ASSESSMENT OF SOILS FOR HEAVY METAL BY ATOMIC ABSORPTION SPECTROMETRY (Zn, Pb, Cd, Cu)

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Abstract. The authors studied the sources of soil contamination with heavy metals and their impact on the environment and human health. The research analysed the content of acid-soluble forms of heavy metals in soils on the territory of Sunzha, the Republic of Ingushetia, The Russian Federation *near 589 km of the Federal Highway 'Kavkaz'. According to the results, authors determined the extent of heavy metal contamination in the locations under study.*

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Introduction

Nowadays, the most important source of environmental pollution are heavy metal ions. They contained in industrial wastewater of various industries enterprises, including chemical, petrochemical, mining, etc. The heavy metals are accumulated in the environment. Moreover, they are not decomposed by microorganisms as organic substances are. High content of heavy metals in ecosystems (plants, water bodies, soil, etc.) provides their accumulation in drinking water, food raw materials, etc. As a result, entering the human body they cause serious harm to health [1-2].

The toxic effect of heavy metals is non-specific. They are able to combine with proteins, nucleotides, coenzymes, phospholipids, i.e. practically with all types of substances involved in cell metabolism [3].

One of the strongest and most widespread chemical pollution is heavy metal pollution. Heavy metals include more than 40 chemical elements of the periodic system of D. I. Mendeleev; their atomic mass is more than 50 atomic units. This group of elements is actively involved in biological processes being part of many enzymes and largely coincides with the concept of 'microelements'.

Heavy metals are released into the environment during the vehicular traffic and the abrasion of road surfaces. It ensures releasing of dissipated lead, cadmium, zinc, iron, and other

metals deposited in the roadside area into the atmosphere. These dissipated elements concerns with harmfull emissions provided by motor vehicle engines

The composition of exhaust gases includes carbon monoxide, nitrogen and sulphur oxides, hydrocarbons, heavy metal compounds, etc. These substances are involved in the metabolic cycle of plants, animals and humans [4]. Moreover, these chemicals substances are extremely toxic for living organisms.

Heavy metals are the second most dangerous pollutants. Only pesticides, carbon dioxide and sulphur dioxide are followed by them. However, heavy metals could become potentially more hazardous than nuclear power plant waste and solid waste. The high level of industrial production is a reason of heavy metal pollution. Due to imperfect treatment systems, heavy metals are released into the environment, including soil polluting and poisoning.

Nowadays, both official and unofficial established standards are used in Russia to assess heavy metal contamination of soils. Their main purpose is to prevent excessive amounts of anthropogenically accumulated solid metals in soil from penetrating the human body and neutralise their negative impact. Heavy metals negatively affect plants, soil water, and soil itself. Soil microorganisms are particularly susceptible to the impact of heavy elements; deterioration of phosphate regime and loss of humus may also occur [5-7].

The study of soil mantle for heavy metal content is of great practical importance. As heavy metals can be of a negative nature, it is necessary consider their content in terms of the Maximum Permissible Concentration (MPC). Therefore, research results may become the basis for monitoring and integrated soil mantle assessment. Moreover, they may also provide a basis for a work plan to reduce heavy metal concentrations.

The purpose of the study is to determine the impact of vehicle transport on the soil composition of arable land. Therefore, we selected a piece of land located in Sunzha, the Republic of Ingushetia, The Russian Federation near 589 km of the Federal Highway 'Kavkaz'. It is necessary to detect the content of heavy metal ions (Zn, Cd, Pb and Cu) in soil sample by atomic absorption spectroscopy.

Hence, there is a necessity to perform the following:

1) To study the operating principle of atomic absorption spectrometer with electrothermal atomisation 'KVANT.Z'.

2) To determine the concentration of each heavy metal (Zn, Pb, Cd, Cu) in soil samples taken at a distance of 5, 10 and 15 metres to the road.

3) To assess the degree of selected samples contamination.

Sources of soil contamination with heavy metals and their impact on the environment and human health

Pollution is divided into natural (caused by natural causes) and anthropogenic (caused by human activity) ones. The atmosphere, water, soil are the direct objects of pollution. Indirect objects of pollution are plants, animals, microorganisms, and humans [5-6].

Chemical pollution is an increase of chemical components in certain environment, penetration (introduction) of chemical substances into it in concentrations exceeding the norm or not peculiar to it. However, chemical pollution is one of the most frequently occurring types

of pollution produced by a variety of human economic activities. Chemical contaminant agents include a wide range of chemical compounds. According to the World Health Organisation (WHO), there are about 500,000 such compounds; about 40,000 are harmful substances and about 12,000 are toxic ones [4, 6].

Heavy metal pollution can affect the environment, but the serious environmental problem and the longest lasting effects of human activity is soil pollution. Accumulation of heavy metals in soil occurs as a result of mining, smelting of metal ores, industrial emissions, the use of pesticides, herbicides and fertilisers. Metals Cd, Cu, Pb, Zn and metalloids (e.g., As) are considered environmental pollutants due to their persistence, bioaccumulative nature, and serious harmful impact on human health and the environment [7].

The gross content of heavy metals in natural unpolluted soils is due to their concentration in the original parent rock. It is impacted by soil formation processes and characteristics such as organic matter content, environmental reaction, and granulometric composition. However, heavy metal levels are now altered by anthropogenic impacts. Soils within urban areas are exposed to chemical, biological, and radioactive contamination [8]. Particular attention in the assessment of soils chemical pollution is paid to contamination by heavy metals and organic toxicants. Moreover, heavy metals monitoring is compulsory in all environments.

MPC is main indicator characterising the impact of pollutants on the environment. In terms of ecology, MPC of a particular substance represent the upper limits of limiting environmental factors (in particular, chemical compounds). Indeed, the content does not exceed the permissible limits of the human ecological sphere.

Approximate permissible concentrations (APC) of heavy metals in soils with different physical and chemical properties (gross content, mg/kg) (supplement to No. 1 to the list of MPC and APC No. 6229-91) for the elements to be determined as follows: for soils close to neutral (loamy and clayey) **Zn** – 220 mg/kg; **Cd** – 2.0 mg/kg; **Pb** – 130 mg/kg; **Cu** – 132 mg/kg [18].

Lead, cadmium, iron, nickel, zinc, manganese, etc. enter the soil from motorways. Lead is the first element to be considered when assessing the impact of transport on soil composition. The widespread use of tetraethyl lead as an additive to petrol causes about 75 % of lead contained in it released in the form of aerosol during its combustion and dispersed in the air [8].

Lead. The most serious source of lead contamination of organisms' habitats is automobile engine exhaust. The anti-detonator tetramethyl – or tetraethyl lead – has been added to most petrols in amounts of about 80 mg/litre since 1923. When a vehicle is driven, between 25 and 75 per cent of this lead is released into the atmosphere. Lead is not a life-sustaining element. It is toxic and belongs to hazard class I. Its inorganic compounds disturb metabolism and enzyme inhibitors (similar to most heavy metals), block -SH groups of proteins, poisoning, damages of the nervous system, etc.

Cadmium and zinc. Cadmium, zinc, and copper are the most important metals in pollution studies because they are widely spread around the world and have toxic properties. Cadmium and zinc (as well as lead and mercury) are found mainly in sulphide sediments [5, 8, 9]. These elements are readily emitted into the oceans by atmospheric processes. Cadmium has a relatively high volatility; it easily penetrates into the atmosphere. Sources of atmospheric pollution by zinc are the same as cadmium. Zinc is the least toxic of all the heavy metals listed above. Cadmium is much more toxic than zinc. It and its compounds are classified as hazard

class I. It penetrates into the human body for a long period, blocks sulfhydride groups of enzymes, disrupts iron and calcium metabolism and DNA synthesis. Inhalation of air for 8 hours at a cadmium concentration of 5 mg/m³ can cause death [9, 18].

Copper. Copper is found in sulphide precipitates co-occurring with lead, cadmium, and zinc. It is present in small amounts in zinc concentrates and can be transported long distances with air and water. Absorption of large amounts of copper by humans causes Wilson's disease, with excess copper deposited in brain tissue, skin, liver, pancreas. Indeed, it can increase cell permeability, inhibits glutathione reductase, disturbs metabolism by interacting with -SH, NH_2, and COOH- groups [8-9].

Experimental part

Atomic-absorption spectrometer 'KVANT-Z' was used for analysis of metal content in solutions of soil extracts. Atomic absorption spectrometer 'KVANT.Z' is designed for quantitative elemental analysis of liquid samples of different origin and composition. The principle of operation of the spectrometers is based on the method of electrothermal Atomic Absorption (AA) spectrometry [16]. The sample to be analysed is vaporised in a graphite tube furnace heated by an electric current. The free atoms of the element to be determined absorb the resonance radiation, with the maximum absorption occurring at the analytical resonance spectral line. It is usually used for AA measurements. The graphite furnace is placed in a longitudinal alternating magnetic field [13-14].

Atomic Absorption Spectrophotometry (AAS) allows ones to determine the gross content of Si, Al, Fe, Ca, Mg, K, Na, Mn, Ti, biologically important trace elements (gross content and mobile forms) – Zn, Cu, Co, Ni, Cr, V, etc. in soils. This method can be used to determine exchangeable bases and absorption capacity, study the composition and number of water-soluble cations in soil [15]. Its main features are versatility and selectivity. Due to its high selectivity, the analyser allows ones to determine the content of a wide range of elements in samples of different composition – without or with minimal sample preparation. Worldwide AAS with Electrothermal Atomisation (ETA) and non-selective absorption corrector is a reference method for determination of low elemental contents in samples of complex composition. Control of the measurement process and processing of the obtained information is performed using a computer with the installed software.

Determination of Zn, Cd, Pb and Cu by atomic absorption spectrometry

The method of atomic absorption spectral analysis is based on the phenomenon of absorption of resonance radiation by free atoms of an element. For each element there are certain allowed states – energy levels. Consequently, there are certain emission and absorption wavelengths for each element [14].

The AA measurement uses resonance lines corresponding to transitions of atoms from unexcited to excited levels. Conversion of the sample to the atomic vapour state is performed in an analytical cell (graphite tube furnace) of an electrothermal atomiser; it is heated to element atomisation temperature to be determined according to a special temperature-time programme; it includes evaporation of the sample to a dry residue, its ashing and atomisation;

those accompanied by measurement of metal absorbance at its resonant spectral line emitted by an appropriate lamp with a hollow cathode [13, 17]. Table 1 shows the conditions of measurements on atomic absorption spectrophotometer with atomisation in graphite cuvette for Zn, Cd, Pb, and Cu.

Table 1. Conditions of analysis

Element	Wave length, nm	Slot width, nm	Ashing temperature, °C	Atomisation temperature, °C
Cd	228.8	0.2	800	1,400
Cu	324.8	0.7	1,200	2,400
Pb	283.3	0.2	1,300	2,200
Zn	213.9	0.2	700	1,600

The main stages of the study

1. Preparation of calibration solutions

We prepared operating calibration solutions in measuring flasks by serial dilution. We used nitric acid with a mass concentration of 0.1 mol/dm^3 for dilution.

When preparing operating calibration solutions, we take the solution in the following volumes: Zn – 1.0 mg/dm^3, Pb – 1.0 mg/dm^3, Cu – 0.50 mg/dm^3, Cd – 0.50 mg/dm^3 in measuring flasks 100 cm^3; mark them with nitric acid of mass concentration 0.1 mol/dm^3; mix them thoroughly. Nitric acid with a concentration of 0.1 mol/dm^3 is used as a reference solution for determining the calibration characteristic.

We added concentrated sulphuric acid to the measuring flasks with the rate of 0.5 cm^3 per 10 cm^3 of the calibration solution.

Preparation of operating calibration solutions for soil analysis is conducted in accordance with Table 2.

Table 2. Values of operating calibration solutions for soil analysis

Metal	Mass concentration of initial solution, mg/dm^3	Volume of selected reference solution, mm				
		Number of operating calibration solution				
		1	2	3	4	5
Copper, lead and zinc	2.0	20	50	100	200	400
Cadmium	0.5	4	10	20	40	80

We took the volumes of intermediate solutions of cadmium, copper, lead, and zinc with mass concentration of 2.0 and 0.5 mg/dm^3 indicated in Table 3 using dosing devices of DPV-1 type with interchangeable tips. Then we put them into measuring flasks of appropriate capacities; marked them with background solution and mixed.

Next, we put a 2 g sample weight of the analysed sample into a glass beaker; added 10 cm^3 of nitric acid with a molar concentration of 0.5 mol/dm^3; stirred and heated the mixture at 90 °C. Then we filtered the sample through a paper filter into a 100 cm^3 measuring flask; marked the solution to with bidistilled water.

2. Preparing the sample for analysis

We added a solution of the appropriate modifier (20 µg/cm^3 Pd for cadmium, copper, and lead, and 100 µg/cm^3 Mg for zinc) to a 2.0 cm^3 Eppendorf tube, marked with a prepared blank

sample and stirred. We converted to the average metal content per filter. The values resulted are subtracted by analysing the solution samples.

3. Preparation of AAS with electrothermal atomisation

The AAS is prepared for operation to measure mass concentrations of metals in accordance with the AAS operating manual.

In accordance with the AAS programme, dosing of the sample into the graphite cuvette made by a doser of the DPV-1 type and the temperature-time heating programme of the AAS atomiser for measuring the mass concentration of metals were also selected [15, 16].

However, the programme automatically sets the required temperature and measurement time for each metal.

4. Establishment of calibration dependencies

Three measurements were made when atomising the calibration sample with zero concentration of metal ion (blank sample) and at least three measurements when atomising the calibration samples in ascending order of their concentrations.

Graduation dependences for each metal are calculated by the least squares method in the coordinates: metal concentration in $\mu g/dm^3$ – analytical signal value in absorbance units using the AAS data processing programme.

5. Measurement procedure

To perform AAS measurements, the prepared solution is dosed into the graphite furnace and the mass concentration of each metal is measured according to the appropriate AAS programme. The measurement is repeated; the values of metal mass concentration are averaged, if the difference between them does not exceed the limit of repeatability.

Then the mass concentration of the element to be analysed; blank solutions is determined by the calibration characteristic according to the average value of the output signal.

The value of mass concentration of the element in solutions (C_{m1}, C_{m2} are parallel determinations and C_X) is indicated automatically when using software.

We calculated the average value of the mass fraction of the element for the two determinations ($\bar{X}^{AAC}$) by the formula:

$$\bar{X}^{AAC} = \frac{X^{AAC_1} + X^{AAC_2}}{2}, \tag{1}$$

and checked the acceptability of the results of parallel determinations by condition:

$$\frac{X^{AAC_1} - X^{AAC_2}}{\bar{X}^{AAC}} \cdot 100 \leq d, \tag{2}$$

where *d* is the standard (limit of repeatability of results of parallel determinations); *d* = 30 % [16].

Results of the analysis

Tables 3 shows the numerical values of metal concentrations obtained during the analysis for soil samples taken at distances of 5, 10 and 15 metres to the road.

Table 3. Numerical values of concentrations of determined metals in soil samples

Numerical values of metal concentrations in a soil sample taken at a distance of 5 metres to the road			
Metal	Value of the blank sample	The closest values	Arithmetic average value
Cu	0.069	0.264±0.395	0.330
Pb	0.160	0.690±0.520	0.605
Cd	0.013	0.035±0.010	0.027
Zn	0.046	0.680±0.557	0.619
Numerical values of metal concentrations in a soil sample taken at a distance of 10 metres to the road			
Metal	Value of the blank sample	The closest values	Arithmetic average value
Cu	0.069	0.270±0.341	0.306
Pb	0.160	0.645±0.523	0.584
Cd	0.013	0.019±0.024	0.021
Zn	0.046	0.462±0.414	0.438
Numerical values of metal concentrations in a soil sample taken at a distance of 15 metres to the road			
Metal	Value of the blank sample	The closest values	Arithmetic average value
Cu	0.044	0.283±0.305	0.294
Pb	0.105	0.525±0.498	0.517
Cd	0.023	0.011±0.013	0.012
Zn	0.031	0.423±0.460	0.428

We then used formulae 1 and 2 to calculate the resulting numerical values given above and obtained the following approximated average values for each individual metal (Table 4).

Table 4. Average values of the mass fraction of determined metals

Metals contained in soil samples at a distance of 5 metres to the road	Average value calculated by formulas 1 and 2	Metals contained in soil samples at a distance of 10 metres to the road	Average value calculated by formulas 1 and 2	Metals contained in soil samples at a distance of 15 metres to the road	Average value calculated by formulas 1 and 2
Cu	39.7	Cu	23.2	Cu	7.5
Pb	28.1	Pb	20.9	Pb	5.2
Cd	59.3	Cd	23.8	Cd	16.7
Zn	19.9	Zn	10.9	Zn	8.3

As a result of the atomic absorption spectrometer analysis, soil samples located closer to the road (at a distance of 5 metres) had higher metal content than soil samples located 10 and 15 metres to the road. Compared to APC and MPC, the indicators do not exceed the values of permissible concentrations (list of MPC and APC No. 6229-91 [17]). Indeed, motor transport has a negative impact on the pollution of soils located near the motorway.

Fig. 1 shows the results of laboratory analyses by atomic absorption spectrometry.
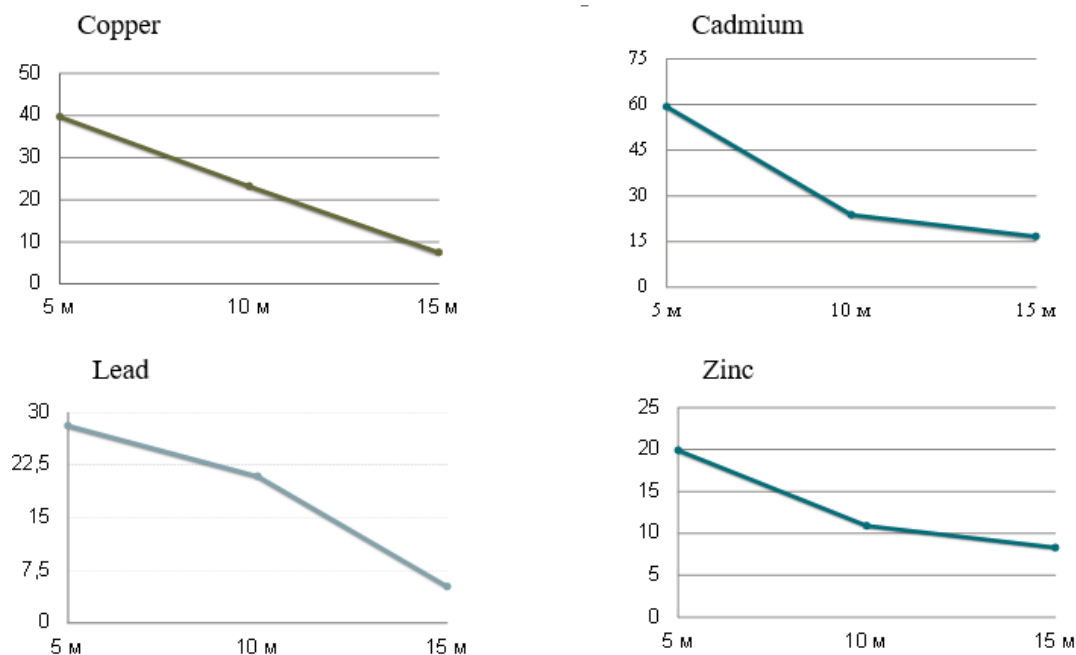
Fig. 1. Value of laboratory analyses by atomic absorption spectrometry

Conclusion

Currently, development of the automotive industry and the constant growth of vehicles have negative impact on the environment and human health. Hence, there is a necessity of this issue detailed study, development its monitoring system and search for solutions to minimise the harmful impact. Increased awareness and attention to this issue will ensure a safe environment and preserve future generations health.

References

1. **Nikiforova T.E., Vokurova D.A., Sofronov A.R.** Extraction of copper ions by a sorbent based on flax fiber modified with L-arginine // *From Chemistry Towards Technology Step-by-Step*. 2022. Vol. 3, Iss. 3. Pp. 17-26. Available at: https://chemintech.ru/ru/nauka/issue/5031/view DOI: 10.52957/27821900_2022_03_17 (accessed 03.07.2024) (in Russian).

2. **Vardhan K.H., Kumar P.S., Panda R.C.** A review on heavy metal pollution, toxicity and remedial measures: current trends and future perspectives // *J. Mol. Liq.* 2019. Vol. 290. 111197. DOI: 10.1016/j.molliq.2019.111197.

3. **Lindholm-Lehto P.** Biosorption of heavy metals by lignocellulosic biomass and chemical analysis // *BioRes.* 2019. Vol. 14(2). Pp. 4952–4995. DOI: 10.15376/biores.14.2.Lindholm-Lehto.

4. **Vodyanitsky Yu.N.** Prirodnye i tekhnogennye soedineniya tyazhelyh metallov v pochvah [Natural and anthropogenic heavy metal compounds in soils] // *Pochvovedenie [Soil Science].* 2014. No. 4. Pp. 1-131. DOI: 10.7868/S0032180X14040108 (in Russian).

5. Technogenic pollution of the natural environment: [website]. URL: https://studfile.net/preview/7615608/page:9/ (accessed 03.07.2024) (in Russian).

6. **Vodyanitsky Yu.N.** Zagryaznenie pochv tyazhelymi metallami i metalloidami i ih ekologicheskaya opasnost' (analiticheskij obzor) [Soil pollution by heavy metals and metalloids and their environmental hazard (analytical review)] // *Pochvovedenie [Soil Science].* 2013. No. 7. P. 872 DOI: 10.7868/S0032180X13050171 (in Russian).

7. **Boltunova A.D., Smirnova S.V., Soltis V.V.** Nakoplenie tyazhelyh metallov v pochvah pod vliyaniem promyshlennogo proizvodstva [Accumulation of heavy metals in soils under the influence of industrial

production] // *Sovremennye problemy nauki i obrazovaniya [Modern problems of science and education]*. 2017. No. 4. URL: https://science-education.ru/ru/article/view?id=26637 (accessed 03.07.2024) (in Russian).

8. **Ladonin, D.V.** Soedineniya tyazhelyh metallov v pochvah - problemy i metody izucheniya [Heavy metal compounds in soils - problems and methods of study] // *Pochvovedenie [Soil Science]*. 2002. No. 6. Pp. 682-692 (in Russian).

9. **Serdyukova. A.F., Barabantshchikov D.A.** Posledstviya zagryazneniya pochvy tyazhelymi metallami [Consequences of soil pollution by heavy metals] // *Molodoj uchenyj [Young Scientist]*. 2017. No. 51 (185). Pp. 131-135. URL: https://moluch.ru/archive/185/47382/ (in Russian).

10. **Vodyanitsky Y.N., Ladonin D.V., Savichev A.T.** Soil pollution by heavy metals. Lomonosov Moscow State University. - Moscow : Typography of Rosselkhozakademia, 2012. - 304 p. (in Russian).

11. **Minkina T.M., Moguzova G.V., Nazarenko O.G.** Composition of heavy metal compounds in soils. – Rostov-on-Don: Southern Federal University, 2009. - 208 p. (in Russian).

12. **Kosheleva N.E., Kasimov N.S., Vlasov D.V.** Faktory nakopleniya tyazhelyh metallov i metalloidov na geohimicheskih bar'erah v gorodskih pochvah [Factors of heavy metal and metalloid accumulation at geochemical barriers in urban soils] // *Pochvovedenie [Soil Science]*. 2015. No. 5. Pp. 536-553 (in Russian).

13. **Ermachenko L.A., Ermachenko V.M.** Atomic absorption analysis with graphite furnace: Methodical manual for practical use in sanitary and hygienic research M.: PAIMS, 1999. 220 p. (in Russian).

14. **Gromovik A.I., Yonko O.A.** Modern instrumental methods in soil science. Theory and practice. Voronezh, 2010. - 60 p. (in Russian).

15. **Pupyshev A.A.** Atomic absorption spectral analysis. - M.: Technosphere., 2009. - 782 p. (in Russian).

16. Atomic absorption spectrometer 'KVANT.Z' Operation Manual GKNZH.84.000.000.000 RE, Moscow, 2019 (in Russian).

17. GD 52.24.535-2019. Guidance document. Mass fraction of cadmium, cobalt, lead and chromium in bottom sediments. Methods of measurements by atomic absorption method using microwave processing of samples (put into application by the Order of Roshydromet on 25.06.2019 N 296) (in Russian).

18. On approval of sanitary rules and norms SanPiN 1.2.3685-21 'Hygienic norms and requirements to ensure safety and (or) harmlessness for humans of habitat factors' (as amended on 30 December 2022) (in Russian).