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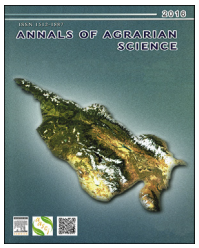

Standards for the contents of heavy metals in soils of some states

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ABSTRACT

In line with the present-day ecological and toxicological data obtained by Dutch ecologists, heavy metals/metalloids form the following succession according to their hazard degree in soils: Se > Tl > Sb > Cd > V > Hg > Ni > Cu > Cr > As > Ba. This sequence substantially differs from the succession of heavy elements presented in the general toxicological Russian GOST (State Norms and Standards), which considers As, Cd, Hg, Se, Pb, and Zn to be strongly hazardous elements, whereas Co, Ni, Mo, Sb, and Cr to be moderately hazardous. As compared to the Dutch general toxicological approach, the hazard of lead, zinc, and cobalt is lower in soils, and that of vanadium, antimony, and barium is higher in Russia. MPC must been adopted for strongly hazardous thallium, selenium, and vanadium in Russia.

Introduction

The soil chemistry distinguishes heavy metals as a special group of elements because of their toxic effect exerted on plants upon their high concentrations. However, there is no common opinion on the hazard degree of any particular heavy metal in soils. Only three heavy metals, i.e., Pb, Cd, and Hg, were men-tioned in the Global Monitoring Program adopted by the UN in 1973 (cited after [1]). Later, in the report delivered by the Executive Director of the UN Envi-ronmental Program (UNEP), seven other heavy metals (Cu, Sn, V, Cr, Mo, Co, and Ni) and three metalloids (Sb, As, and Se) were added to the list of the most hazardous elements [2].

These recommendations still form the basis for monitoring heavy elements in soils. The Ministry of Natural Resources and Ecology of the Russian Federation controls the total content of nine heavy metals in soils [3]. For some metals (V, Mn, Pb), maximum permissible concentrations (MPC) were adopted; for others (Cd, Cu, Ni, and Zn), approximate permissible concentrations (APC) were introduced; and, for the third group of metals that are not described by any standards (Co, Cr), the soil's contamination degree is estimated by the empiric criterion, i.e., a fourfold excess of the background values.

The Russian sanitary hygienic GOST 17.4.102–83 classifies As, Cd, Hg, Se, Pb, and Zn as highly hazardous elements, whereas Ni, Mo, Cu, and Sb as moderately hazardous ones [4]. This list of general toxicity is also applied for assessing the hazard of metals/metalloids in the soils despite the fact that it ignores the interaction between the pollutants and soil components, which leads to misinterpretation of their toxicity. Later, special attention was paid to six heavy elements in soils, i.e., Ni, Cu, Zn, Cd, Pb, and As; and APC criteria were developed for them (cited after [5].

In western countries worried about the environment condition, the development of standards is intensely promoted. The toxicity was assessed on the basis of the impact of heavy metals/metalloids on biological objects in soils and soil

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solutions. Dutch ecologists have generalized the research data on the toxicity of heavy metals/metalloids in soils.

The aim of this paper is to compare the Russian and the Dutch lists of hazardous metals/metalloids in soils and to attract attention to the most dangerous elements.

The group of heavy metals, case of Russia

The metals with their atomic mass heavier than 50 are scientists regarded as heavy metals usually [6]. However, the known lists of heavy metals are not precise. The number of heavy metals is not usually specified: the vague phrase "more than 40 chemical elements" is common [7]. Nevertheless, a list comprising 19 elements (Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Mo, Cd, Sn, Sb, Te, W, Hg, Tl, Pb, and Bi) is often cited [7]. This list of metals does not contain Ba, lanthanides, and actinides. In the later edition of textbook [8], only eleven elements are classified as the most typical contaminating heavy metals: Pb, Cd, Hg, Zn, Mo, Ni, Co, Sn, Ni, Cu, and V. It appears appropriate to add heavy metalloids (their former name was semimetals) to the group of heavy metals. Two of them, i.e., Sb and As, are included as hazardous metalloids on many lists of heavy elements. In this case, all the elements from V (atomic mass 50.9) to U (atomic mass 238) constitute the group of natural heavy metals and metalloids, except for halogens (the 17th group) and noble gases (the 18th group), which do not refer to heavy metals and metalloids. The transuranium elements were artificially obtained; therefore, we don't consider them. Thus, 57 elements form the group of heavy metals and metalloids.

Not all heavy elements entering soils as pollutants are similarly hazardous for plants, biota, and groundwater. At present, the general toxicological GOST operates in Russia, dividing heavy metals/metalloids into three classes by their hazard degree [4]. However, this versatile classification of elements does not take into account the specific features of the depositing environments; therefore, it appears to be more suitable for the air and water than for soils. Pollutants entering soil interact with its active phase (clay minerals, oxides and hydroxides of iron and manganese, and organic substance) and change their own activity either increasing or decreasing their hazard. Let us take Pb as an example. The high biological hazard of Pb is manifested in experiments with its salts. However, in soil, lead forms stable complex compounds with organic ligands, which become much less hazardous for living organisms than metal ions are [9]. In this case, the share of these complexes in the water extract can exceed 90% of the total lead content. As we show below, the lead hazard in soils is assessed now as low.

Assessment of heavy metals and metalloids toxicity in soils according to the Russian and Dutch criteria

Let us scrutinize the paper by Dutch ecologists [10] dealing with the standardization of the heavy metal/metalloid content in soils and sediments. The essence of this paper consists in the mathematical harmonization of a large number of experimental studies on the influence of heavy metals/metalloids on the biota and plants. The list of references includes 160 titles of publications. The maximum permissible addition (MPA) of the heavy metal/metalloid content in the soil is the key idea upon the standardization of the soil contamination. The MPA is calculated proceeding from the following condition:

$$\mathrm{MPA} = \mathrm{NOEC} : 10, \quad (1)$$

where the abbreviation NOEC stands for *no observed effect concentration*, i.e., the maximal concentration exerting no significant influence on the growth and reproduction of the test organisms. The Dutch ecologists took into account the influence of contaminated soils on soil fauna representatives (earthworms and arthropods), on the development of microbiological processes, and the response of plants. In addition, the biological effect of heavy elements passing into the solution (in laboratory experiments with suspensions) and into the ground and surface water (under natural conditions) was taken into consideration. Maximal permissible addition MPA of heavy metals and metalloids by the data of Dutch ecologists [10] is presents in Table 1.

Let us analyze the MPA values; they permit us to rank a large set (17) of heavy metals/metalloids and to distinguish the most hazardous among them in the soils. Let us compare the set of elements toxicity according to the general toxicological criterion with the set of their toxicity in soil according to the MPA value.

Hazard of metals/metalloids according to the Russian general toxicological standard and according to the standard for soil

The MPA values vary very widely, i.e., from 0.0061 mg/kg for a light metal Be (the most toxic element) to 253 mg/kg for Mo (the least toxic element). The wide range reflects the

Table 1 – Maximal permissible addition MPA of heavy metals and metalloids by the data of Dutch ecologists [10] in mg/kg.

Metal/metalloid	MPA
Beryllium (Be)	0.0061
Selenium (Se)	0.11
Thallium (Tl)	0.25
Antimony (Sb)	0.53
Cadmium (Cd)	0.76
Vanadium (V)	1.1
Mercury (Hg)	1.9
Nickel (Ni)	2.6
Copper (Cu)	3.5
Chromium (Cr)	3.8
Arsenic (As)	4.5
Barium (Ba)	9.0
Zinc (Zn)	16
Cobalt (Co)	24
Tin (Sn)	34
Lead (Pb)	55
Molybdenum (Mo)	253

Note: A dash stands for not determined.

difference in the hazard degree of the elements in the soils. For subdividing the elements by their hazard on the MPA basis, we refer the elements with MPA <1 mg/kg to the first class; the elements with 1 mg/kg < MPA <10 mg/kg, to the second class; and those with MPA >10 mg/kg, to the third class (Table 2). Above all, the absence of elements recognized as very hazardous in soils (beryllium and thallium) on the list of elements standardized in Russia stands out. At the same time, the hazard of Pb and Zn in the soils is not as high as in other media: they may be classified as the low dangerous third group according to the MPA values for the soil. This is also true for Mo, which may be moved from the second group of moderately dangerous substances to the low dangerous third group.

On the contrary, the hazard of the other elements in the soil appears to exceed the general toxicological level. For example, this is true for Sb, which has proved to be highly hazardous in soil. The first group of highly hazardous elements in the soil contains the light metal Be and the heavy metal Tl. The hazard of Ba and V is underestimated in soil; they should be referred to the second group of moderately hazardous elements.

Role of different toxicity of heavy metal for integration evaluating of soils contamination

Usually the soil contaminated not only pollutant, but several. Therefore, it is important to determine the total contamination of soil by heavy metals. To do this in Russia, Yu.E. Saet proposed a formula to count the total pollution of soil by heavy metals [11]:

$$Zc = \sum Kki - (n - 1), \quad (2)$$

where Kki is the coefficient of the concentration i-th element's; n – number of elements, as pollutants.

It is proposed critical values of total heavy metal pollution hazard. With Zc < 16 contamination is considered as non-dangerous; with 16 < Zc < 32 contamination is moderately dangerous; with 32 < Zc < 128 contamination is dangerous; with Zc > 128 contamination is extremely dangerous [11]. Formula (2) is widely used in Russia for the total characteristics of soil pollution by heavy metals.

But formula (2) does not take into account the differences in toxicity of heavy metals in soil. Meanwhile, the degree of toxicity (and hazard) of heavy elements is different. According to the Russian Standard - GOST 17.4.102–83—heavy metals and metalloids are specified into three classes of hazard: the first (high-hazard) class includes As, Cd, Hg, Se, Pb, and Zn; the second (medium-hazard) class contains B, Co, Ni, Mo, Cu, Sb, and Cr; and the third (low-hazard) class encompasses Ba, V, W, Mn, and Sr [4]. For the same values of the concentration coefficient Kk, the total contamination will apparently be more hazardous in the case when the most toxic elements belonging to the first group are accumulated in soils rather than the low-toxic elements of the third group. To introduce the appropriate corrections for the toxicity, the different elements should be given different weights in the equation according to their hazard group.

Before passing to correction coefficients, let us revise the list of hazardous elements of the first group. It does not contain chromium, which is classified as a medium-hazard element. Meanwhile, lately, particular attention is being paid to chromium because of its high biological activity and carcinogenicity [12]. Along with arsenic, the study chromium ranks first in the dataflow among other heavy metals and metalloids. It is necessity of moving Cr to the first hazard class.

Having introduced the correction coefficient for toxicity, the author suggested calculates the ecological index of the total contamination Zct according to the equation:

$$Zct = \sum (Kki \times Kti) - (n - 1), \quad (3)$$

where Kti is the coefficient of the i-th element's toxicity. Upon adopting the Kti coefficients, we proceeded from the necessity to preserve the schedule of the critical summary indices Zc proposed by Saet. To preserve it, the coefficient $Kt = 1.0$ should be assigned to the medium (second) hazard class elements in order to keep their input unchanged, a reducing coefficient ($Kt < 1$) should be given to the third hazard class elements, and a raising coefficient ($Kt > 1$) should be added to the first hazard class elements. The average value for the (0–1) interval was accepted for the chemical elements of the third hazard class, i.e., $Kt = 0.5$. For the elements of the first hazard class, the second-class coefficient was increased by 0.5, i.e., $Kk = 1.5$. The values of the element toxicity coefficients are listed in Table 2.

In the case when six elements are revealed in the geochemical anomaly grouped by two belonging to three different hazard classes, the total indices of the contamination (both the old one and the new one, which takes into consideration the toxicity coefficients) coincide. Since many heavy metals have not been distributed into hazard classes yet, we may temporarily take a neutral toxicity coefficient $Kt = 1.0$ for them.

As the first example, let us calculate the new index of the total soil contamination (with account for the toxicity) Zct of the natural geochemical anomalies in Altai region [13], where

Table 2 – Hazard of metals/metalloids according to the Russian general toxicological standard (cited after [4]) and according to the Dutch standards for soils [10].

Hazard class	Russia	The Dutch MPA for soils
1. Highly hazardous	0As, Cd, Hg, Se, Pb, Zn	<1: Be, Se, Tl, Sb, Cd
2. Moderately hazardous	Co, Ni, Mo, Cu, Sb, Cr	1–10: V, Hg, Ni, Cu, Cr, As, Ba
3. Low hazardous	Ba, V, W, Mn, Sr00	>10: Zn, Co, Sn, Ce, Pb, Mo00

Note: For the numbers, the dimension is in mg/kg.

the concentration of elements in the humus horizons was studied in three anomalies of the foothills and low mountains. One of the anomalies is developed over complex ores; the second, over chromium-containing serpentinites; and the third, over sulfide-containing effusive rocks. As is seen from Table 3, all the values of the new coefficient of the total contamination Zct have increased by 10–20 units as compared to Saet's index (Zc).

As the second example, let us calculate the indices of the total soil contamination in Ust-Kamenogorsk in Kazakhstan [14], where the technical impact is very strongly pronounced. As is seen from Table 4, all the values of the new total contamination index taking into account the elements' toxicity have increased as compared to the Saet index. This is due to the soil contamination with the most toxic elements referred to the first hazard class. The new index rose most significantly (by 100–300 units) in the zone of extremely hazardous contamination; it rose by only 20 units in the zone of hazardous contamination and by only 7–9 units in the zone of moderately hazardous contamination. Thus, the new ecological index of the total contamination permits us to distinguish the contaminated areas depending on the hazard of the individual pollutants.

Standards of mobile form contents of heavy metals in soils case of Russia

Gross content includes inert (usually silicate) form of heavy metals, which has no toxic effect on plants and soil biota. That is why mobile content, easily soluble (potentially toxic) compounds of heavy metals are normalized in Russia [7]. Practically, the hazard of heavy metals is assessed in Russia according to the MPC_{mob} criterion for mobile compounds soluble in an acetate–ammonium buffering solution with pH 4.8.

Such standards were proposed for the five elements (mg/kg): copper – 3, nickel – 4, cobalt – 5, chromium – 6, zinc – 23. They as gross content are used also for characteristics of soil pollution by heavy metals [7].

But this does not take into account the important fact: dependency of content mobile iron compounds from the weather conditions at the time of the selection of soil samples. Turn to extended analysis (for 11 years), M.G. Opekunova the mobile forms of heavy metals in background territories in Bashkir Trans-Ural, Russia [15]. Repeat her table by adding the values of the coefficient of variation (V) of the contents for mobile forms of heavy metals (Table 5).

As you can see, variation by year of mobile forms of heavy metals is very considerably: from 45% (Mn), up 188% (Cd). Variation depends on weather conditions and, above all, rainfall and soil moisture, so for years at the same venues there are significant differences in the concentration of mobile forms of heavy metals [15]. Such a strong variation in the contents of mobile forms of heavy metals is due to the activities of soil organisms, rhythmic changes acquisitions chemical elements by plants and other factors.

Simple correlation analysis can reveal some features of heavy metals varying by year. To do this, let us calculate correlation coefficients (r) of heavy metals with macro elements: Fe and Mn. Mobility of these metals is increasing when humidity increase the reducing of (hydr)oxides of Fe and Mn and metals are moving into the solution. Manganese oxides are reduced under light reduction of redox potential E_H than Fe-hydroxides; this explains the higher mobility of the Mn than Fe. Most heavy metals mobility change (zinc, nickel, lead, cobalt) stronger correlate with change of manganese mobility than iron mobility: $r(Zn–Mn) = 0.65^*$ but $r(Zn–Fe) = 0.40$; $r(Ni–Mn) = 0.83^*$ but $r(Ni–Fe) = 0.45$; $r(Pb–Mn) = 0.47$, but $r(Pb–Fe) = 0.27$; $r(Co–Mn) = 0.43$, but $r(Co–Fe) = 0.09$. Probably at humidifying the microorganisms are activated and heavy metals are released in sync with reductions of oxides of manganese, which requires only a small reduction in yen less than the reduction of ferric hydroxide.

To use motile forms of heavy metals for soil contamination assessment, obviously, should standardize the procedure for selection of a soil sample. It is necessary to come to an agreement, in what period of time you want to selection of a soil sample. Probably best to selection of a soil sample in spring when soil moisture is maximal and slightly varies from year to year, rather than in the summer, when humidity varies strongly and during the season and from year to year.

Toxic metals in the soils, requiring the monitoring

Let us discuss in more detail those elements whose hazard in the soils is underestimated.

Table 3 – The concentration coefficients Kk for the heavy metals and metalloids in the natural geochemical anomalies of Altai region according to [13] and the indices of the total soil contamination: Zc, the Saet index and Zct, the index taking into account the toxicity of the elements.

Contamination	Horizon	Coefficients of the element concentration (in brackets)	Zc	Zct
Soils on complex ores				
Moderately hazardous	Asod	Zn(11.4) Pb(9.7) Cr(8.5) Cu(4.0) Cd(2.5) Mn(2.1)	29	49
	A	Cd(16.9) Zn(10.8) Pb(8.0) Cu(4.9)	38	55
Soils on Cr-containing serpentinites				
Hazardous	Asod	Ni(24.0) Cr(17.8) Co(7.4) Zn(2.8) Mn(2.2)	50	72
	A	Ni(26.7) Cr(23.0) Co(9.5) Mn(2.8) Zn(2.7)	62	88
Soils on sulfide effusive rocks				
Moderately hazardous	Asod	Cd(12.3) Zn(3.9) Cr(3.8) Co(2.3) Cu(2.0)	21	30
	A	Cd(29.1) Cr(3.3) Zn(2.0) Co(2.0) Ni(2.0)	34	52
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Table 4 – The concentration coefficients Kk for the heavy metals and metalloids in the technogenically contaminated soils in Ust-Kamenogorsk, Kazakhstan according to [14] and the indices of the total soil contamination.

Contamination	Horizon	Coefficients of the element concentration (in brackets)	Zc	Zct
Extremely hazardous	1990–1992	Sb(624) Pb(406) Ag(189) As(100) Cd(62) Zn(49) Cu(42) Sn(38) Bi(21) Hg(8) Mo(3) Ba(2)	1533	1844
	2004	Pb(70) Sb(53) Zn(32) Cd(31) Ag(17) As(9) Bi(9) Cu(8) Hg(6) Sn(3) Ba(2)	230	303
Hazardous	1990–1992	Pb(16) Hg(15) Cd(11) Zn(8) Ag(8) Cu(3) Sb(3) Sn(2)	59	84
	2004	Pb(18) Sb(11)Zn(11) Cd(11) Ag(9) Bi(3) Cu(2) Ba(2) Sn(2) Hg(2)	62	82
Moderately hazardous	1990–1992	Hg(8) Pb(7) Zn(3) Ag(4) Cu(2) Sn(2)	23	30
	2004	Ag(10) Pb(9) Zn(6) Cd(2) Sn(1.5)	24.5	33
Permissible	1990–1992	Pb(4) Zn(3) Ag(2) Cu(2) Hg(2)	9	13.5
	2004	Pb(4) Zn(2) Ag(2) Sn(1.5)	6.5	9.5

Table 5 – *The contents of mobile heavy metals (mg/kg) and their variations V* (according to Opekunova [15]).

Year	Fe	Cu	Zn	Mn	Pb	Ni	Cd	Co
1999	00.29	1.8	2.6	23.7	0.2	0.1	0.01	0.10
2000	06.00	0.1	7.6	28.3	0.1	0.1	0.01	0.10
2001	07.40	0.5	7.6	52.1	0.4	0.7	0.70	0.10
2002	16.3	0.6	6.6	50.8	1.6	0.6	0.10	0.30
2003	18.0	0.7	5.8	48.0	0.9	0.5	0.20	0.20
2004	05.90	0.2	5.5	42.8	0.8	0.1	0.03	0.20
2005	15.20	1.0	8.1	29.1	2.0	0.3	0.03	0.10
2006	03.71	0.2	7.0	71.1	2.1	0.7	0.07	0.28
2007	02.20	1.5	6.3	19.6	3.1	0.3	0.03	0.01
2009	17.0	1.3	21.40	73.7	4.7	1.6	0.08	0.01
2010	11.8	0.4	0.6	23.5	<0.02	<0.015	<0.12	<0.01
V, %	6800	7600	7300	4500	101,000	9800	188,000	8100

Thallium ranks 58th among the elements in the earth's crust with its clarke being 0.7 mg/kg [16]. It is regarded to be a very dangerous metal [17], more dangerous than mercury [18]. This is proved by its lower MPA value - 0.25 and 1.9 mg/kg for thallium and mercury, respectively—although there is no MPC/APC for Tl in soils.

Thallium inhibits the germination of seeds, chlorophyll formation, and the operation of many enzymes. Its ionic radius is close to that of K^+; as a result, Tl^+ replaces potassium in metabolism processes. Thallium is very mobile in soils; its availability for plants depends on its total content in the soil and on the form of its compounds [17]. The content of Tl in plants usually reaches (and often even exceeds) half of its total content in the soil [17]. The coefficient of the biological consumption of Tl reaches 80 in acidic soils with a low content of organic matter. Thallium is toxic for organisms in both its oxidation forms (Tl^+ and Tl^{3+}), and its toxicity is comparable to that of Cd and Hg.

Vast provinces with a positive thallium anomaly have been revealed, i.e., soils almost everywhere in France are enriched in thallium (they contain 1.51 mg Tl/kg on the average) [19]. The zonal soils of the Russian Plain contain 0.4–0.6 mg Tl/kg [20]. In the south of Western Siberia, the average content of thallium in the soils is much higher, namely, 2.8 mg/kg [21]. This territory represents a positive geochemical anomaly. In the center of the population's intoxication with thallium in Western Ukraine, the concentration of this metal reached 20–130 mg Tl/kg in the soot of brickwork chimneys [22].

Vanadium ranks 19th among the earth's crust elements with its clarke being equal to 136 mg/kg [16]. It is referred to the hazardous heavy elements in soils [22]. Vanadium mainly forms anionic complexes; however, these complexes are neutral and cationic in an acidic environment. This difference in charge results in the widely varying chemical properties of the metal. In acidic soils, the vanadyl cation VO_2, is more stable; it is firmly fixed by humus. More vanadium is fixed in stable humic acids than in fulvic acids. The situation becomes more dangerous in a neutral medium.

The vanadate anion VO^-_3, predominates there and becomes more mobile and toxic for plants and biota [22]. Let us specify that the vanadium hazard is higher in the cities, where soils are alkalized. A very notice-ably negative effect of vanadium on human health is registered in the town of Chusovoy, where the operating metallurgical enterprise emanates vanadium among other metals [23].

Vanadium is not referred to biophilic elements with its coefficient of biological consumption being about 0.1. The accumulation of V decreases the crop yield [22]. The background content of V is thrice exceeded in Moscow soils [24].

Antimony occupies the 62nd place among the earth's crust elements with its clarke being 0.2 mg/kg [16]. Sb has a low MPA (0.53), which testifies to its high hazard. Antimony is regarded to be a hazardous pollutant of soils in the USA and EU [25,26]. According to its toxicity and distribution, it occurs among the first ten most hazardous pollutants of the biosphere [27]. Antimony is accumulated in coal and in Sb–Au ores. In coal ash, the content of Sb varies from 10 to 500 mg/kg [28].

Soils are contaminated with technical antimony in the vicinity of ferrous and nonferrous metallurgical plants upon

cement and brick production and upon coal combustion [28]. In Great Britain, soils and plants in the zones of formerly developed mineral deposits are highly contaminated with antimony. The industrial contamination may raise the Sb content in the soils up to extreme values (200–280 mg/kg) [28].

Chromium ranks 21st among the earth's crust elements with its clarke being 122 mg/kg [16]. The chromium clarke in the world soils is 59.5 mg/kg [29].

Contamination with Cr considerably affects the biological activity of the soil. The catalyses activity of chernozems and the soil's ability for cellulose decomposition are decrease. The worsening of the soil's respiration inhibits important biochemical processes [30]. Chromium exerts a highly toxic effect on the chernozem's biota [31].

In a small amount, chromium stimulates the growth of agricultural crops; an excess of it however promotes various diseases. A wide distribution of technical Cr in the environment is unfavorable for humans and animals. In the USA, Cr ranks third among the pollutants by its abundance at waste disposal sites, and it ranks second (after Pb) among the inorganic pollutants [32]. The chromium toxicity depends on its oxidation status. Cr occurs in two states in soils. The oxyanion chromate CrO^{2-}_4, is highly mobile and more toxic in soils and groundwater. On the contrary, the reduced ion Cr(III) forms either a weakly soluble hydroxide or stable complexes with soil minerals [33].

A large amount of Cr is accumulated in urban soils [34]. The content of Cr reaches 1000–2000 mg/kg in the *urbic* horizon of urban soils in the town of Chusovoi [35]. Industrial waste water flows into rivers and contaminates alluvial soils in that industrial town. In Perm, the content of Cr reaches 600–1400 mg/kg in the alluvial soils of minor river floodplains upon its background content averaging 80 mg of Cr/kg [36]. Although the soil is contaminated with chromium via ground water only locally, the contamination degree may be very high.

Barium. The clarke of this metal in the earth's crust is 390 mg/kg [16]. The barium clarke in the world soils is 460 mg/kg [29].

In Russia, the Ba hazard in soils is underestimated, now it should be referred to the group of moderately dangerous elements. A barium excess in soil, water, and food (especially in combination with a Sr excess) may disturb the calcium metabolism and results in a serious skeletal-system disease known as endemic osteoarthritis. It is not by chance that a strict MPA for Ba equal to 100 mg/kg is adopted for the wastewater sediments used as an organic fertilizer in the USA [22]. At the same time, the maximal level of Pb and Zn in the wastewater sediments in the USA is 500 and 1500 mg/kg, respectively, whereas the content of Co is not standardized at all. This difference points unambiguously to the greater danger of Ba as compared to Pb, Zn, and Co in organic fertilizers, which agrees with the low value of the barium MPA obtained by Dutch ecologists.

Barium is accumulated in the dust of some industries: it is a by-product of coke plants, engineering works (foundries and cast iron processing shops), and cement production. Hazardous emissions are produced by Ba-processing plants as well as ore-processing enterprises specialized in mining and beneficiation of barite, strontium, and manganese ores [22].

Soils are contaminated with Ba in many cities. In Tomsk, the barium content in urban soils 5 times exceeds the background value [37]. In the town of Chusovoi contaminated with metallurgical industrial wastes, the share of technogenic Ba is considerable (35–74%). The content of Ba in a technozem in the town of Chusovoi constitutes 270–1000 mg/kg [38]. About one-third of the Ba is of technogenic nature in the air-contaminated urban soils in the city of Perm [38].

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