Chapter 19
Heavy Metals in Soils Under the Heel of Heavy Industry

Georgii Lysychenko, Iryna Kuraieva, Anatolij Samchuk, Viacheslav Manichev, Yuliia Voitiuk and Oleksandra Matvienko

Abstract The soils of urban agglomerations dominated by heavy industry exhibit specific geochemical behaviour. New data are presented on total and mobile forms of heavy metals in soils contaminated by steelworks and chemical plants in different parts of Ukraine. The distribution of heavy metals in technogenic soils and the soil geochemical factors influencing the mobility of heavy metals and the mobile forms of metals in soil solution are assessed, and biogeochemical indices of polluted areas are determined. Heavy metal concentrations in soils of polluted areas are tens or hundreds of times higher than background values and maximum allowable concentrations, the soils' buffer capacity is much diminished, and the mobility of heavy metals is increased. Microscopic fungi may be a supplementary criterion for ecological and geochemical studies.

Keywords Heavy metals · Geochemical distribution · Forms of occurrence · Biogeochemical indices

Introduction

Soil is a unique natural resource, the font of terrestrial life, and the original natural indicator of pollution. The degree and the character of soil contamination by heavy metals are of special interest in the field of environmental geochemistry—which embraces the role and significance of natural and technogenic geochemical fields, processes and phenomena in the formation and evolution of life on Earth, and the

G. Lysychenko (✉) · V. Manichev
Department of Ecological Safety Problems, Institute of Environmental Geochemistry, Kyiv, Ukraine
e-mail: lysychenko@ukr.net

I. Kuraieva · A. Samchuk · Y. Voitiuk · O. Matvienko
Department of Geochemistry of Anthropogenic Metals and Analytical Chemistry, Semenenko Institute of Geochemistry, Mineralogy and Ore Formation, NAS Ukraine, 34a Palladina Av, Kyiv-142 03680, Ukraine

D. Dent and Y. Dmytruk (eds.), *Soil Science Working for a Living*,
DOI 10.1007/978-3-319-45417-7_19

functioning of the biota, including the influence of anthropogenic factors on ecosystems (Kuraieva et al. 2009). Here we investigate the distribution and geochemical behaviour of heavy metals in soils of Ukraine subjected to the impact of heavy industries. Contamination with heavy metals diminishes the activity of microorganisms and the ecological condition of soils (Kashin 2013). Although there is a considerable Russian and Ukrainian literature (Bondarenko 2011; Dolin 2011; Glazovskaya 1990; Il'in 1997; Mitskevich 1971; Saet et al. 1989; Samchuk et al. 1993, 1998; Vodyanitsky et al. 2012; Zhovinsky 2002), research on the geochemical component of technogenic pollution of soils is increasingly urgent.

Materials and Methods

Study Area

Research was carried out in eastern and northeastern Ukraine on soils under the influence of heavy industries: the steel industry in Mariupol, Alchevsk, and Dniprodzerzhyns'k, and the surrounding areas (the village of Melekine, the Streltsovskaya Steppe, and Dnyprovsko-Orylsky Nature Reserve); and the chemical industry in Shostka and surrounding areas (the Bogdanivsky reserve, and the villages of Obrazhiyivka and Lazarevka).

Field and Laboratory Methods

For each location, one large bulk sample was taken from various soils common in the urban areas. Sampling was stratified in 0–5 and 5–10 cm layers. In the laboratory, the samples were air-dried, crushed with a wooden rolling pin, and screened through a 2 mm steel sieve. Arinushkina's methodology was used to determine the soils' physical and chemical properties (Arinushkina 1970). Subsamples were finely ground in an agate mill and dissolved in concentrated HCl and HNO_3 (3:1) in a microwave system. The total content of heavy metals was assessed by ICP-AES using a PerkinElmer Optima 3200RL instrument. Mobile forms of heavy metals were determined following Pavlotskaya (1974). Statistical analysis was performed using the MS Excel package and maps drawn with the MapInfo program.

Results and Discussion

Soil Chemical and Physical Properties

We have studied both industrially contaminated soils and the soils of surrounding areas (Table 19.1). Soil organic carbon (C_{org}), pH, and the content of adsorbed

Table 19.1 Physicochemical properties of topsoils in contaminated areas and background values

Location of soil samples	C_{org} (mg/kg)	pH	Exchangeable cations * meq/100 g					
			H^+	Ca^{2+}	Mg^{2+}	K^+	Na^+	CEC
Technogenic soils affected by the steel industry								
Mariupol area	4.7	7.7	7.2	2.3	1.2	0.1	1.0	11.8
Alchevsk area	4.5	7.2	7.3	2.4	1.1	0.1	1.1	12
Dniprodzerzhyns'k area	4.6	6.7	10.1	2.3	1.1	0.2	1.2	14.9
Soils of background areas								
Melekine village	6.4	7.4	8.4	38.2	13.0	0.6	0.5	60.7
Shooting Steppe nature reserve	4.8	6.6	5.8	28.2	12	0.3	0.4	46.7
Dnyprovsko-Orilskyy nature reserve	7.8	6.4	10.8	49.3	18.4	0.8	0.6	79.9
Technogenic soils under the influence of the chemical industry								
Chemical factory at Shostka	0.75	5.1	–	2.3	0.9	0.08	0.3	3.58
Zirka	0.96	4.8	–	1.9	0.7	0.1	0.4	3.1
Svema	0.83	4.9	–	1.7	0.6	–	0.3	2.6
Soils of background areas								
Bogdanivsky reserve	0.85	6.3	–	5	2	0.14	0.9	8.04
Obrazhiyivka village	1.42	6.5	–	12.3	0.7	0.1	0.68	13.78
Lazarevka village	1.61	6.4	–	2	1	–	0.57	3.57

cations all decrease in technogenically contaminated soil compared with the background values and, as noted in earlier papers (Zhovinskiy 2002; Kuraieva 2013, 2014), soil physical and chemical properties affect the distribution of heavy metals.

Total Content of Heavy Metals

The content of some heavy metals in samples of soil from the towns of Mariupol and Shostka is presented in Tables 19.2 and 19.3, respectively. Since the contents of metals are specific and depend on the soil parent material and the conditions of soil formation, pollution levels are measured by comparison with control samples that are taken as a background level. The gross concentrations of heavy metals in each of the studied areas are as much as an order of magnitude greater than the background values. Maximum concentrations are found in industrial areas of the cities; contaminants are distributed according to the wind rose.

Table 19.2 Total content of heavy metals in topsoils from steel towns, mg/kg

Element / Sample location	Ni	Cr	Cu	Pb	Co	Ag
Mariupol area, *n* = 39	$\frac{2100}{500}$	$\frac{204}{50}$	$\frac{308}{20}$	$\frac{184}{18}$	$\frac{9}{5}$	n.a.
Alchevsk area, *n* = 51	$\frac{59}{23}$	$\frac{140}{80}$	$\frac{73}{21}$	$\frac{101}{13}$	$\frac{6}{6}$	n.a.
Dniprodzerzhyns'k area, *n* = 36	$\frac{36}{20}$	$\frac{113}{50}$	$\frac{60}{20}$	$\frac{119}{12}$	$\frac{4}{3}$	n.a.

Note Above the line—total concentration of heavy metals in contaminated soils; below the line—background value; *n*—number of samples; n.a.—not analyzed

Table 19.3 Total content of heavy metals in topsoils of the town of Shostka, mg/kg

Element / Sample location	Ni	Cr	Cu	Pb	Co	Ag
Svema, *n* = 55	$\frac{250}{10}$	$\frac{140}{5}$	$\frac{60}{10}$	$\frac{55}{15}$	$\frac{15}{4}$	$\frac{10}{1}$
Zirka, *n* = 50	$\frac{85}{10}$	$\frac{60}{5}$	$\frac{300}{10}$	$\frac{130}{15}$	$\frac{6}{4}$	$\frac{5}{1}$
Shostka plant chemicals, *n* = 44	$\frac{25}{10}$	$\frac{20}{5}$	$\frac{210}{10}$	$\frac{40}{15}$	$\frac{4}{4}$	$\frac{5}{1}$

Note Above the line—total concentration of heavy metals in contaminated soils; below the line—background value; *n*—number of samples

Total Soil Contamination

The geochemical association of heavy metals in the topsoils of Mariupol comprises the following elements: $Pb_{14.4} > Cu_{8.8} > Zn_{5.3} > Cr_{4.3} > Mn_{3.5}$; and for Shostka: $Pb_{53} > Ni_{16} > Cr_{9} > Co_{5} > Ag_{4} > Cu_{2}$ (the numbers next to the elemental symbol represent concentration ratios).

For the two towns, total contamination index (Z_C) is determined by the method of Saet et al. (1989):

$$Z_C = \sum_{1}^{n} K_C - (n-1), \quad \text{where } K_C = \frac{C_i}{C_\Phi} \tag{19.1}$$

K_c—coefficient of concentration, *n*—number of accounted anomalous elements; C_i—concentration of the element in the investigated object, C_Φ—background content element.

For Mariupol, the total contamination index (Z_C) was calculated for the following elements: Mn, Ni, Co, V, Cr, Mo, Cu, Pb, Zn, and Sn. For the upper 5-cm layer, Z_C ranges from 3 to 581 with a mean of 38. Almost half of the city suffers dangerously high soil pollution ($Z_C > 32$); high concentrations of heavy metals are found not only around the steel works but also in residential areas. There are two anomalous areas with extremely dangerous levels of contamination ($Z_C > 128$)—one in the town centre and the other in the northwest part of the town. The least contaminated area is the southeastern part of town, upwind of the steel works. For the 5–10 cm soil layer, the contamination index 3–591 with a mean of 43; the 5–10 cm soil layer has a greater loading of heavy metals than the surface layer. Four areas of anomalously high and extremely dangerous level of contamination ($Z_C > 128$) were located: two in the central part of the town (northern Azovstal) and the other two in the west. About two-thirds of the town is characterized by high and dangerous pollution ($Z_C > 32$).

The total soil contamination of the soils in Shostka by Cr, Cu, Pb, Co, and Ag reaches a maximum in the vicinity of the industrial enterprises. The figure is 170 around the facility for production of hydroquinone (Shostka Plant Chemicals) compared with the average of 7; once again, pollution is attenuated downwind of the industrial plants.

Forms of Heavy Metals in Soils

Using Pavlotska's selective extraction, we separated exchangeable (ammonium acetate buffer), reserve and fixed forms of the heavy metals in the soils (Fig. 19.1).

The content of exchangeable forms of heavy metals in the measured soils decreases in the sequence (%): Zn (16.9–18.5) > Pb (5.2–10.6) > Ni (4.5–5.2) > Cu (1.8–3.4) > Cr (0.8–1.4). The share of reserve forms of heavy metals decreases in the sequence: Pb (55.2–57) > Cu (40.7–45.3) > Zn (31.6–39.2) > Ni (23.2–35.4) > Cr (16.9–19.1). Fixed forms of heavy metals decrease in the sequence Cr (79.4–82.3) > Ni (60.1–71.6) > Cu (51.3–57.5) > Zn (40.7–50.3) > Pb (32.4–39.6). In the background areas, the sequence of heavy metals

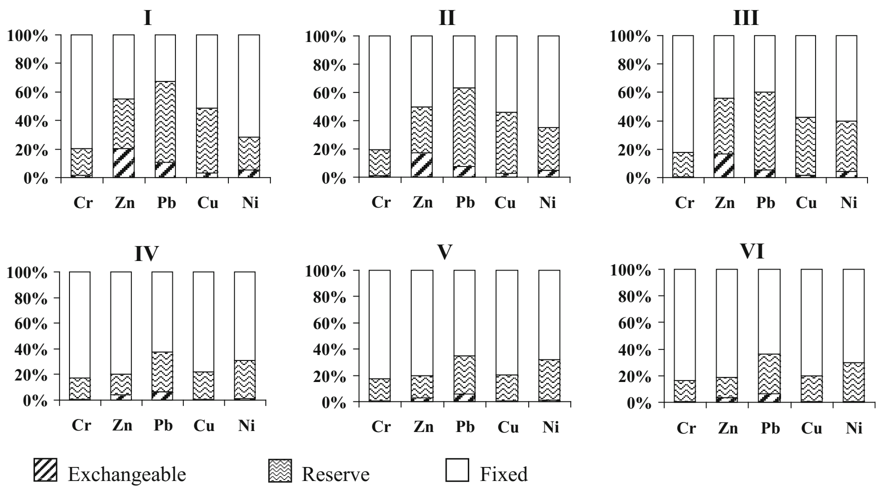

Fig. 19.1 Forms of heavy metals in soils (0–5 cm) around steelworks—**I** Mariupol, **II** Alchevsk, **III** Dniprodzerzhyns'k; and the surrounding areas—**IV** Melekine village, **V** Streltsovskaya Steppe reserve, **VI** Dnyprovsko-Orilsky reserve

content is (%): exchangeable—Pb (5.9–6.3) > Zn (3–4) > Ni (0.8–1.2) > Cr (0.7–0.8) > Cu (0.6–0.7); reserve—Pb (29–31.3) > Ni (29–31) > Cu (19–21.5) > Cr (16.4–17) > Zn (15–16.7); and the fixed form—Cr (82.8–83.4) > Zn (79.6–81.5) > Cu (77.8–80.2) > Ni (67.8–70.2) > Pb (62.5–65.1).

Using selective extractants, Samchuk et al. (1998) distinguished different forms of heavy metals in the soils around the Mariupol steelworks. The least amount of heavy metals occurred in water-soluble form (0.1–1%); in spite of the very high level of soil contamination, the concentration of heavy metals in aqueous solution is relatively low—exceeding the maximum permissible concentration only in the most contaminated spots. In the soils of background areas, most of the heavy metals are held firmly in the insoluble form.

In the town of Shostka (Fig. 19.2), the content of exchangeable forms of heavy metals decreases in the sequence %: Zn (25–62) > Pb (10–19) > Co (2–12) > Cu (5–10) > Ni (1–3) > Cr (0.04–4). The share of reserve forms decreases in the sequence %: Cu (25–75) > Co (17–51) > Zn (29 35) > Pb (28–71) > Ni (6–5) > Cr (1 7–22). The content of fixed forms decreases in the range: Cr (73–98) > Ni (73–91) > Co (48–72) > Cu (15–67) > Pb (20–53) > Zn (5–46). In the background areas, the sequence of the exchangeable form of heavy metals is (%)—Zn (10–28) > Cu (11–26) > Pb (12–19) > Co (1–3) > Ni (1–2) > Cr (0.4–2);

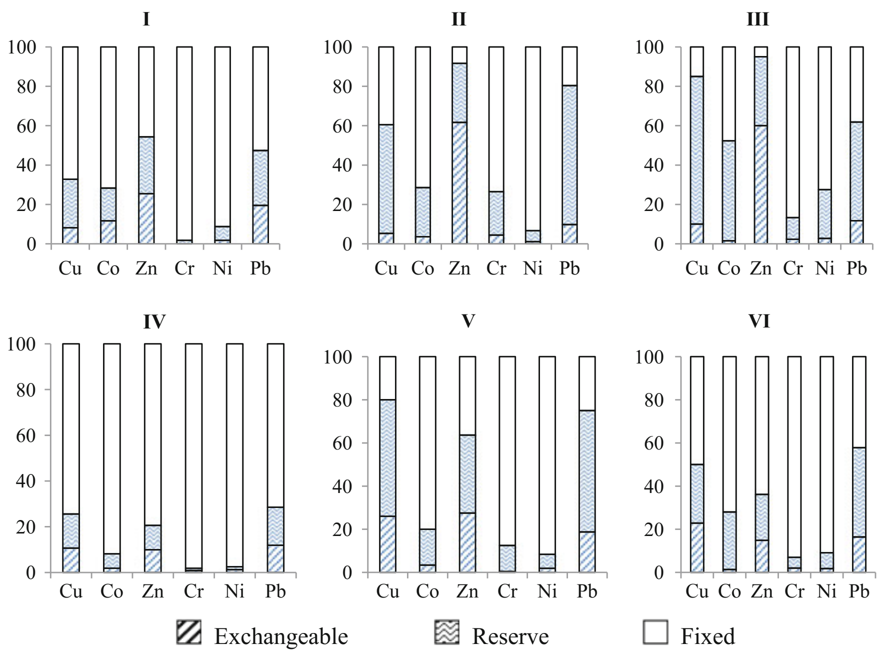

Fig. 19.2 Forms of heavy metals in soils affected by the chemical industry (0–5 cm)—**I** Svema, **II** Zirka, **III** Shostka plant chemicals; and surrounding areas—**IV** Bogdanivsky reserve, **V** Obrazhiyivka village, **VI** Lazarivka village

reserve form—Pb (17–56) > Cu (15–54) > Zn (11 36) > Co (6–27) > Cr (1–12) > Ni (1–6); and fixed form—Ni (91–98) > Cr (87–92) > Co (72–92) > Zn (36–79) > Cu (20–74) > Pb (25–71).

Soil Buffer Capacity

To investigate the buffering by soils impacted by the steel industry, we used Samchuk's method (1998) and, as a criterion for the quantitative assessment of ecological and geochemical stability of the soil solution, calculated the buffering coefficient K_b = CE/ΔpH (where CE is the capacity of the soil absorbing complex).

In both the Mariopol area and the Shostka area, technogenically contaminated areas have a lower buffer capacity than similar, uncontaminated soil landscapes (Table 19.4).

Soil Microbiology

Anthropogenic loading of heavy metals has a severe impact on ecosystems, leading to changes in the biota including, significantly, microscopic fungi. During the investigations of soil affected by the steel and chemical industries, 15 genera, 27 species, and 61 strains of microscopic fungi have been isolated and identified.

Table 19.4 Index of buffering of soils

Location of soil samples	K_b
Technogenic soils affected by the steel industry	
Mariupol area	4.2
Alchevsk area	4.8
Dniprodzerzhyns'k area	4.5
Soils of background areas	
Melekine village	55.2
Shooting Steppe nature reserve	28.8
Dnyprovsko-Orilskyy nature reserve	87.7
Technogenic soils affected by the chemical industry	
Shostka plant chemicals	3.6
Zirka	2.8
Svema	2.3
Soils of background areas	
Bogdanivsky reserve	11.8
Obrazhiyïvka village	10.5
Lazarivka village	11.5

In soil samples taken near the Azovstal Metallurgical Combine at Mariupol, the dominant fungi were *Mucor plumbeus*, *Aspergillus fumigatus*, and *Aspergillus flavus* (species not typical for background plots). The last two species are Group III pathogens able to produce mycotoxins dangerous to humans and animals. Soil samples taken near the Illich Steel and Iron Works at Mariupol were dominated by *Rhizopus stolonifer* and *Aspergillus niger; Aspergillus flavus* and *Aspergillus fumigatus* were also encountered.

Soil samples taken near the Svema plant at Shostka were dominated by *Penicillium spp.,* among them many species with high biochemical activity (*P. harzianum* Rifai, *P. Thomii* Maire, *P. Godlevsky* Zalessky, *P. decumbens* Thom) producing biologically active substances that are important for the national economy: enzymes, antibiotics, etc. Soil samples taken near Shostka Plant Chemicals were dominated by *Aspergillus sulphureus* Thom et Church*, Botrytis cinerea* Persoon ex Fries*, Chaetomium homopilatum* Omvik, dark-coloured *Cladosporium cladosporiodes*, and *Clonostacchis rosea*—all tolerant of extreme environmental conditions. We may conclude that certain sets of species of microorganisms may be sensitive indicators of soil contamination by heavy metals.

Conclusions

- Soil organic carbon, pH, and the content of adsorbed cations decrease in technogenically contaminated soil compared with background areas.
- The geochemical association of heavy metals in the topsoil of Shostka town, affected by the heavy chemicals industry, is represented by (%): Pb53 > Ni16 > Cr9 > Co5 > Ag4 > Cu2. The geochemical association of heavy metals in soils of Mariupol that are affected by the steel industry is represented by (%): Pb14 > Cu9 > Zn5 > Cr4 > Mn3.5.
- For areas affected by the steel industry, total pollution index (Z_C) is 3–581 with a mean of 38. The index for soils affected by the chemical industry at Shostka reaches 170 the industrial areas and diminishes to 2–3 at some distance from the industrial plants.
- Contamination of soil by the steel industry disturbs the natural form of heavy metals; in both *Chernozem* and *Sod podzolic soils* (*Albeluvisols*, IUSS WRB 2006; *Retisols*, WRB 2014), the incidence of mobile forms is increased. Their higher migration capacity is explained by an order of magnitude reduction in the buffering capacity of soils from emissions of anhydrides of strong acids.
- Some species of fungi are specific and may indicate concentrations of particular elements.

References

Arinushkina EV (1970) Manual of methods for soil chemical analysis. Moscow University Publishing House, Moscow (Russian)

Bondarenko GN (2011) Development of geochemistry technogenesis after the Chernobyl disaster. In: Scientific papers of the Institute of Environmental Geochemistry, vol 19. Kyiv, pp 19–40 (Russian)

Dolin VV (2011) Technogenic and ecological safety ecogeosystematics of the Bug Estuary in terms of heavy metal pollution. RAL-Poligrafiya, Kyiv-Nikolaev (Russian)

Glazovskaya MA (1990) Principles of soil classification of the danger of contamination by heavy metals. Biol Sci 9:38–52 (Russian)

Il'in VB (1997) Buffer properties of soil and the allowable level of pollution by heavy metals. Agrochemistry 11:65–70 (Russian)

IUSS WRB (2006/2014) World reference base for soil resources. World Soil Resources Reports 103/106, FAO, Rome

Kashin VK (2013) Features of accumulation of trace elements in oat grain in the Western Baikal. Agrochemistry 10:55–65 (Russian)

Kuraieva IV (2013) Forms of heavy metals in soils in Ukraine. In: Collected works UkrNDMI NANU, Kyiv, pp 331–339 (Ukrainian)

Kuraieva IV (2014) Forms of occurrence of heavy metals in technogenicaly contaminated soils affected by the steel industry (for example, the city of Alchevsk). Sci Pap Inst Environ Geochem 23:105–109 (Russian)

Kuraieva IV, Manichev VJ, Olishevskaja SV et al (2009) Biogeochemical indicators of soil in the area affected by the Kostyanetskiy lead-nickel plant. Mineral Mag 1:58–61 (Ukrainian)

Mitskevich BF (1971) Geochemical landscapes of the Ukrainian Shield. Naukova Dumka, Kiev (Russian)

Pavlotskaya FI (1974) Migration of radioactive products of global attacks on soils. Atomizdat, Moscow (Russian)

Saet YE, Revich BA, Yanin EP (1989) Environmental geochemistry. Nedra, Moscow (Russian)

Samchuk AI, Mitskevich BF, Sushchik YY, Shramarenko IF (1993) Mobile forms of heavy metals in the soils of the Kievskogo Poles'ya. Geol J 1:81–86 (Russian)

Samchuk AI, Bondarenko GN, Dolin VV et al (1998) Physico-chemical conditions of the mobile forms of toxic metals in soils. Mineral J 2:48–60 (Russian)

Vodyanitsky YN, Ladonin DV, Savichev AT (2012) Soil pollution by heavy metals. RASKhN, Moscow (Russian)

Zhovinsky EY (2002) Geochemistry of heavy metals in soils in Ukraine. Naukova Dumka, Kyiv (Russian)