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Nature and Science

MARSLAND PRESS
Multidisciplinary Academic Journal Publisher

Synergetic and Competitive Relations between Metallic Ions in Soils with Various Man-Caused Impacts

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Abstract: The goal of the research is to evaluate the heavy metals content in soils with various man-caused impacts taking into account their synergetic and antagonistic relations on the example of Orenburg Oblast. It is estimated that the gross content of lead, nickel, chrome, and cobalt in all the zones of Orenburg Oblast under study (the Eastern, Western and Central zone) is increased while the content of cadmium is decreased in comparison with the maximum allowable concentration (MAC). These differences can be caused by the polyelemental contamination of the territory as well as by synergetic and competitive relations between metallic ions.
[Mikhailova I.V., Barysheva E.S., Voronkova I.P., Kuzmicheva N.A. **Synergetic and Competitive Relations between Metallic Ions in Soils with Various Man-Caused Impacts.** *Nat Sci* 2020;18(1):150-154]. ISSN 1545-0740 (print); ISSN 2375-7167 (online). http://www.sciencepub.net/nature. 20. doi:10.7537/marsnsj180120.20.

Keywords: Soil contamination; MPC; competitive interaction of metals; heavy metals; anthropogenic impact

1. Introduction

Being an essential part of the ecological system, soil is a key component of human and animal environment. Therefore, it is becoming increasingly important in studying comprehensive man-caused impacts. One of the traditional man-caused contaminations is heavy metal inputs to soil from metal processing wastes, fuel combustion products, car exhaust emissions, pesticides and fertilizers (Barsova et al., 2019; Boev, 2009; Brusseau et al., 2019; Ettler, 2016; Evseev, 2017). Being contaminated by chemical substances, soil may adversely affect contacting environments (air, water, food) and a human. The level of soil contamination enables to define the state of water reservoirs and air, since soil is a depositing environment (Csavina et al., 2011; Setko and Boev, 2006).

Soil degradation, lower biological value of soil and its lower ability to purify itself causes a chain reaction, which may have a negative effect of people's health in case of long unfavorable impact, since biological interaction between soil and a human is mostly provided by metabolism (Brusseau, 2019; Li et al., 2014; Boev et al, 2013; Huang et al., 2018; Sumenko et al, 2012). In view of the above, investigating the level of heavy metal deposition in soils with various a man-caused impact seems relevant. The goal of the research is to evaluate the heavy metal content in soils with various man-caused impacts taking into account their synergetic and antagonistic relations on the example of Orenburg Oblast.

2. Material and Methods

The Orenburg Oblast occupies the 4th place in the Volga District according to the level of man-caused impact on nature (Boev, 2009). The Orenburg Oblast lies in the central part of Eurasia and is situated both in Europe and Asia. The main contaminators of environment in the central part of the region are Orenburg gas processing factory, Orenburg helium factory, Orenburg gas production department, mechanical engineering and metal-working companies, as well as energy and transport companies. Ferrous and non-ferrous metallurgy companies are concentrated in the eastern part of the Orenburg Oblast. In the Western part of the Oblast, the main contaminators are oil-processing companies. Some towns and villages in Totskoe, Grachevka, Sorochinsk, Krasnogvardeisk and Aleksandrovka districts are situated in the zone of Totskoe nuclear exercise. Having multi-sectoral industry, the Orenburg Oblast is among the regions with the highest emissions of harmful substances (more than 500 thousand tones). Soil contamination is evaluated (320 studies) using the gross content of lead, nickel, strontium, cobalt, nickel, chrome, cadmium and labile lead, chrome, cadmium, and nickel according to the "Guidelines on Evaluating the Danger of Soil

Contamination by Chemical Substances" № 4266-87 and SanPin 2.1.7.1287-03. Chemical contamination of soil in the regions under study was evaluated using the total for soil contamination Csoil defined as the sum of coefficients for individual chemical substances concentrations. Concentration coefficients were calculated for substances with MAC as the ratio of the actual content of substance and its maximum allowable value.

The results of the studies are processed by means of variation statistics using the "Microsoft Excel 7.0," and "STATISTICA 10.0" including parametric (Student-Fisher test) and non-parametric (Wilcoxon test) methods. They are represented as a mean value (M±m). The groups were compared by means of Mann-Whitney and Student test.

3. Results

The analysis of the gross content of toxic microelements in the soils of Orenburg Oblast has shown that MAC of lead, nickel, chrome, and cobalt is increased in all the zones under study, while the content of cadmium was lower than MAC. Thus, it is established that the content of lead in the Central zone is 1.4 times higher (p<0.01) than in the Eastern and the Western zones, while in the Western zone, it is 1.03 times higher (p>0.05) than in the Eastern zone. The concentration of nickel in the Eastern zone is 2.3 times higher (p<0.001) than in the Western zone and 2.7 times (p<0,001) higher than in the Central zone, while in the Western zone, it is 1.17 times higher (p>0.05) than in the Central zone (Table 1).

Table 1. Gross Content of Toxic Microelements in the Soils of Orenburg Oblast (M±m, mg/kg).

Element	Eastern zone	Western zone	Central zone	Background value (mg/kg)	MAC (mg/kg)
Lead	33.25±1.59**	34.47±3.76**	47.96±5.03**	11.4±3.3	32
Nickel	405.6±45.3**	172.8±27.6***	146.8±8.6***	63.84±12.1	80
Strontium	122.6±9.6***	133.2±9.9***	125.6±8.2***	26.25±5.8	-
Cobalt	48.68±4.79***	26.66±3.71***	21.31±0.00***	6.72±2.9	50
Chrome	558.1±53.7***	459.5±37.8***	350±13.9***	160.5±	100
Cadmium	-	-	0.083±0.008	-	0.5-1.0

Note: * - significant differences relative to MAC are defined (* - p<0.05; ** - p<0.01; *** - p<0.001; «-» - the element is absent or non-defined).

The concentration of strontium in the Western zone is higher than in other zones: in the Central zone, it is 1.25 times higher (p>0.05) than in the Eastern zone. The content of cobalt in the Eastern zone is 1.8 times higher (p<0.001) than in the Western zone and 2.3 times (p<0.001) higher than in the Central zone.

In the Western zone, it is 1.25 times higher (p>0.05) than in the Central zone. The content of cobalt in the Eastern zone is 1.2 times higher (p>0.05) than in the Western zone and 1.5 times (p<0.001) higher than in the Central zone. In the Western zone, the content of chrome is 1.31 times higher (p<0.001) than in the Central zone. Cadmium was found only in the soil of the Central zone.

Therefore, the analysis of soil contamination with heavy metals in the zones of Orenburg Oblast has revealed the high content of nickel, cobalt, and chrome (the Western and the Eastern zones).

On the next stage of the research, we evaluated total labile toxic elements, which provide the most reliable information on the contamination of environment, since gross elements in the chemical compounds and the organic part of the soil are not labile. The analysis of total labile toxic elements has revealed that the concentration of nickel in the Eastern zone in the Western Zone is 1.09 times higher (p>0.05) than in the Central zone (Table 2).

Table 2. Total Labile Toxic Elements (M±m, mg/kg).

Element	Eastern zone	Western zone	Central zone	MAC
Lead	1.89±0.11	1.92±0.12	1.71±0.17	6
Cadmium	0.23±0.02**	0.17±0.01	0.21±0.03	0.3
Nickel	1.54±0.09	1.50±0.24	1.37±0.12	4
Chrome	1.55±0.09	1.34±0.05	1.76±0.17*	6
K_{tot}	**1.72**	**1.49**	**1.61**	

Note: * - significant differences relative to MAC are defined (* - p<0.05; ** - p0.01; *** - p<0.01; «-» - the element is absent or not defined).

The concentration of cadmium in the Eastern zone is 1.3 times higher ($p<0.01$) than in the Western zone and 1.09 times ($p>0.05$) higher than in the Central zone, while the concentration of cadmium in the Central zone is 1/23 times higher ($p>0.05$) than in the Western zone. The concentration of strontium in the Western zone is higher than in other zones: it is 1.01 times higher than in the Eastern zone and in 1.1 times higher than in the Central zone ($p>0.05$). In the Eastern zone, it is 1.1 times higher ($p>0.05$) than in the Central zone.

The content of liable chrome is the highest in the soil of the Central zone: it is 1.13 times higher than in the Eastern zone ($p>0.05$) and 1.3 times higher than in the Western zone ($p<0.05$). In the Eastern zone, the concentration of chrome is 1.12 times higher ($p>0.05$) than in the Western zone. Thus, we can arrange the zones of the Orenburg Oblast under study in the following order according to total labile toxic elements: The Eastern zone (C_{tot} =1.72) > the Western zone (C_{tot}= 1.49) > Central zone (C_{tot} =1.61). In the Eastern zone, the concentration of C_{tot} is 1.15 times and 1.06 times higher than in the Western and Central zones respectively.

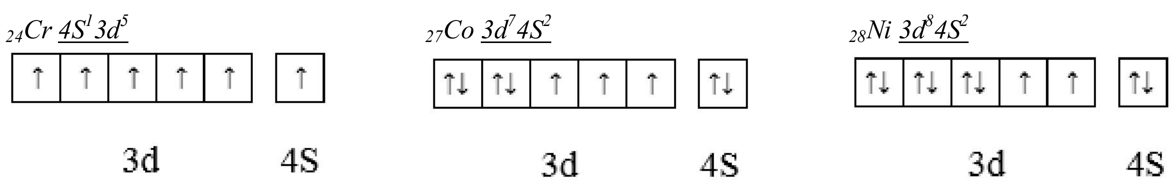
In general, the analysis of soil contamination with heavy metals in the zones of the Orenburg Oblast has revealed the high content of nickel, cobalt and chrome (the Western and the Eastern zones). It should be noted that the increase in the content of chrome in soil is caused by the increase in cobalt and nickel content. It is interesting that in the soil of the Western zone, the level of Co, Ni and Cr content is higher (relative to the Central zone), while the level of air impact in these elements in the Central zone is much higher.

4. Discussions

When discussing the obtained results, we should take into account the polyelemental contamination of territory and the fact that the behavior of elements in soil and neighboring environments as well as their labiality depends on some factors. Among these factors are synergetic and competitive relations between the metallic ions. Thus, in case of polyelemental contamination, the various metallic ions will tend to interact with one and the same soil reaction centers. Here, the absorption of the element with less affinity to soil reaction centers inevitably decreases.

The similarity of biological effect is caused by the electronic structure of atoms and ions. Chrome, cobalt and nickel have horizontal similarity in the Mendeleev periodic system.

These are d-elements. Cobalt and nickel belong to the same family (iron family) and their ions have similar electronic structure (Figure 1).



(a) *(b)* *(c)*

Figure 1. Electronic and Graphic Formulas: (a) - Chrome; (b) - Nickel; (c) - Cobalt.

Cobalt, nickel and chrome are typical complexing agents; their coordination values are in most cases 4 and 6. The soil contains a whole range of components with different origin, structure and properties. It can interact with heavy metallic ions. Most of soil organic matter is represented by humic acids. Humic acids play an important role in the adsorptive stabilization of heavy metals by soil. The metals are absorbed by humus substances due to the exchange of H^+ -ions of acidic functional groups of humus acids with the stabilization of metals in the structure of intracompex compounds. The intensity of the interaction between metallic ions and humic acids depends on the stability constant a (C_{sta}) of metal complexes with humic acids. Relatively high value of C_{sta} of nickel, cobalt and chrome ions enables to assume that these metals will readily form complexes with organic substances. Cobalt has three unpaired electrons in the pre-outer orbital, while nickel has two unpaired electrons. They give these electrons back and form trivalent and bivalent cations (Co^{+3}; Ni^{+2}). It is these peculiarities of Co and Ni atom configuration that increase their response ability in the interaction with humic acids and their absorption values.

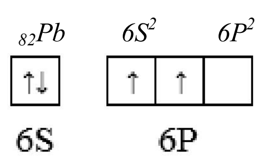


Figure 2. Electronic and Graphic Formula of Lead.

Chrome is close to nickel and cobalt in the durability of connection between electrons in the atom. It refers to this group because of the small amount of low-valent connections, which is important for joint migration. Chrome has six unpaired elections in the outer and pre-outer energetic levels. Having a large atomic radius, it gives electrons back easily and then turns to positively charged ions. Besides, we have established antagonism between the lead ions and cobalt, nickel and chrome ions, which is manifested in the decreased content of lead in soil and the increased content of cobalt, nickel and chrome.

As mentioned above, cobalt, nickel and chrome are d-elements, which are stronger complexing agents than p-elements (Pb^{2+}) (Figure 2).

Atoms of d-elements have an uncompleted d-electron layer. Using the pairs of d-electrons that are not filled by d-orbites and are not divided (in sub-outer electronic layer), d-elements form more stable complex compounds with the organic matter of soil than p-elements (picture 2). Thus, synergism and antagonism of ions is related to the peculiarities of atom electronic structure. It is apparent that these antagonistic interactions result in the decreased content of Pb in the soil of the Eastern zone (relative to the Central and Western zones). Thus, the increased content of Co, Ni and Cr in the soil of the Western zone is possibly related to both natural content and synergetic effect of ions.

5. Conclusion

The obtained results enable to make the following conclusions.

1. The gross forms of chrome, nickel and cobalt are the major contaminators of soil in the Eastern zone. The gross forms of strontium and chrome are the major contaminators in the Western zone, while the gross forms of lead and cadmium are the main contaminators in the Western zones.

2. The higher level of contamination by labile elements is found in the soils of the Eastern zone. Cadmium and nickel are the major contaminators (labile) in the Eastern zones, lead and nickel - in the Western zones, and cadmium and chrome - in the Central zone.

3. It is established that the increased (decreased) content of the elements in soil in case of low (high) level of aerogenic impact may be caused by synergism and antagonism of ions.

4. It is revealed that the increased content of nickel and cobalt in soil leads to the increased content of chrome (synergism). Besides, the increased content of cobalt, nickel and chrome (antagonism) results in the decreased content of lead.

5. Synergism and antagonism of ions in soil can be caused by the ability of metal ions to form intracomplex compounds with soil organic matter. The electronic structure of atoms and ions defines complexing properties of the element.

Acknowledgements:

The authors express gratitude and deep appreciation to Viktor M. Boev, MD, Professor, the head of the department of general and communal hygiene of the Orenburg State Medical University for assistance in this research.

Foundation item: The National Project of India. Authors are grateful to the Department of Science and Technology, Government of India for financial support to carry out this work.

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11/28/2019