contribute up to 370 and 1,236 mg kg⁻¹ of As and Pb to the diet, respectively. However, different factors affect the actual oral uptake of PHEs into the system.

For a correct estimation of PHEs' oral intake, it is very important to consider the size of the ingested soil particles, as smaller particles have larger surfaces, on which PHEs can be adsorbed. In their study on the size distribution of soil particles adhered to children's hands, Yamamoto et al. (2006), for example, pointed out that the cut-off diameter of 2 mm defined by the Japanese Ministry of the Environment is too permissive and may lead to an underestimation of the risk posed by contaminated soil intake. A considerable percentage of PHEs is released into the environment in the particulate forms, which are highly mobile and can easily interact with other chemicals. The size of the particulate matter (PM) varies, e.g. PM_{2.5} and PM₁₀ for particles with diameter smaller than 2.5 µm and 10 µm, respectively, which are further divided into narrow classes (Kampa and Castanas 2008). Small particles can enter the human body also via inhalation, leading to a significant PHE absorption in the respiratory tract, in addition to the gastrointestinal absorption due to the ingestion of soil particles and to the consumption of vegetables and water contaminated with airborne particles. In a study on the relationship between soil particle-size fractions and Cr, Cu, Ni, Pb and Zn content in five European cities, Ajmone-Marsan et al. (2008) reported that all the PHEs were concentrated in the <10 µm fraction. Interestingly, the accumulation factors in the finest fractions were higher where the overall soil contamination was lower, indicating, that relying on PHEs' concentration values in the soil solely may lead to an underestimation of the health risk for humans. Similarly, Cai et al. (2013) reported about significantly higher mean PHE concentration in urban dusts than in urban soils. While 89 % of investigated park soil and all residential areas were classified as lowly-moderately polluted, and 86 % of roadside soils and 91 % of sport ground soils were described as moderately polluted, all dusts were classified as highly polluted.

PHEs are known to have significant negative effects on human health at different levels, ranging from acute reactions due to the exposure to increased levels of PHEs, to chronic illness, including cancer (Kampa and Castanas 2008). Exposure to mercury due to the industrial activity, for example, has been found to be correlated to the increased kidney disease mortality among the population in the nearby residential zone (Hodgson et al. 2007). Similarly, epidemiological studies have reported an elevated incidence of beryllium sensitization (BeS) among workers occupationally exposed to Be-bearing dust particles, which may develop into the potentially fatal lung disease, the chronic Be disease (CBD) (Virji et al. 2011). Long-time exposure to PHEs may also impair fertility. Louis et al. (2012) found the Pb and Cd blood levels to be significantly associated with reduced couple fecundity, prolonging thus the conceiving time. It should be also highlighted that maternal exposure to PHEs, in particular to Pb, resulting in maternal blood levels $>1 \mu\text{L L}^{-1}$, can have severe negative effects on the developing fetus, impairing the cognitive and motor abilities of the child, or even inducing spontaneous abortion (Bellinger 2005; Schell et al. 2006).

Many studies have focused on children, since they represent the most vulnerable group of people. Children are exposed to soil PHEs by dust and/or soil tracked into homes on shoes or family pets (Hunt et al. 2006), by dust deposition in closed spaces (Laidlaw and Filipelli 2008), by their mouthing behavior and during their recreational outdoor activities (Ko et al. 2007; Abrahams 2012). In addition, children stature usually coincides with the lower airborne mixing layer produced by vehicular traffic vibrations. The suggested values of daily ingested soil are different, with values up to 137 mg d^{-1} , or even $1,432 \text{ mg d}^{-1}$, when pica behavior is present (Moya et al. 2004). The ingestion values proposed by the US EPA differ in relation to the routes of intake and are of 50 mg d^{-1} for soil solely, 100 mg d^{-1} for soil and dust and 1 g d^{-1} for soil pica behavior (US EPA 2008). So far, much attention has been given especially to Pb, which remains one of the major public health problems in the United States (Todd et al. 1996). As reported by Mielke et al. (2010) in a study on the Pb legacy from vehicle traffic in Californian urban areas, about 5.4 million tons of Pb additives were used in the USA in the period between 1927 and 1994. Another important source of soil pollution in urban areas is the Pb-based painting, which can substantially contribute to the overall Pb dust emissions, e.g. by power sanding and paint scraping (Mielke et al. 2001). Pb has a high uptake percentage into the children's organism; 50 % of the ingested Pb is retained into the organism, compared to the 5 % in adults (Laidlaw and Filipelli 2008). As Pb accumulates in the developing neural system and in bones, it may lead to permanent neural deficiencies, such as impaired intellectual performance, learning disorders and attention-deficit/hyperactivity disorder (ADHD) (Oskarsson et al. 1995; Nigg et al. 2008). An extensive overview of the existing studies concerning the soil/dust Pb in urbanized areas within the United States and the blood Pb in children can be found in Mielke et al. (2010). Similarly, in a study on children Pb-blood levels in New York City, Billick et al. (1980) reported a significant relationship between Pb-blood levels and gasoline Pb content.

Not only Pb, but also Zn, Cr, Cu, Cd and Ni are largely present in urban soils and dusts (Mielke et al. 2000; Wei and Yang 2010). Some PHEs, such as Cu, are harmless in small quantities, whereas some other PHEs, including Pb and Cd, may have neurotoxic effects. No homeostasis mechanisms are known so far for many PHEs, and exposure to high levels of PHEs could have serious negative effects on humans, e.g. accumulation in fatty tissues, negative effects on central nervous system and internal organs (Dockery and Pope 1996). Long-term exposure to PHEs may lead to several diseases, among them a high potential to develop cancer (Nriagu 1988; Kurt-Karakus 2012). Hubbard et al. (1996), for example, reported about significant exposure-response effects regarding the cryptogenic fibrose alveolitis among subjects occupationally exposed to metal or wood dust. Willis et al. (2010) have studied the connection between the incidence of Parkinson disease and PHE (Cu, Pb and Mn) emission in urban areas. The results showed that a significant increase of Parkinson disease (PD) risk was statistically significantly associated to the long-term residence of the observed subjects in U.S. counties with high cumulative industrial Cu or Mn release. Also worksite conditions implying exposure to Fe, Cu, Mn, Hg, Zn and Pb showed a significant association with the PD (Gorell et al. 1997). Interestingly, the more than 20 years' exposure to combinations of Pb-Cu, Pb-Fe and Fe-Cu showed a greater association with PD than with any of these metals alone. It has been reported that significant correlations can be found among different PHEs in soil or dust, e.g. between Pb and Cd, Zn and Cd, Pb and Zn, Cd and Zn, Cu and Pb, Pb and Zn, respectively (Cai et al. 2013). Such correlations indicate the source of PHEs: the significant correlations (at 99 %) between Pb and Zn in soil ($r = 0.381$) and dust ($r = 0.363$) indicate a traffic source coupled with industrial emissions. Further, significant correlations (at 95 %) between Zn and Cu in soil ($r = 0.351$) and dust ($r = 0.341$) indicate a possible origin in mechanical abrasions of vehicles (Jiries et al. 2001). However, the toxicological impact of PHE mixtures on human health still remains poorly understood.

4 Assessment of PHEs in Soils

Total PHE concentration in soil is the most common measure of soil contamination, and further, of environmental and human exposure. One of the most used standard analytical methods for the determination of elemental concentrations is the *aqua regia* leaching followed by AAS, ICP-MS, or similar analysis. The *aqua regia* leaching is a partial (pseudototal) extraction, where carbonates, mostly sulphide minerals, some silicates, clay minerals, salts and hydroxides are dissolved in a mixture of nitric and hydrochloric acid (ISO 11466 1995). However, different extraction methods may be preferred, according to the physical and chemical characteristics of the soil sample. In a study on selected PHEs in top soils of the main urban areas in Campania, Albanese (2008) reported that anthropogenic elements are easily extractable owing to their weak association with the crystalline

lattice of the soil minerals and, as a consequence, can be dangerous to human health. The ammonium acetate–EDTA extraction method (AA-EDTA) could be a more suitable method for the risk assessment purpose. In a comparative study on the suitability of three methods of PHE determination in soil samples, Sastre et al. (2002) proposed a decision chart for the selection of the most appropriate digestion procedure considering the sample nature and the purpose of the analysis. In addition to the *aqua regia* leaching, the microwave-assisted digestion (US EPA 2007) and the nitric acid extraction (Tam and Yao 1999) were tested by the authors. Recently, also the non-destructive XRF spectrometry has gained attention for its simple use for quick PHE screening in soils and other materials (US EPA 1998; Bachofer 2004). Additionally, several studies have tested simpler extraction procedures to be used as predictors of the total PHE content in soil. Wharton et al. (2012), for example, compared three commonly used screening tests, i.e. the modified Morgan, Mechlich 3 1-M HNO₃ extraction with the standard total Pb testing method (US EPA 2007). In their study, the 1-M HNO₃ extraction test resulted to be the best predictor of the total Pb content in soil.

The derivation methods for screening values used to regulate land contamination are widely variable among countries, due to different geographical, biological, sociological, regulatory and political needs (Carlson 2007). Although the total concentrations of PHEs in soil are still largely used as direct measures of maximum PHE intake, the urge of considering the complexity and heterogeneity of soil for the assessment of health risks for humans is gaining attention (Wragg and Cave 2002; Latawiec et al. 2010). PHEs are present in soil bound to soil fractions with different solubility and chemical characteristics. Consequently, they may have different toxic effects on organisms (Rieuwerts et al. 1998; Rodriguez et al. 1999; Oomen et al. 2000; Arnold et al. 2003; Geebelen et al. 2003; Krishnamurti and Naidu 2008; Buccolieri et al. 2010). The risk posed by contaminated soils to human health depends on the potential of the PHEs to leave the soil and enter the human bloodstream (Wragg and Cave 2002). The fraction of PHEs that can be absorbed by the body in the central blood compartment through the gastrointestinal system, the pulmonary system and the skin is defined as bioavailability (Ruby et al. 1996; Paustenbach 2000). Since bioavailability can be measured only in time consuming and expensive *in vivo* animal studies subject also to ethical considerations, *in vitro* bioaccessibility tests are preferred for the evaluation of the risk posed by PHEs to human and environmental health (Whitford 2006). Here bioaccessibility is defined as the fraction of PHEs, which is available for absorption. Innovative physiologically based extraction tests are the most comprehensive existing methods for the assessment of PHE bioaccessibility in soil. They aim to simulate human physiological processes, which affect the uptake of PHEs into the human body (Wragg and Cave 2002; Dean 2007; Peijnenburg et al. 2007). So far, most of the attention was given to the development of a unified *in vitro* method for the simulation of the human uptake of metals through the digestive system, especially by children (Wragg and Cave 2002; Oomen et al. 2003). For the implementation of the EU Soil Thematic Strategy, which dictates to the EU state members to identify areas where pollution has adverse effects on human and environmental health, a unified

methodology is needed. For this propose the standardization of the novel UBM (Unified BARGE Bioaccessibility Method) (Wragg et al. 2011) is very important. A first step was made by Denys et al. (2012), which validated the UBM procedure with an *in vivo* animal (swine) model.

PHE uptake into the human body through dust particle inhalation is less known. After dust particles enter into the lungs, the PHEs are affected by three chemically different environments: the extracellular lung solution, the cytoplasm of the alveolar macrophages and the lysosom (Collier et al. 1992). Currently only a few existing methods are available providing an approximate simulation of only one of the three environments, either by simulating the PHE solubility in the artificial extracellular lung solution (Ansoborlo et al. 1999; Twining et al. 2005), or with *in vivo* tests using primate lung macrophages (Poncy et al. 1992). It is therefore needed to develop a unified method for the assessment of PHE uptake through the respiratory system, which should comprise all the three mentioned environments.

The assessment of the lability of PHEs using diffusive gradients in thin films (DGT) is another innovative *in situ* method for the evaluation of the dynamics of PHEs between the solid soil and the liquid soil phases (Zhang et al. 1998; Peijnenburg et al. 2007). The DGT method is very suitable for the assessment of PHE uptake into plants (Tandy et al. 2011) and in soil organisms (Koster et al. 2005), which allows us to evaluate the human uptake of PHEs from the consumption of food produced on polluted soils.

Literature data reference levels on some PHE in world rocks and soils are reported in Table 6.6, while a data collection from some selected urban areas are displayed in Table 6.7.

5 Platinum Group Elements (PGEs)

In relation to economic and living standard conditions changes and with the introduction and development of new technologies, new chemical species and related pollutants have been continuously released into the environment. Among these we can mention PGEs (Platinum Group Elements) and REEs (Rare Earth Elements), both present in many industrial processes and in particular in car catalysts, to reduce traffic emissions of Pb, NO_x etc. (Morrison and Rauch 2007; Zereini and Alt 2006). The strong development of electronics and computer industry has required the use of large amounts of tantalum, gallium and REEs such as cerium, lanthanum, etc.; in fact, their chemical and physical properties are essential for the operation of televisions, computers and mobile phones.

Recently PGEs, mainly Pt, Pd, and Rh gained attention as possible threat for human and environmental health. These heavy metals are considered to be mostly inert and non-mobile, but there is evidence of their spread and bioaccumulation in the environment. Occurring in airborne particulate matter PGEs accumulate in organisms with time, as shown in studies reporting their enhanced levels in humans working in certain occupational environment (e.g. refineries and catalyst

Table 6.6 Reference levels of some PHEs in rocks and soils (mg/kg)

	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Sb	Zn	Reference
UCC ^a	2.0	0.10	11.6	35	14.3	0.056	18.6	17	0.31	52	Wedepohl (1995)
UCC	4.8	0.09	17.3	92	28	0.050	47	17	0.40	67	Rudnick and Gao (2003)
European soils		0.79		53	19.5		27	39		68	Angelone and Bini (1992)
World soils		0.30		200	20		40	10		50	Angelone and Bini (1992)
				68	22		22	30		66	Kabata-Pendias (2000)
	6.0	0.35	8.0	70	30	0.06	50	35		90	Adriano (2001)
Excessive levels		5.00		100	100		100	200		250	Kabata-Pendias (2000)
Pre industrial levels		0.55		48	34		40	22			Callender (2003)

^aUpper continental crust

productions). Even if elemental (metallic) PGEs have generally no biological effect, some of their salts, such as hexachloro platinate and tetrachloro palatinate, may have severe allergic and sensitization effects (Merget and Rosner 2001). Moreover, their accumulation in humans have been associated with long-term effects, e.g. asthma, nausea, increased hair loss, increased spontaneous abortion, dermatitis etc. (Ravindra et al. 2004).

Conspicuous is the literature available on PGEs. For evident space limitation all information can't be thoroughly presented in the present work. However, more information may be found in the following papers and in the enclosed references: Barefoot (1999), Ravindra et al. (2004), Morrison and Rauch (2007), Rauch et al. (2005), Angelone et al. (2006), Zereini and Alt (2000, 2006), Kalavrouziotis and Koukoulakis (2009).

As previously mentioned, PGEs are present in car catalysts which convert dangerous compounds, such as NO_x, carbon monoxide (CO) and the unburned hydrocarbons (HC) into less dangerous compounds, such as CO₂, N₂ and H₂O. Despite these evident advantages, their use gives rise to new environmental concerns. As an example, the continuous thermal and mechanical wearing out of the catalyst causes the release of PGE wash-coat particles. These particles are emitted in the order of few ng km⁻¹ in a wide range of sizes. i.e. <3.1 μm (~13 %), from 3.1 to 10 μm (~21 %) and >10 μm (~66 %) (Artelt et al. 1999). A data collection of PGEs released from various catalysts in different operative conditions is reported in Table 6.8, while the levels of Pt, Pd and Rh in two different European catalysts are reported in Table 6.9.

Even though PGEs have long been considered to be non-reactive (inert) elements, it has been recently observed that the effect of PGEs on human health depends on the degree of their bioavailability and that the proportion of soluble and hence quite reactive PGEs chemical forms may reach levels up to 10 % (Klaassen 1996). Literature data show evidence that PGE compounds are toxic,

Table 6.7 Potentially harmful element concentration in urban top soils in some world cities (mg/kg) n/a, information not available. Where available, the information on soil usage is specified

Location	Soil usage	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Sb	V	Zn	Reference
Warsaw, Poland	n/a	0.73	5.1	32	31	12	57	166	Czarnowska (1980)				
Glasgow, UK	n/a	0.53			97	216	207	Gibson and Farmer (1986)					
Brussel, Belgium	Urban gardens		42	55	55	207	Albarel and Cottenie (1985)						
Glasgow, UK	n/a	0.53		97	216	516	Gibson and Farmer (1986)						
Hamburg, Germany	n/a	2.0	95	146	62	218	Lux (1986)						
London, UK	n/a	1.0	73	294	183	Thornton (1991)							
Hamburg, Germany	n/a	23	1.2	52	81	0.60	31	168	Lux (1993)				
Rome, Italy	Urban area	0.31			47	8	67	331	Angelone et al. (1995)				
Prague, Czech Rep.	Urban parks	1.07			30	158	108	Scharova and Suchara (1995)					
Richmond, UK	n/a	<0.2			62	106	231	Kelly et al. (1996)					
Wolverhampton, UK	n/a	0.80			6.4	23.9	27	14.9	94.4	Paterson et al. (1996)			
Aberdeen, UK	Park soils		6.2	22.9	44.6	15.9	173	113					
	Road soils			104	71	71	102	138	Bini et al. (1995)				
	Urban parks		6	75	72	14	161	210	De Miguel et al. (1998)				
Florence, Italy	n/a		0.29	26	42	25	48	118	Wilcke et al. (1998)				
Madrid, Spain	n/a		0.57	114	99	21	214	440	Pfeiffer et al. (1988)				
Bangkok, Thailand	n/a			35	79	0.42	11	243	Birke and Rauch (2000)				
Manila, Philippines	City limits	5.1	0.92	5.2	39.9	45	16	75.3	31.7	156	Bityukova et al. (2000)		
Berlin, Germany	n/a		0.8	34	92.2	76	22.6	3.6	95.3	141.8	Thuy et al. (2000)		
Tallinn, Estonia	n/a		0.4	17.4	103.7	55.9	14.6	1.8	100.7	81.3			
Danang-Hoian, Vietnam	Soil particle <63 µm												
Conuña, Spain	n/a		0.3	11	39	60	28	309	3	206	Cal-Prieto et al. (2001)		
Hong Kong	n/a		2.18		25	93	168	Li et al. (2001)					
Oslo, Norway	n/a		5.48	0.41	9.98	32.5	31.7	0.13	28.4	55.6	51.3	160	Tijhuis et al. (2002)
Palermo, Italy	Urban areas		0.68	5.2	34	63	0.68	17.8	202	3.0	138	54	Salvagio Manta et al. (2002)
Aviles, Spain	n/a		15	2.4	18	20	11	107	477	Gallego et al. (2002)			
Nanjing, China	n/a			85	66	163	Lu et al. (2003)						

Jakobstad, Finland	n/a	2.7	0.25	23	22	7.9	59	82	Peltola and Aström (2003)				
Naples, Italy	Urban soils			11	74	262	251	Imperato et al. (2003)					
Beijing, China	n/a				71.2	22.2	66.2	87.6	Chen et al. (2005)				
Miami, USA	Residential areas					161			Chirenje et al. (2004)				
	Commercial areas					223							
	Public parks					107							
Gamesville, USA	Residential areas					67							
	Commercial areas					37							
	Public parks					22							
Damascus, Syria	Agricultural soils			13	57	39	17	103	Moller et al. (2005)				
Hong Kong	Urban areas			0.36	3.55	17.8	16.2	103	Lee et al., (2006a)				
Naples, Italy	n/a			0.56	28.2	97.5	158	111	Maisto et al. (2006a)				
Tuscany, Italy	n/a				85	59	219	128	Bretzel and Calderisi (2006)				
Torino, Italy	Urban soils			191	90	209	149	183	Biasioli et al. (2006)				
Torino, Italy	Urban soils	11	1.30	27	233	94	0.90	164	124	2.8	86	170	Biasioli and Ajmone-Marsan (2007)
Ibadan, Nigeria	n/a	3	0.15	56	32	17	47	94	Odewande and Abimbola (2008)				
Baltimore, USA	n/a			1.1	15	72	45	27	231	141	Yesilonis et al. (2008)		
Shanghai, China	n/a			0.52	108	59.3	31.1	70.4	301	Shi et al. (2008)			
Aveiro (Portugal)	Parks, road sides, gardens			7	46	12	72	86	Ajmone-Marsan et al. (2008)				
Glasgow (UK)				52	62	41	195	178					
Ljubljana (Slovenia)				43	48	22	102	177					
Sevilla (Spain)				32	55	31	223	157					
Torino (Italy)				303	107	260	277	235					
Kavala, Greece	n/a	38	0.2	240	48	0.1	77	571	175	Christoforidis and Stamatidis (2009)			
Moscow, Russia	n/a			2.0	4.3	79	59	19	37	208	Plyaskina and Ladonin (2009)		
Mexico City, Mexico	n/a				117	101	40	140	307	Morton-Bermea et al. (2009)			
Chicago, USA	n/a	20		11	71	150	0.64	36	395	397	Cannon and Horton (2009)		
Izmit, Turkey	n/a			0.23	17	34	37	39	35	72	Canbay et al. (2010)		
Trondheim, Norway	(Survey 2004)	4	0.19	65	39	0.15	45	81	112	Anderson et al. (2010)			

(continued)

Table 6.7 (continued)

Location	Soil usage	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Sb	V	Zn	Reference
	(Survey 1994)	3	0.24		73	42	0.21	48	52			151	
Sialkot, Pakistan	n/a		46	36	107	19		83	122			78	Malik et al. (2010)
Islamabd, Pakistan	n/a		3.5	17		18		91	208			1643	Ali and Malik (2011)
Torino, Italy	parks				116	57		127	57			106	Sialelli et al. (2011)
	road soils				464	202		415	454			275	
China, 21 cities	n/a	12	0.39	14	69	40	0.31	25	55			109	Luo et al. (2012)
Estarreja, Portugal	n/a	10	0.26		15	28			35			59	Cachada et al. (2012)
Rome	Parks					107		48	417			220	Calace et al. (2012)
Ghaziabad, India	n/a		0.40		288	122		147	147			187	Chabukhara and Nema (2013)
Tianjin, China	n/a		1.01		96.4	41.7		34.0	30.8			199	Wu et al. (2013)
Las Tunas, Cuba	n/a			14	97	94		35	42			277	Diaz Rizzo et al. (2013)
Guangzhou, China	n/a		0.23		22.4	41.6		11.1	65.4				Quan et al. (2013)

Table 6.8 PGEs released from various catalysts in different operative conditions

Catalyst model	Operative condition test	Emissions rate	References
Pellet type	48 km h ⁻¹ 96 km h ⁻¹	Pt: 1.2 µg km ⁻¹ Pt: 1.9 µg km ⁻¹	Hill e Mayer (1977)
Monolith type	Engine at the lowest r.p.m.	Pt :67 ng m ⁻³	Rosner and Hertel (1986)
Monolith type	80 km h ⁻¹ (new catalyst) 80 km h ⁻¹ (old catalyst) 130 km h ⁻¹ (new catalyst) 130 km h ⁻¹ (old catalyst)	Pt: 12 ng km ⁻¹ Pt: 9 ng km ⁻¹ Pt: 90 ng km ⁻¹ Pt: 18 ng km ⁻¹	Artlet et al. (1999)
Pt/Pd/Rh, Pd/Rh catalysers (18,000 km)	Test at constant speed (80 km h ⁻¹) Standard test drive	Pt: 6.3–7.5 ng km ⁻¹ Pd: 1.2–1.9 ng km ⁻¹ Rh: 0.6–1.2 ng km ⁻¹ Pt: 11–58 ng km ⁻¹ Pd: 2–24 ng km ⁻¹ Rh: 1.5–7 ng km ⁻¹	Moldovan et al. (1999)
Pt/Pd/Rh catalysers Pd/Rh	Gasoline	Pt: 27–313 ng km ⁻¹ Pd: 6–108 ng km ⁻¹ Rh: 8–60 ng km ⁻¹	
Monolith type	Diesel Gasoline	Pt: 47–170 ng km ⁻¹ Pt: 10.2 ng km ⁻¹ Pd: 14.2 ng km ⁻¹ Rh: 2.6 ng km ⁻¹	Rauch et al. (2002)
	Diesel	Pt: 223 ng km ⁻¹ Pd: 75.8 ng km ⁻¹ Rh: 33.7 ng km ⁻¹	

Table 6.9 PGEs levels in two European auto catalysers adopted before 2004

Catalyst type	Pt µg g ⁻¹	Pd µg g ⁻¹	Rh µg g ⁻¹
Ceramic-based	990 ± 21	307 ± 3	218 ± 2
Metallic-based	2,424 ± 89	16 ± 1	567 ± 2

while Pd and Rh are also potentially carcinogenic elements (Leikin and Paloucek 1995). However, Pt has been used as an anti-cancer drug, while Pd chloride has been employed for the treatment of tuberculosis without too many side effects.

PGEs released in the environment are mostly deposited on the roadsides. Available data on PGEs concentrations in urban environment in some world cities are reported in Table 6.10.

Since the size of a large amount of catalyst particles is <10 µm (referred to as PM10) health problems can arise from their direct inhalation of dust particles. The size fraction between 2.5 and 10 µm can easily reach the nose-pharynx region, while the size fraction <2.5 µm can reach the alveolar region.

The chemical transformations of PGEs, which can occur after their release in the environment, may increase their bioavailability, as for Pt⁺⁶ which is known to be a powerful oxidizing agent (Barefoot 1999).

Table 6.10 PGEs concentration levels in urban environment from some world cities (ng g^{-1})

Location	Pt	Pd	Rh	Matrix	Reference
San Diego, USA	100–600	38–280		Suburban road dust (high traffic)	Hodge and Stallard (1986)
	300	15–24		Road dust (resi- dential area)	
Germany	1,000	100	110	Road dust (high traffic)	Shäfer et al. (1996)
Rome, Italy	14.4–62.2	102–504	1.9–11.1	Urban road dust	Petrucci et al. (2000)
Austria	55–81	4–5.5	10–12	Tunnel dust from airshaft	Schramel et al. (2000)
Frankfurt, Germany	72	6	18	Highway soil	Zereini and Alt (2000)
	46	4	9	Urban soil	
Rome, Italy	0.8–6.3			Urban soil (1992)	Cinti et al. (2002)
	7.0–23.7			Urban soil (2001)	
Madrid, Spain	144–339		44–64	Road dust ($<63 \mu\text{m}$)	Gómez et al. (2002)
Honolulu, USA	15–160			Road dust	Sutherland (2003)
	2–160			Soil	
Accra, Ghana	39 \pm 24			Road dust	Kylander et al. (2003)
	15 \pm 5.3			Road side soil	
Perth, Australia	8.8–91	58–440	53–419	Road dust	Whiteley and Mur- ray (2003)
	3.5–27	13.8–108	31–107	Road side soil	
Naples, Italy	4.2 \pm 6.5	12.7 \pm 13.2		Urban soil	Cicchella et al. (2003)
London, UK	4.6–356.2			Road dust ($<75 \mu\text{m}$)	Ward and Dudding (2004)
Austria	1–134	0.79–21.2	.17–13.2	Soil	Fritsche and Meisel (2004)
Białystok, Poland	111 \pm 13	42 \pm 1	19.7 \pm 2.7	Road dust	Lesniewska et al. (2004)
	23.3 \pm 3.8	23.9 \pm 1.2	6.76 \pm 1.3	($<75 \mu\text{m}$)Tunnel dust	
Perth, Australia	20.5–419	19.8–440	3.7–91.4	Road dust ($<63 \mu\text{m}$)	Whiteley (2005)
	13.9–153	9.4–100	1.2–26.6	Soil	
São Paulo, Brasil	0.3–17	1.1–58	0.07–8.2	Road soil (high traffic)	Morcelli et al. (2005)
Seoul, Korea	0.4÷444			Soil and Road dust	Lee et al. (2006b)
Athens, Greece	127÷54.5	112÷52.8		Road side soil	Riga-Karandinos et al. (2006)
Sheffield, UK	8–606	8–1,050		Road side soil	Jackson et al. (2007)
	27–408	26–453		Road dust	
Beijing, China	4–356	0.1–125	2.7–97	Road dust	Wang et al. (2007)
Germany	50.4	43.3	10.7	Road side soil	Wichmann et al. (2007)
Beijing, China	7.60–126	3.38–57.5	.97–31.4	Urban soil	Pan et al. (2009)
	6.56 90.9	6.68–120	1.99–31.7		

(continued)

Table 6.10 (continued)

Location	Pt	Pd	Rh	Matrix	Reference
Guangzhou, China					
Hong Kong	15.4–160	6.93–107	1.61–34.5		
Macao, China	3.58–21.9	2.01–27.3	0.44–5.63		
Qingdao, China	3.72–9.72	3.26–13.4	1.00–2.88		
Mumbai, India	3.20–9.40	1.32–42.4	0.24–1.36		
Calcutta, India	2.59–9.43	1.31–4.07	0.40–2.27		
Hyderabad, India	1.5–43	1.2–58	0.2–14.2	Road dust	Mathur et al. (2011)
Palermo, Italy	0.6–2,240 0.3–16			Upper urban soil Lower urban soil	Orecchio and Amorello (2011)
Prague- Ostrava, Czech Rep.	<0.7–7.7	<0.45–50.0	<0.08– 3.86	Urban park	Mihaljevič et al. (2013)

Data on body fluids among the occupationally exposed population, e.g. PGE manufacturing workers, or among the population exposed to road traffic, show levels of Pt ranging between 150 and 450 mg L⁻¹ (Kalavrouziotis and Koukoulakis 2009), while the normal levels fall in the range from 0.1 to 2.8 µg L⁻¹. Merget and Rosner (2001) reported that halogenated platinum salts act as sensitizing substances causing asthma, rhinoconjunctivitis and contact urticaria in the exposed population.

Recent studies on the effects of PGE-graded salts on the human health suggest that these compounds foster lymphocyte proliferation and cytokine release while, in addition, speciation influences their immune capacity. Chemical and biological interactions among trace elements and PGEs may affect their absorption and metabolism resulting in modified toxic effects. Correlations between Pt and Pd blood and serum concentrations suggest this kind of interaction (Barany et al. 2002).

It is generally accepted that, similarly to Cd and Cr, also Pt²⁺, Pt⁵⁺ and Pd²⁺ give rise to toxic effects on cellular level, but with much worse damages than in the case of Cd. A lower toxic potential is reported for Rh (Krug et al. 2006; Nel et al. 2006).

According to Boscolo et al. 2004, in vitro activity of Pd compounds is higher than that of other PGE salts. This experimental result agrees with the increment of sensitization and allergenic contact dermatitis in relation to the increase of Pd levels in the urban population. In addition, as reported by Paolucci et al. (2007), PGEs can amplify the immune response to allergens while Linnett and Hughes (1999) report that PGE risk assessment could be based on the results of respiratory sensitizing potential of halogenated Pt salts.

6 Pt and PGE in Italian Urban Environment: A Case Study

With the aim to determine Pt background levels and the Pt time dependent accumulation factor in Italian urban and 'natural' soils, since 1992 a sampling campaign was carried out in some Italian cities. Globally, two hundred eight soil samples were collected from selected sites in the urban areas of Rome, Naples, Palermo and Padua, taking into account traffic intensity, pollution source distance, green areas extension, number of inhabitants and morphology. Soil parent materials were selected in order to be really representative of Italian geological setting and variability.

Preliminary results evidence that Pt concentration levels in urban soils are, in some cases, slightly higher than the average level in Italian "natural" soils. Moreover, a comparison between data from samples collected in 1992 and data from 2001 campaign, shows a slight but analytically significant increase of Pt, paralleling a Pb level decrease, clearly related to the large introduction of unleaded fuel.

In some cases, Pt in urban soils resulted to be slightly higher than the background concentration of Italian 'natural soils' ($3.1 \pm 2.1 \text{ ng g}^{-1}$), developed mainly on sedimentary and volcanic rocks. As a general consideration, soils deriving from limestone rocks evidence a wide concentration range for Pt ($<1\text{--}6 \text{ ng g}^{-1}$), reflecting the variable contents of insoluble residue of these rocks.

No data on Pd and Rh levels in natural soils and related parent materials are reported for Latium (central Italy) because all concentrations were below the detection limit.

The Pt levels in various soil materials from Latium are plotted in Fig. 6.1 while the variation of the Pt levels in different environmental condition in Latium and Rome are reported in Fig. 6.2.

As a general consideration, Pt concentrations in the studied samples are higher in the dumped soils collected close to the main traffic roads (mean 10, max 13.8 ng g^{-1}), compared to the relatively undisturbed soils. Top soils are enriched in Pt, compared to bottom soils, confirming the explanation of a recent deposition of atmospheric particulate matter containing Pt particles emitted from vehicle exhaust.

While grain-size distribution generally affects PHEs (generally the Pb, Zn, Cd and Hg content increases with decreasing soil grain size), no significant relation was observed for Pt. This could be related to the low Pt concentration in soils which, at the present time, does not allow a clear discrimination between the background Pt levels and the contribution of Pt particles of size 5–10 μm released by vehicle catalysts. Moreover, it has been observed that Pt associated to particular matter is generally not readily mobilized, but redistributed in the various grain size fractions of soils (Fig. 6.3).

Similar data on Pt in urban soils have been reported by Cichella et al. (2003, 2008) in a study on PGEs in soils from urban areas of the Campania region, southern Italy, along with data on Pd and Rh. The authors also discuss on the relationship between high population density and traffic, and PGE levels in soils. Data on Pt distribution in Palermo urban soils (Sicily) have been discussed by

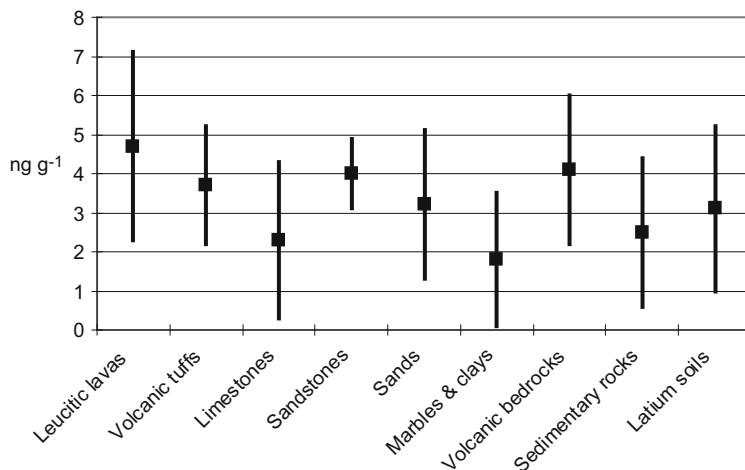


Fig. 6.1 Platinum in different soil parent materials from Latium, Central Italy

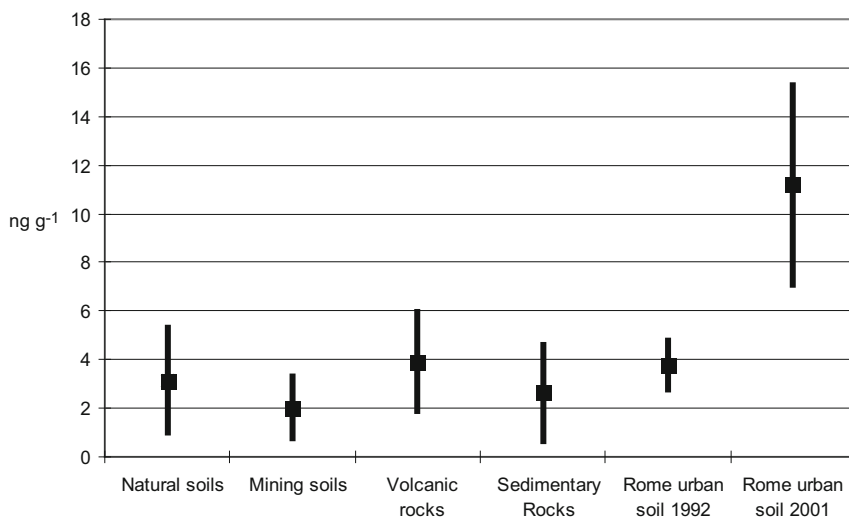


Fig. 6.2 Comparison of Pt levels in different matrices in the Latium Region and Rome (Italy)

Orecchio and Amorello (2010, 2011), while interesting data on Pt and Pd in pine needles from Palermo urban area have been reported by Dongarra et al. 2003. A data collection of PGE in urban soils from some Italian cities is reported in Table 6.11.

Among the various particulate fractions emitted, the most abundant fraction ($>10 \mu\text{m}$) falls down and settle on the road-side within a few hours. The smaller particles ($<10 \mu\text{m}$) can remain in suspension even for several days while the smallest may be transported over long distances. As a consequence PGE accumulation in soils alters their natural geochemical background, which is very low,

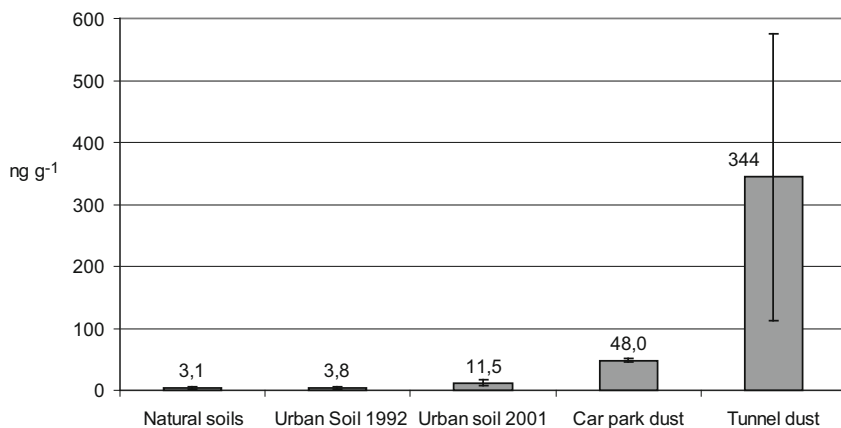


Fig. 6.3 Differences in Pt concentration in urban matrices in Rome, Italy

Table 6.11 PGEs in urban soils in some Italian cities (ng g⁻¹)

City	Element	Mean	Median	Min.	Max.	Reference
Padova	Pt	1.4 ± 1.3	0.9	0.1	5.7	Cinti et al. (2002)
Rome	Pt	11.5 ± 4.7	10.6	7.0	19.4	
Viterbo	Pt	10.3 ± 3.6	9.6	4.9	20.0	
Naples	Pt	8.5 ± 2.5	8.4	4.7	14.3	
Palermo	Pt	1.0 ± 0.9	0.7	0.2	3.9	
Latium natural soils	Pt	3.1 ± 2.1	2.9	<1.0	5.0	Cinti et al. (2002)
Avellino	Pt	2.4 ± 1	2.1	1	6.1	Cicchella et al. (2008)
	Pd	2.2 ± 6.4	1.0 <0.05	<.5	38	
	Rh	<.06 ± .13		<.05	0.61	
Benevento	Pt	2 ± 3.3	1.0	0.4	18.4	
	Pd	1.5 ± 1.8	0.9	<0.5		
	Rh	<.05 ± .09	< 0.05	<0.05	8.7	
Salerno	Pt	13.1	2.1	<0.1	278	
	Pd	15.3	2.4		432	
	Rh	1.79	0.28	<0.5	47	
Palermo	Pt (range)			0.3	2,240	Orecchio and Amorello (2011)

usually in the order of few ng g⁻¹ (Cinti et al. 2002). Winds and run-off waters can disperse and redistribute the top soil and dust PGE enriched particles at a considerable distance from their original source. (Barbante et al. 2001; Rauch et al. 2005).

Owing to transport modality in urban environment, road dusts are particularly enriched in PGEs, in fact their concentrations reach levels of one or more orders of magnitude higher compared to the levels of urban soils. As a consequence, dust is

Table 6.12 PGEs in tunnel and road dusts in some Italian cities (ng g^{-1})

City	Matrix	Pt	Rh	Pd	Reference
Naples	Tunnel dust	533 ± 564	73 ± 39	n/a	Angelone et al. (2007)
	Road dust	133 ± 106	$23 \pm 10,3$	n/a	
Rome	Tunnel dust	344 ± 232	69 ± 49	563 ± 244	
	Road dust	$44.3 \pm 6,3$	n/a	n/a	
Viterbo	Road dust	110 ± 26	n/a	n/a	

n/a, data non available

the most polluted matrix in the urban areas. Data on PGEs in urban soils and dusts from some Italian cities are reported in Tables 6.11 and 6.12.

The large standard deviation shows a great lack of homogeneity for the analyzed samples, which may be related to traffic conditions, roads morphology, wind direction, and presence of barriers. However, the data are generally in agreement with those reported in the literature (Ravindra et al. 2004).

7 Conclusions

Since ancient times, human activities have poured large amounts of hazardous substances into the environment, but issues related to urban environment pollution have started to gain attention only in the 60s. In the last 25 years we have witnessed a rapid expansion of urban and industrial areas without any control of the sources of contamination and with absolute lack of policies or regulations.

In natural conditions most of the PHEs are present at low concentration levels in soil. However, pollutant emissions due to human activity have become predominant compared to natural emissions. This fact is particularly evident when we consider the releases of some PHEs into the atmosphere due to, for example, mining activities or fossil material combustion. In addition to the consequences concerning strictly the environment, increased PHE levels have also affected the population health, especially in urban areas, where higher incidence of diseases related to an excessive presence of PHEs (e.g. Pb, Cd, Ni, As and Hg) is recorded. Moreover, until the mid-90s of the last century, the long-term negative effects of urban pollution on biota have been neglected. Nowadays, toxicological studies help us understand the potential effects of PHEs on the human and environmental health. The role of relatively recent industrial components, such as PGEs and REEs, is also considered, since there is a high concern about their impact on human health.

From the geological point of view, the research approach has hanged lately in order to better understand the complexity of the urban environment. While geochemical early studies involved only individual elements, a gradual tendency towards a multi-element approach can be now observed. This includes studies on the spatial distribution and interaction among different environments, which were

made possible by the availability of recent technological innovations in the field of environmental analysis.

It is evident that, in urban environment, the vehicular traffic is still one of the most significant sources of contamination. Although the replacement of the gasoline Pb with alternative additives in new catalytic devices, which use high quantity of REEs, PGEs and Mn, has caused a substantial reduction of Pb in urban areas, it has also led to the introduction of previously unknown compounds and particles into the environment. The PHE potential hazard to humans is mainly related to their very fine dimensions and their consequent chemical-physical properties. Besides, their interactions with the biota are yet to be understood fully. The increasing frequency of respiratory diseases in the urban population, in particular among children and workers, is a clear evidence of the effect of the exposure to PHEs in urban road dusts.

Because the urban environment is the preeminent habitat for humans at the present time, a comprehensive assessment of urban soil resources and quality planning should be considered as a priority, in order to balance the effects of anthropic pollution. An harmonized assessment and comprehensive understanding of the legacy of PHEs in urban environment is the next challenge in order to create a sound platform for a sustainable management of urban areas along with the constraint of negative health consequences.

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