EXPERIMENTAL INVESTIGATIONS OF HEAVY METALS CONCENTRATIONS IN THE GROUND OF SECTION KAZLU RUDA – JURE

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Abstract. The extent of exploited railways in Lithuania makes 1905 km. Railway section Kazlu Rūda – Jūrė was selected for ground pollution with heavy metals investigations due big intensity of train transport in this section: about 40 trains pass this section per day. The distance of this section is about 5 km. Sampling places were in the similar ground level as railway bed. That is why relief's influence to pollutants dispersion in many ground sampling places was very small and was not evaluated. Several authors calculated that zone of maximum pollutants fall out intensivity can reach till the Sanitary Protection Zone (SAZ) of railway - 100 meters. Different distance from railway bed was selected (10, 50, 100, and 200 m) for research. Sampling was carried out in both sides of railway ground. Concentrations of heavy metals: nickel (Ni) and zinc (Zn) were determinated with help of atomic absorption spectrophotometric method with acetylene-air flame and with graphite furnace. The results of research showed that concentrations of Zn and Ni did not exceed permissible concentrations common for Marijampolė region ground in distance of SAZ and further except first point (100 m) for zinc.

Keywords: railway, ground pollution, heavy metals, zinc, nickel.

1. Introduction

Heavy metals falls to environment from different sources: industry, energetic objects, agriculture, roads and railway transport. They are toxic and harmful even at low concentrations [1]. Heavy metals have complex negative impact on human health, animals, flora and fauna [2-8]. Zinc, copper and lead are three of the most common heavy metals released from road travel, accounting for at least 90 of the total metals in road runoff. Lead concentrations, however, consistently have been decreasing since leaded gasoline was discontinued. Smaller amounts of many other metals, such as nickel and cadmium, are also found in road runoff and exhaust. About half of the zinc and copper contribution to the environment from urbanization is from automobiles [9]. Brakes release copper, while tire wear releases zinc. Motor oil also tends to accumulate metals as it comes into contact with surrounding parts as the engine runs, so oil leaks become another pathway by which metals enter the environment [10]. Most heavy metals are cations, meaning they carry a positive charge. Soil particles and loose dust also carry charges. Most clay minerals have a net negative charge. Soil organic matter tends to have a variety of charged sites on their surfaces, some positive and some negative. The negative charges of these various soil particles tend to attract and bind the metal cations and prevent them from becoming soluble and dissolved in water. The soluble form of metals is thought to be more dangerous because it easily is transported and more readily available to plants and animals. By contrast, soil bound metals tend to stay in place. Today, the use of locomotives to transport freight is on the rise, and nearly all locomotives are powered by diesel engines. As a result, these "smokestacks on rails" contribute significantly to national air pollution [11].

Direct or from air they falls in the soil and for that reason can pollute groundwaters. Also heavy metals can fall in nutrite chain by plants. These both ways cause negative impact for human health. In Lithuania were investigated others sources of heavy metals impact, but railway pollution was not still investigated so widely. The main works are concerned with railway pollution with oil products [12].
Carried out experimental investigations in the ground of chosen railway section Kazlų Rūda – Jūrė will be helpful to evaluate impact of railway to the environment. Purpose of the work was to evaluate pollution of heavy metals (Zn and Ni) in the ground of chosen railway section section Kazlų Rūda – Jūrė.

2. Methodology of investigation

The objective of researches: evaluation of heavy metals concentration (Ni and Zn) in the ground near railway with help of atomic absorption spectrophotometer. For determination of heavy metals concentrations in the ground were taken samples of ground in 40 points of chosen railway section Kazlų Rūda – Jūrė. Envelope principle was used for ground sampling: were taken 5 sub samples from 0-20 cm depth and then mixed and this mixture was analysed. Roots, leaves, stones and etc. was eliminated from samples. Sample mass was approximately 100 g.

Samples of ground were taken in 10-17 th of September in 2007. Temperature of ambient air was 14 -19 °C, atmospheric pressure – 101.1-102.2 kPa, specific humidity of air – 58 - 76%.

The experimental research on the heavy metals concentrations measurement in the ground was carried out in the scientific laboratory of the Department of Environmental Protection at Vilnius Gediminas Technical University. The map of the research object is presented in Fig. 1.

Necessary solutions to compose calibration graph
1. Preparation of blank solution for calibration curve: mix 180 ml HCl (37%) and 60 ml HNO3 (65 %) with 500 ml deionised water in 1000 ml measuring flask and dilute with deionised water till the mark.

Solutions of metals (chrome, nickel) for calibration curve are prepared from standard metals solutions (≈ 1000 mg/l metal, 2% HNO3).

Add with pipette 0.20 ml, 0.50 ml, 1.00 ml, 1.50 ml and 2.00 ml of nickel solution (≈ 1000 mg/l) to the 1000 ml volume measuring flask. To every flask added 180 ml HCl and 60 ml HNO3. Concentration of nickel in these solutions is equal to 0.20 mg/l, 0.50 mg/l, 1.00 mg/l, 1.50 mg/l and 2 mg/l.

100 g of ground sample must be dried in porcelain plates in 105 °C temperature 2 hours. After this sample of ground passed through 1 mm mesh sieve.

100 g of ground sample additionally was dried in 105 °C 30 min. After this sample is cooled in dessicator and weighted. After this sample is poured in to the plastic vessel and 12 ml of „Aqua Regia“ was added. Mineralization is carried out according description of EPA method. Temperature and time of digestion was selected according EPA (Environmental Protection Agency) method. After digestion vessel with sample was cooled till the room temperature and solution was filtered thorough glass filter to 50 ml measuring flask. Vessel was rinsed with 10 ml of
deionised water. These liquid was filtered thorough glass filter also. After it solution in flask was diluted till the mark with deionised water. Heavy metals concentrations in ground samples are analyzed with AAS finishing [13-17] Buck Scientific 210 VGP atomic absorption spectrometric with air-acetylene flame and with graphite furnace [14-17] was used. The concentration of heavy metals in the ground was determined from the following equation:

\[ c_{\text{dry soil}} = \frac{c_{\text{solution}} \cdot 0.05 \cdot 1000}{m_{\text{soil}}}; \text{mg/kg}, \]  

(1)

where: \( c_{\text{solution}} \) – concentration of metal in solution, mg/l, 
\( m_{\text{soil}} \) – taken weight of dry soil, g.

For comparison of chemical elements concentrations with background concentrations in Marijampolė region level of technogenic pollution illustrating index – concentration coefficient (K_k) was calculated. It can be calculated from the following equation [18]:

\[ K_k = \frac{C}{F}; \]  

(2)

where: \( C \) - concentration of element in the ground, mg/kg; 
\( F \) – background concentration of element in the ground, mg/kg.

After summation of all potentially toxic heavy metals K_k it was determined level of pollution. Index Z was calculated from the following equation [18]:

\[ Z = \sum_{i=1}^{n} K_k - (n - 1), \]  

(3)

where: \( n \) – number of elements-pollutants, 
\( K_k \) – concentration coefficients.

3. Results of the investigation

In Lithuania geochemical mapping of urban areas was started in Vilnius city in 1985. Topsoil, stream sediments, snow cover, manufactory dust and other sampling media are used in ecogeochimical investigations. Furthermore, a sanitary assessment of urban soil is carried out on the basis of available geochemical data and the soil quality standard of Lithuania HN 60:2004. The soil contamination with heavy metals is estimated according to the highest allowable concentrations (HAC) and the total contamination index Z.

The soil geochemical background values obtained by geochemical mapping of natural areas are always used for assessment of contaminated urban areas. Part of geochemical background and contamination data is published in Geochemical Atlas of Lithuania.

The extent of exploited railways in Lithuania makes 1905 km. There are not experimental data about ground near railway pollution with heavy metals. That is why it was very important to do experimental research on heavy metals concentration evaluation in ground. Railway section Kazlų Rūda – Jūrė was selected for ground pollution with heavy metals investigations. Big intensity of train transport is common for this section: about 40 trains pass this section per day. The distance of this range is about 5 km. Sampling places were in the similar ground level as railway bed. That is why relief’s influence to pollutants dispersion in ground sampling places was very small. Several authors calculated that zone of maximum pollutants fall out intensivity can reach till the Sanitary Protection Zone (SAZ) of railway - 100 meters. Different distance from railway bed was selected (10, 50, 100, and 200 m) for research. Sampling was carried out in both sides of railway ground. There are many heavy metals spreaded in the environment especially in the ground, but not all of them are typical for railway transport. Zinc and nickel can be connected with emissions to the air from train’s fuel and with other reasons.

Concentrations of selected heavy metals: nickel (Ni) and zinc (Zn) were determined with help of atomic absorption spectrophotometric method with acetylene-air flame and graphite furnace and recalculated to dry soil.

Maximum allowed concentrations of heavy metals in ground are presented in the hygienic norm HN 60:2004 [19]. Maximum allowed concentration for zinc is equal to 300 mg/kg and for nickel – 75 mg/kg.

After measurement of heavy metals concentrations they were compared with median values of heavy metals in Marijampolė region. Median values of heavy metals concentrations in ground are presented in geochemical atlas of Lithuania [20]. Median values of microelements in topsoil of administrative districts of region of Marijampolė are equal to 15,1 mg/kg for nickel and 26,5 mg/kg for zinc. Description of selected points for heavy metals research in the ground near railway is presented below.

First point is 1 km from Jūrė railway station. There are no houses, many trees, around grass, no agriculture.

Second point is 2 km from Jūrė railway station, very close from forest, in this area was not houses and no agriculture.

Third point is 3 km from Jūrė station. No houses, many trees, around grass, no agriculture.

Fourth point is 4 km from Jūrė. There are a few houses.

Fifth point is 5 km from Jūrė, near Kazlų Rūda. There are a few houses.
The results of the experimental research on heavy metals concentrations in the ground in 10 meters distance from railway are presented in Fig. 3. Experimental research of Zinc concentrations measurement in the ground of right side in 10 metres distance from railway showed that minimal concentration was 26.8 mg/kg (second point) and maximal concentration - 31.13 mg/kg (first point). Analogical measurements carried out in the ground of left side in 10 metres distance from railway showed that minimal concentration was 25.26 mg/kg (second point) and maximal concentration - 30.60 mg/kg (fifth point). If we compare these values of zinc concentration in the ground with permissible in Marijampolė region we will see, that zinc concentration in the ground in ten metres distance from railway are bigger than permissible concentrations (26.5 mg/kg) (Fig. 3) in all points except left side of second point. The reason of this exceeding could be anthropogenic pollution of railway transport.

![Fig 3. Zinc concentration in the ground in 10 m distance from railway](image)

Zinc concentrations in the ground in 50 m distance from railway are presented in Fig. 4. Experimental research of Zinc concentrations measurement in the ground of right side in 50 metres distance from railway showed that minimal concentration was 25.4 mg/kg (second point) and maximal concentration - 29.33 mg/kg (first point). Analogical measurements carried out in the ground of left side in 100 metres distance from railway showed that minimal concentration was 21.43 mg/kg (third point) and maximal concentration - 26.59 mg/kg (first point). If we compare these values of zinc concentration in the ground with permissible in Marijampolė region we will see, that zinc concentration in the ground in 100 metres distance from railway are bigger just in the first point in the right side than permissible concentrations (26.5 mg/kg) (Fig. 5).

The reason of this exceeding could be anthropogenic pollution of railway transport. Zinc concentrations in the ground in 100 m distance from railway (Sanitary Protection Zone) are presented in Fig. 5. Experimental research of zinc concentrations measurement in the ground of right side in 100 metres distance from railway showed that minimal concentration was 23.76 mg/kg (second point) and maximal concentration - 27.54 mg/kg (first point). Analogical measurements carried out in the ground of left side in 100 metres distance from railway showed that minimal concentration was 21.43 mg/kg (third point) and maximal concentration - 26.59 mg/kg (first point). If we compare these values of zinc concentration in the ground with permissible in Marijampolė region we will see, that zinc concentration in the ground in 100 metres distance from railway are bigger just in the first point in the right side than permissible concentrations (26.5 mg/kg) (Fig. 5).

The reason of this situation could be also anthropogenic pollution of railway transport and of course the distance from the railway. Zinc concentrations in the ground in 200 m distance from railway (after SAZ) are presented in Fig. 6. Experimental research of zinc concentrations measurement in the ground of right side in 200 metres distance from railway showed that in this distance the received concentrations were not bigger than permissible concentrations (26.5 mg/kg) in Marijampolė region (Fig. 6).

In all selected point in both sides of railway section Kazlų Rūda – Jūrė ground concentrations of zinc were smaller than highest allowable concentrations (HAC). The total contamination index $Z$ is related to the criteria of human. According to this parameter in all selected points common pollution level belong to first pollution category ($Z<16$).
Nickel concentration in the ground in 10 m distance from railway is presented in Fig. 7. Experimental research of nickel concentrations measurement in the ground of right side in 10 metres distance from railway showed that minimal concentration was 15,66 mg/kg (third point) and maximal concentration - 16,32 mg/kg (fourth point). Analogical measurements carried out in the ground of left side in 10 metres distance from railway showed that minimal concentration was 15,61 mg/kg (second point) and maximal concentration - 16,42 mg/kg (third point). If we compare these values of nickel concentration in the ground with permissible in Marijampolė region we will see, that nickel concentration in the ground in ten metres distance from railway are bigger than permissible concentrations (15,1 mg/kg) just in third point on left side in all others points concentrations are smaller than permissible (Fig. 7). The reason of this situation could be the distance from railway road and also environment impact, because there are around some trees.

Experimental research of nickel concentrations measurement in the ground of right side in 50 metres distance from railway showed that maximal concentration 14,55 mg/kg (fifth point) and minimal concentration - 12,43 mg/kg (fourth point). Analogical measurements carried out in the ground of left side in 50 metres distance from railway showed that minimal concentration was 13,12 mg/kg (fourth point) and maximal concentration - 15,53 mg/kg (third point). If we compare these values of nickel concentration in the ground with permissible in Marijampolė region we will see, that nickel concentration in the ground in fifty metres distance from railway are bigger than permissible concentrations (15,1 mg/kg) just in third point on left side in all others points concentrations are smaller than permissible (Fig. 8). The reason of this situation could be the distance from railway road and also environment impact, because there are around some trees.

Experimental research of nickel concentrations measurement in the ground of right side in 100 metres distance from railway showed that maximal concentration 12,43 mg/kg (third point). Analogical measurements carried out in the ground of left side in 100 metres distance from railway showed that maximal concentration - 13,45 mg/kg (first point). If we compare these values of nickel concentration in the ground with permissible in Marijampolė region we will see, that nickel concentration in the ground in one hundred metres distance from railway are smaller than permissible concentrations (15,1 mg/kg) in all points (Fig. 9).
Nickel concentrations in the ground in 100 m distance from railway (SAZ) are presented in Fig. 9.

The reason of this situation could be also the distance from railway road and also environment impact, because there are around trees.

Nickel concentrations in the ground in 200 m distance from railway (after Sanitary Protection Zone) are presented in Fig. 10.

In all selected point in both sides of railway section Kazlų Rūda – Jūrė ground concentrations of nickel were smaller than highest allowable concentrations (HAC). According to parameter Z in all selected points common pollution level belong to first pollution category (Z<16).

The same situation is connected with zinc. That is why pollution with Ni and Zn level in all selected points of ground is acceptable and there are no dangerous to human health.

4. Conclusions

1. Results of carried out experimental research shows that concentrations of zinc in the ground in ten metres distance from railway are bigger than permissible in Marijampolė region in all selected points except left side of second pint. Concentrations of zinc in ground are smaller than permissible in Marijampolė region just in both sides of second point and in left side of third point (50 m). Concentrations of zinc in ground are bigger than permissible in Marijampolė region just in first point and in distance of 200 m concentrations of Zn in the ground are in the similar level or smaller than permissible concentration.

2. Results of carried out experimental research shows that concentrations of nickel in the ground in ten metres distance from railway are bigger than permissible in Marijampolė region in all points.
Concentrations of nickel in ground are bigger than permissible in Marijampolė region in left side of third point (50 m). In distance of SAZ (100 m) and further – 200 m - concentrations of Ni were smaller than permissible in all points.

3. According to the data of 40 ground samples analysis were are determined these biggest values of heavy metals concentration coefficients: Ni (1,09) and Zn (1,17).

4. In all selected point in both sides of railway section Kazlų Rūda–Jūrė ground concentrations of zinc and nickel were smaller than highest allowable concentrations (HAC) – 300 mg/kg (Zn) and 75 mg/kg (Ni).

5. According to the total contamination index Z in all selected points common ground pollution level belong to first pollution category (Z<16).

References


