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Soil contamination with heavy metals as a potential and real risk to the environment

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ABSTRACT

The heavy metal content (Cu, Zn, Pb, Cd and Ni) in soils of natural landscapes and soils contaminated by these metals under technogenic and artificial conditions was investigated. Ecological hazards caused by heavy metal compounds in soils were evaluated. The concept of a real and potential risk to the ecosystem in addition to soil contamination with heavy metals was formulated. The ratio of weekly bound heavy metal content to the strongly bound content of metals was very informative parameter for the assessment of the ecological state of the polluted soils and evaluation of ameliorant effect to metal fixation in the soil.

1. Introduction

The environment contamination poses a serious hazard at present so putting in jeopardy the very basis of human existence at the planet. The real danger of environmental pollution is obvious (Bowen, 1979). But the doctrine about the potential threat of pollution for soils, about the relationship between actual and potential dangers of the pollutants for soils is weakly developed.

The present paper is aimed at discussing the concept of ecological hazard to the biosphere through its pollution by different substances. Special attention is paid to approaches for evaluating the soil contamination with heavy metals and for describing informative indices, methods and results of their practical application under different conditions, thus answering the question about soil contamination with heavy metals as a potential and real risk to the environment.

1.1. Approaches for solving the above objectives

Contaminants are substances released into the environment from man-made sources in amounts exceeding the natural level of their content (Motuzova, 1999). Heavy metals are referred to the most dangerous group of contaminants and their chemical criteria (atomic weight, density) have proved far from sufficient in environmental research because the effect exerted by them on the behavior of chemical elements reveals no manifestation in landscape. Nevertheless, the effects of interaction between heavy metals and living organisms and the processes of their biogenic migration are of great importance (Weber and Karczewska, 2004). Essentially, heavy metals are microelements that are released into the environment from technogenic sources. In biochemistry, agrochemistry and soil science the heavy metals represent chemical elements, the small quantities of which (10^{-3}–10^{-6}%) in natural habitats contribute to the most important biochemical processes in living organisms.

In heterogenous natural landscapes the heavy metals are distributed creating diverse biogeochemical provinces. They are intrazonal by character and confined to areas with different distribution degrees of chemical elements (and their compounds) to be specifically interacted with living organisms. The concept of biogeochemical provinces has been first formulated by Vinogradov (1957). Kovalsky (1982) studied in detail the interaction between different organisms (crops, animals, human) and biogeochemical indices of their habitat. As a result of biogeochemical zonation at the territory of the former USSR, 14 biogeochemical provinces have been distinguished according to surplus or deficit of microelements in natural habitats (Kovalsky, 1982). Having used the data about the living organisms in natural habitats, Kovalsky (1982) was the first to determine an optimal (threshold) level of microelement content in the environment (prototype of the currently used maximum allowable concentration or critical load). The areas have been distinguished by him to show insufficient or abundant content of microelements caused harm to living organisms including higher and lower plants, zoocoenoses, and microbiocoenoses. At present, there are provinces that provide a breeding ground for endemic diseases due to deficiency or abundance of chemical elements in rocks and

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soils (Avtsin et al., 1991). Among them are provinces characterized by abundance of molybdenum (endemic podagra), fluorine (fluorosis), strontium, barium and the other elements.

Apart from natural biogeochemical provinces, technogenic landscapes are developed with a higher concentration of heavy metals (Meers et al., 2006). Only a comprehensive analysis of soils and their state makes possible to evaluate the hazard of these elements for living organisms. Just the soil plays a decisive role in the formation of substance flows in landscape directly combined with plants, surface and ground waters.

Soil compounds of microelements have a system organization being represented by a great diversity of strongly bound solid phases (organic, mineral, organo-mineral, primary, secondary formations), mobile compounds, soluble and gaseous forms, and soil biota. It is formed under the influence of hierarchically organized soil-chemical and landscape-geochemical processes of migration, accumulation and transformation of these compounds.

The following objectives of this study were to:

- investigate the heavy metal content (Cu, Zn, Pb, Cd, Ni) in soils of natural landscapes and contaminated by these metals under technogenic and artificial conditions;
- evaluate ecological hazards caused by heavy metal compounds in soils;
- formulate the concept of a real and potential risk to the ecosystem in addition to soil contamination with heavy metals.

2. Materials and methods

2.1. Study area

The study area presents the landscapes of the most significant territories of Russia. These are forest landscapes of Murmansk surrounding area (Kola Peninsula, North-Western Federal District of Russia) and Rostov surrounding area (Southern Federal District of Russia).

The first group presents the forest landscapes that characterize the highest share of the European part of Russia. Soils of this group are presented by podzols, derived on the moraine deposits. Soils of the natural and technogenic landscapes of this region were analyzed.

The second group of the investigated objects is the steppe landscapes that are the most actively used in agriculture of Russia. Soils of this group are presented by chernozem, derived on the loess sediments. On the steppe soils two series of experiments were carried out. In the first series soils of the natural and technogenic landscapes were investigated. The other part of work with chernozem is consisted of vegetation experiments with artificial contamination of soils by heavy metals and their subsequent remediation by using some ameliorants.

We can compare the ecological situation that takes place in these regions under the influence of pollution by heavy metals.

2.2. Field experiment

To evaluate a real and potential risk of contaminated soils to the environment, a long-term (2006–2011) field experiment was established on a clay loamy ordinary chernozem on loess-like loam (Haplic Chernozem, FAO).

The soil was contaminated with salts Zn^{2+} and Pb^{2+} acetate. The metals were applied separately as dry acetate salts to the plow (0 to 20-cm) horizon in fall. The application rates were 300 mg kg^{-1} for Zn and 100 mg kg^{-1} for Pb, which corresponded to 3 maximum permissible concentration (MPC) for these metals in the soil and to the real level of soil contamination of Zn and Pb in the Rostov region (Russia).

Three months later the chalk (5 mg m^{-2}) and semidecomposed cattle manure (5 mg m^{-2}) were applied as ameliorants according to the following experimental design:

(1) Without metal addition;
(2) Metal (Me);
(3) Me + chalk, 5 mg m^{-2} + manure.

Experiments were conducted in triplicate. The previous results of the pot experience has shown that the most significant effect of decreasing metal mobility in soil was at the simultaneous application of chalk and manure (Minkina et al., 2008, 2010).

Spring barley (*Hordeum sativum distichum*), cultivar Odesskii-100, was planted in experimental plots. The crop management practice recommended for this zone was used. Samples of soil (0–20 cm layer) and plants were taken at the complete maturity stage of barley after 1 year from the beginning of the experiment.

The establishment of experiments, observations, and recordings, and sampling of soils and plants were performed in accordance with procedures of field experiments (Dospekhov, 1968).

2.3. Methods of soil investigations

Soil properties were analyzed using Russian traditional methods (Arinushkina, 1970). Soil organic carbon was measured using 0.4 N potassium bichromate (the Tyurin method modified by Simakov). Soil particle size distribution (silt and clay content) was determined by the pipette method after the pyrophosphate treatment. Cation exchange capacity (CEC) of the soil was determined using 1 M ammonium chloride (the Bobko–Askinazi method). The exchangeable potassium was determined by the Machigin (molybdenum blue) method. Adsorbed Na was analyzed by flame atomic adsorption spectrophotometry (FAAS). Soil pH was measured with a pH electrode using a 1:5 suspension of a soil to water ratio. Exchangeable calcium and magnesium were measured by the titration at pH 12.5–13 and 10 respectively. Carbonates were measured by the Kudrin method using 0.005 NH_2SO_4 and then an excess of the acid was titrated with alkali.

2.4. Analytical procedure

Soil samples for determining metal total concentrations were ground to pass through a 0.25 mm sieve. The total content of heavy metals was determined by heating with HF + H_2SO_4 and analyzed with the metals in ground water samples by atomic absorption spectrophotometry (Scientific Buck 200 A).

To detect the metal content that weakly bound with soil components (mobile compounds) was used following the protocol of Mineev (1989):

1) extraction for 1 h shaking, using a 1:10 suspension of a soil to H_2O ratio — extract of water soluble metal form.
2) extraction for 18 h, using a 1:10 suspension of a soil to 1 N NH_4OAc, pH 4.8, ratio — extract of exchangeable water soluble metals form including water soluble form.

The content of metals in strongly bound compounds was determined as the difference between the total amount of metals in soils and their weakly bound compound forms.

The extract from each step were filtered through paper (pore size 2–3 μm) and analyzed by atomic absorption spectrophotometry (Scientific Buck 200 A).

Heavy metals in plants were prepared for analyzing by dry combustion at 450 °C, the rest was dissolved by an acid mixture (HNO_3 + HCl) (Methodological Guidelines on the Determination of Heavy Metals in Agricultural Soils and Crops, 1992). The content of heavy metals in extracts from plants was determined by atomic absorption spectrophotometry (Scientific Buck 200 A). The nitrogen content in grain of barley was analyzed by the optical method with indophenol greens (Mineev, 1989).

2.5. Ecological situation in Murmansky District under the influence of the pollution by heavy metals

The Monchegorsk place (Murmansky region) is represented by natural and technogenically transformed landscapes. Its sufficient part is