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ARTICLE

Change in the Content of Mobile Microelements in Typical Sierozems Under the Influence of the Cement Industry

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Abstract

In this article, the problem of environmental pollution under the influence of the cement industry is discussed. It is proven that in irrigated typical sierozems, the amount of mobile forms of biomicroelements increases with proximity to cement production areas. It is also determined that under the influence of a cement plant, at a distance of 100 m, a geochemical province is formed that is saturated with cobalt while being deficient in zinc and manganese.

Keywords: typical sierozem, biomicroelement, cement, pollution, province, copper, zinc, manganese, cobalt, iron.

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1 Introduction

Sierozem soils are divided into the following types: ordinary, solonchakous, and pebble. In the International Classification (World reference base for soil resources 2014: International soil classification system for naming soils and creating legends for soil maps. FAO. Rome, 2015.), soils are classified in the Calcisols group. According to the World Health Organization (WHO), out of more than 6 million chemical compounds, only about 500,000 are currently in use, of which approximately 40,000 possess harmful properties for humans and more than 12,000 are toxic. In recent decades, the consumption of mineral and organic raw materials has sharply increased. For instance, in 1913 the annual per capita consumption of mineral raw materials was 5 tons; in 1940 it reached 7.4 tons; in 1960, 14.3 tons; and by 2000 it had increased to 40–50 tons. Consequently, the volume of waste generated by industry, agriculture, and communal services is also continuously growing.

By the end of the 20th century and the beginning of the 21st century, the pollution of the environment—especially soils—by industrial, agricultural, and domestic wastes has become a global issue, leading to a worldwide ecological catastrophe and soil degradation.

Environmental pollution is understood as the introduction into the biosphere of any substances or forms of energy (in solid, liquid, or gaseous state—including heat, sound, radioactivity, etc.) in amounts that directly or indirectly cause harm to humans, animals, and plants. The pollution of the biosphere is classified according to its spatial extent as follows:

- **Local pollution** – pollution typical of cities, large industrial enterprises, mining regions for various mineral resources, and large livestock complexes;

- **Regional pollution** – covers large areas and water bodies under the influence of major industrial enterprises;
- **Global pollution** – usually arises from wastes discharged into the atmosphere, dispersing over long distances and affecting vast regions or even the entire planet.

The sources of pollutants are varied, and the impact of cement plant emissions on the biosphere components—particularly on irrigated typical sierozems—has not been sufficiently investigated. In this respect, studying soils within the pollution chain is of great scientific and practical significance.

Soils are polluted by solid and gaseous emissions from metallurgical plants, production facilities for construction materials, and machine-building factories. In addition, the widespread use of chemicals in the production of mineral fertilizers and for plant protection leads to the contamination of the atmosphere, soils, and natural waters with substances such as pesticides, nitrates, and heavy metals [1].

According to static sources, the discharge of harmful substances into the atmosphere results in the exceedance of permissible threshold levels of toxic substances in the soil cover as well as in surface and groundwater in areas near the pollution source. Primary pollutants—delivered as atmospheric dust, aerosols, and acid rains—cause catastrophic environmental conditions in many major industrial cities. Consequently, the technogenic load of certain chemical elements on the Earth's surface has significantly increased; for example, for Na, Cl, Ca, and Fe it reaches 500–1000 kg/(km^2·year), for S, N, K, Al, and P it is 500–200 kg/(km^2·year), and for toxic elements such as F, Cu, Zn, Pb, Ni, As, Cd it is 10–0.1 kg/(km^2·year).

These data indicate that the expansion of technogenic impact is associated with the intensive dispersion of substances on the Earth's surface, atmospheric dust and chemical pollution, aerosols, anthropogenic dust, and the redeposition of chemical compounds onto soils and waters. These processes lead not only to pollution but even to the transformation of the biosphere, hydrosphere, and soil cover.

The rapid development of industrial activities has led to the pollution of the atmosphere, hydrosphere, and pedosphere, the emergence of global environmental problems, the loss of many plant and animal species, and an increase in the concentration of heavy metals, metalloids, and radionuclides in soils. Major sources of environmental pollution include the oil refining industry, metallurgy, construction industries, thermal power stations, and domestic enterprises, along with cement manufacturing companies. The cement industry is considered one of the sectors with a harmful impact on the environment. Annually, cement plants emit over 27 million tons of dust—of which two-thirds is solid and 44 percent is gaseous. Besides dust, cement plant emissions contain nitrogen oxides, sulfur dioxide, carbon monoxide, heavy metals, and metalloids (Ba, Be, Cr, As, Ni, Al, Ca, Fe, Mn, Cu, Ag, Sb, Cd, Pb, Se, Zn, K, Na, Tl, Hg) and their compounds, which are the main pollutants of the atmosphere, hydrosphere, and pedosphere [2, 3]. Studies have also demonstrated that emissions from cement plants adversely affect not only the environment but also human health.

2 Materials and Methods

The objective of this study was to determine the effect of cement plant emissions on the properties of irrigated typical sierozem soils and on the composition and quantity of their mobile microelements. For this purpose, the "Quvasoysement" Joint Stock Company—located in Quvasoy city of the Fergana region—and the lands and crop fields within its influence zone were selected. The "Quvasoysement" enterprise, which began operating on February 1, 1932, produces cement using the dry process. The total land area of the enterprise is 57.73 hectares, of which the production area covers 8.14 hectares.

Cement production is based on two stages: clinker production and the subsequent grinding of clinker with mineral additives. Each stage of the technological process involves the grinding of raw materials, which results in significant dust emissions into the atmosphere and the contamination of soils and plants within the enterprise area and the boundaries of the sanitary protection zone. The sources of pollution affecting nearby field areas and the atmosphere include the stone crushing plant, the clay processing plant, and the dry cement production lines (storage and mixing bunkers, raw material mills, rotary kilns, clinker cooling boxes, raw material mixture compaction parts, cement mills, open warehouses for raw materials and wastes, coal grinding section, slag drying plant, and cement milling plant).

Quvasoy city is located in the southeastern part of the Fergana Valley, with its southern part surrounded by ridges and mountains. This city is distinguished by its unique landscape, natural resources, and raw material wealth. The climate in Quvasoy is continental, characterized by hot summers, cold winters, and relatively mild autumns and springs. The area is predominantly covered by typical sierozem soils, most of which are irrigated. The relatively high humidity in the foothills and mountain slopes makes the region favorable for agriculture.

Soil analysis was carried out in several stages: preparation, field surveys, soil sectioning, and laboratory analysis. The mobile fractions of heavy metals in the soils were determined using a Shimadzu AA-7000 atomic absorption spectrophotometer (GOST: M-MBI-8-2008). Each element was analyzed based on its characteristic resonance wavelength. The wavelengths applied for the microelements were: copper (Cu) – 324.8 nm, iron (Fe) – 248.3 nm, manganese (Mn) – 279.5 nm, zinc (Zn) – 213.9 nm, and cobalt (Co) – 340.6 nm.

Soil samples were collected in accordance with the standards (GOST 28168-89) and placed in sterile parchment bags. A composite soil sample was obtained using the "composite method." To determine the nature of the changes in soil properties under the influence of pollution, soil samples were taken at distances of 0.1, 0.5, 1.0, and 10 km from the cement plant, taking into account the wind direction and topography.

3 Results and Discussion

Investigations in the study areas indicate that the coarse particles of cement dust are concentrated near the pollution source, while the fine particles are distributed over various distances. This observation was also confirmed by Ciobanu, Voicu, Toma, and Tudor [2]. The signs of pollution decrease significantly with increasing distance from the cement plant, as evidenced by the chemical analysis of the soil samples (see Tab.1). Due to the toxic effects of high concentrations of certain chemical elements on plants, heavy metals are categorized as a separate group. However, there is no unanimous opinion regarding the hazard level of each heavy metal in soils—a factor that depends on the buffering capacity (resistance, resilience) of the soil, its organisms, and the resident plants.

Heavy metals in soils are divided into two groups: toxic elements and microelements that are utilized in small quantities in agriculture. Among these microelements, cobalt, copper, iron, manganese, molybdenum, nickel, and zinc, among others, are vital for the biological functions of living organisms when present in trace amounts. An increase in the concentration of these elements in cells can also enhance their toxic properties. Consequently, while many authors refer to these elements as microelements at low concentrations, they are often classified as heavy metals when present in high concentrations [4]. The hazard level of a chemical element is determined by the carcinogenicity of its compounds, which is directly related to its atomic mass and the solubility of its stable compounds in water—and inversely related to their permissible threshold limits (PTLs) [5].

In this regard, chemical elements are divided into three classes according to their hazard level:

1. **Highly hazardous:** As, Cd, Hg, Se, Pb, Zn, F;
2. **Moderately hazardous:** B, Co, Ni, Mo, Cu, Sb, Cr;
3. **Less hazardous:** Ba, V, W, Mn, Sr.

Iron, manganese, copper, zinc, and cobalt occur in varying quantities in the lithosphere and soils. According to A.P. Vinogradov, their average total contents in the lithosphere are approximately 4.65 percent, 0.10 percent, 0.0083 percent, 0.0037 percent, and 0.0018 percent, respectively, while in soils they constitute about 3.8 percent, 0.085 percent, 0.002 percent, 0.005 percent, and 0.0008 percent, respectively [6].

The geochemistry of the studied elements is complex, and their quantities in soils vary accordingly. The migration of these elements is directly related to the soil's redox potential and reaction dynamics. Furthermore, the mobile fractions of these elements in soils vary under the influence of the cement plant, as shown in Table 1.

Table 1. Mobile Forms of Microelements in Irrigated Typical Sierozems (mg/kg)

Distance: 100 m

Depth (cm)	Cu	Zn	Mn	Co	Fe
0–26	0.75	1.31	39.8	7.40	5.20
26–48	0.75	1.28	41.0	13.70	7.60
48–58	0.41	1.05	46.8	11.60	1.94
58–79	2.10	1.40	15.3	9.50	5.95
79–112	2.10	1.21	19.4	5.30	7.60

Distance: 500 m

Depth (cm)	Cu	Zn	Mn	Co	Fe
0–5	0.79	1.21	13.0	3.62	1.79
5–10	1.20	1.25	12.3	2.77	0.54
10–20	0.89	1.30	12.5	1.60	2.88
30–45	1.30	1.32	26.4	4.46	3.20

Distance: 1000 m

Depth (cm)	Cu	Zn	Mn	Co	Fe
0–5	0.68	1.27	48.7	3.28	3.20
5–10	1.51	1.15	51.6	2.95	0.75
10–20	0.68	1.30	49.7	2.10	2.26
30–45	1.82	1.38	15.3	2.61	3.51

Distance: 10,000 m

Depth (cm)	Cu	Zn	Mn	Co	Fe
0–35	2.75	1.50	35.8	5.47	12.10
35–46	3.30	1.87	14.5	2.61	14.50
46–82	2.44	1.52	22.2	4.79	6.31
82–115	2.01	1.32	16.6	4.46	6.64
115–130	1.51	1.21	24.6	4.78	3.30

The table data indicate that in areas close to the industrial facility, the amounts of mobile heavy metals (specifically Zn, Co, Fe) increase, while they decrease with increasing distance from the facility. The accumulation of heavy metals adversely affects many soil processes, primarily by reducing biological activity, which disrupts the formation of organic matter and alters the physical and physico-chemical properties of the soil.

In the irrigated soils of Uzbekistan, the gradation of nutrient microelements—developed for major fodder crops and their complexes—is presented in Table 2. According to the classification, the levels of nutrient microelements vary by a factor of 0.4 to 150. In terms of quantity, the nutrient microelements decrease in the following order: Mn > Co > Zn > Cu.

Table 2. Level of Nutrient Microelements in Soils (mg/kg)

Lev. of Sup.	Cu	Zn	Mn	Co
Ins.	< 0.4	< 1.5	< 80	< 1.0
Ade.	0.4–0.8	1.5–2.5	80–100	1.1–2.5
High	0.8–1.0	> 2.5	100–150	2.51–3.0
Sat. Prov.	> 1.0	–	> 150	> 3.0

Based on the classification developed by Ye.K. Kruglova et al. [3] for the irrigated soils of our republic, it has been shown that mobile copper (0.4–0.8 mg/kg), zinc (1.5–2.5 mg/kg), manganese (80–100 mg/kg), and cobalt (0.15–0.25 mg/kg) exist in "borderline" amounts in soils, which is considered normal and conducive to good crop development. According to Jardal's data, in irrigated typical sierozems at 100 m from the cement plant, copper is within the adequately supplied group while cobalt forms a saturated province. At 10 km, a saturated province with respect to copper was observed. At this distance, manganese appears in a deficient provincial state, ranging from 12.3 to 51.6 mg/kg in the soil layers. Zinc, however, is in the insufficient group at 1 km and in the adequate group at 10 km.

Although the total content of iron in most agricultural soils—which are neutral or weakly alkaline—is excessive, crop productivity is limited by the insufficient availability of mobile iron. In the topsoil near the cement plant (at 100 m), a 2.33-fold lower amount of mobile iron was observed compared to that at 10 km.

4 Conclusions

The technogenic impact of the cement production enterprise results in an increased mobile fraction of iron and cobalt in the soil cover of irrigated typical sierozems. Under the influence of dust emitted from the cement plant, the mobile fractions of most microelements increase as one approaches the cement production area—with the notable exception of zinc. Consequently, relatively clean typical sierozem soils are transformed into a polluted group due to cement industry emissions.

The findings of this study serve as a primary basis for establishing environmental monitoring and protection measures, as well as for setting standards for microfertilizers. It is important to conduct further studies within the soil–plant system to determine the geochemical conditions of environments affected by industrial wastes, and to assess the presence and relative significance of macro- and microelement deficiencies and toxicities in specific areas.

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Abbreviations

The following abbreviations are used in this manuscript:

Lev. of Sup.	Level of Supply
Ins.	Insufficient
Ade.	Adequate
Sat. Prov.	Saturated Province

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