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Heavy Metal Emissions from Linear Sources and Polluted Soil in The Capital City of Poland

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Abstract: Human activities such as transport contribute to the environmental degradation. Therefore, the aim of the study was to determine the level of contamination of soils, from different districts of big cities of central Europe, with heavy metals: zinc, lead, and nickel. The samples were taken from the top, sodded soil layer. Each single sample weigh was about 1 kg taken from 1 m^2 measuring station. Soil samples were dried at room temperature. The airborne dry soil was thoroughly mixed and sieved through a 1 mm nylon sieve. The study included analysis of which type of metals is washed out under the influence of abiotic factors (bioavailable forms) and demonstrating how spatial development affects the accumulation of selected heavy metals in the soil. The results indicated that heavy metals emitted to the ground layer of the atmosphere accumulate in the immediate vicinity of communication routes. Moreover, based on the analysis of interrelationships of zinc, lead, and nickel concentrations, it has been shown that there is a common source of their emission to soil. Furthermore, the thesis that the concentration of metals was dependent on the soil reaction was not confirmed.

Keywords: soil degradation; heavy metals contamination; zinc, lead and nickel contamination

1. Introduction

The constant development of urban agglomerations impose protection of natural environmental surrounding this area by improving the soil's condition, polluted from different sources, e.g. washing the soil with rainwater rich with heavy metals (Piecuch et al. 2015, Polanczyk et al. 2018, Peng et al. 2020). Soils are contaminated with various chemical compounds, e.g. atmospheric dust, sewage runoff, waste dumps, industrial settlers as well as waste sediments, sewage and liming of soils (Nathanail and Bardos 2004, Polanczyk et al. 2018). Urban soils accumulate pollution from many local sources, that have the potential to migrate inside soil (Pierzynski et al. 2005, Zieminska-Stolarska et al. 2015). The form of soil's contamination is strongly dependent on the source of emissions, the physical and chemical properties of soils, the amount and quality of colloids in soils, the pH, sorption properties, as well as the soil redox potential (Liu et al. 2019, Polanczyk et al. 2019). Drinking water resources should be particularly protected against the penetration of pollutants (Czapczuk et al. 2017).

Depending on the climatic conditions and the character of terrain, dust and aerosol particles can be transported by wind over long distances and then get into the soil in the form of dry precipitation, with rainfall, snowfall, and surface runoff. According to Kabaty-Pendias (Ebrahimi-Najafabadi et al. 2019) research, in Poland during the year falls: cadmium – 5 g/ha/year, copper – 39 g/ha/year, lead – 200 g/ha/year, zinc – 540 g/ha/year. For example, precipitation dust in Krakow consists mainly of fine particles of silicate enamel, sulphate calcium and iron oxides. Whereas tests of heavy metal content in precipitation dust carried out in residential and industrial districts of Lublin showed that the maximum concentrations of selected heavy metals were in: zinc – 3154 ppm, manganese – 2479 ppm, copper – 612 ppm, lead – 479 ppm and nickel – 132 ppm (Vehicles 2004). Concentration of heavy metals in rainwater is a sensitive indicator of atmospheric air pollution and is strongly correlated with dust pollution. Street dust is relatively rich in lead and other heavy metals. The lead content of Zurich's street dust is 2000 ppm, which is more than 20 times higher than the natural value (Zhang et al. 2019). Equally high concentrations of selected heavy metals were observed in precipitation dust collected along the Lazienkowska street in Warsaw. Lead aerosol, expelled from the exhaust system of vehicles, moves along with the air currents falling to the areas adjacent to the motorway traffic routes, the significant range of this precipitation is about 100 m. The movement of lead compounds from linear emission sources, which are communication routes, is forced mainly through air mass movements. Metals generated when burning gasoline are stable for 4 up to 7 days and then transform into less soluble forms such as sulfates, carbonates, phosphates and oxides (Pernille et al. 2006, Guan et al. 2018). The process of converting halogenated lead into insoluble forms strongly depends on climatic conditions. Despite restrictions on the use of heavy metal compounds in fuels, the greatest risk of soil pollution with heavy metals still comes from motor vehicles. The specificity of this threat is the banded arrangement of polluted areas. The content of heavy metals in soils adjacent to communication routes, parking areas as well as distance from the road (Martínez 2001). The level of the negative impact of road transport on the quality of the urban environment depends on the following factors: the number of vehicles, vehicle structure, speed, technical condition of the vehicle, the quality of fuel, traffic appearance as well as road quality. The source of lead compounds' emission are fuels. The introduction of lead tetraethyl and tetramethyl lead as a means of increasing octane number has caused that communication routes have become the main source of this metals (Zhao et al. 2019). Data in the literature indicate that communication sources account for 50 to 75% of lead emissions in urban areas (Backstrom et al. 2003). Despite the withdrawal from sales with the beginning of universal petrol replacing lead and restrictions to 0.005 mg/l at the producer and 0.013 mg/l at the distributor of lead compounds, there was no drastic decrease in the content of lead in soils. The reason for this is that the accumulation of metal in earlier years was so great that even limiting its content in fuel, did not cause a significant decrease its concentration in soil. In addition, lead-fueled cars, despite the change in gasoline used, contain in the engine installation residues of lead compounds accumulated in engine oils, lubricants and others (Ebrahimi-Najafabadi et al. 2019). The battery electrodes contain lead, zinc, iron, nickel, or cadmium. Lubricating oils contain heavy metals as well as oxidation and thermal decomposition products of oil and fuel. Zinc, calcium, lead, and magnesium oxides are used as additives to accelerate the vulcanization process of tires. For example, zinc oxide has been detected in the tire tread in an amount of 1-2%. When the tires wear off, it gets into the environment, thus increasing the level of zinc up to several hundred mg/kg in soils along roads (Öborn & Linde 2001). Corrosion of vehicle parts contributes to soil pollution with dust containing substances used to manufacture these parts. Traces of elements such as vanadium, nickel, iron, magnesium and others are also present in bitumens (Ashayeri & Keshavarzi 2019).

Therefore, the aim of the study was to determine the level of contamination of soils, from different districts of big city of central Europe, with heavy metals: zinc, lead, and nickel. In the introduction chapter analyzed problem was described. In the methodology the samples, applied devices and area of sample collecting was described. Finally, the results were presented in the results chapter and concluded in conclusion chapter.

2. Materials and methods

2.1. Characterization of the analyzed urban area

In the area of central Warsaw seven points for sample collection were chosen (Fig. 1). 1 – South Praga, Przyczółek Grochowski, al. The United States; a green belt between traffic lanes over the Gocławski Canal; From the north – allotments; from the south – Gocławskie Lake with adjacent green areas and newly built apartment blocks. Six-lane roadway. 2 – Center, Łazienki Królewskie near the Łazienki Ponds; From the east – Łazienki Ponds, park area. 3 – Mokotow, al. Independence at the height of the National Library; a green belt between the track and the lane; Buildings a few hundred meters from the road, park area. Six-lane road, track, bus stop. 4 – Center, intersection of Solidarnosci al. with Andersa street and Square Banking; Urban buildings, compact. The intersection of an eight-lane roadway with a six-lane roadway; track crossing; subway. 5 – Ochota, Wawelska street, approximately 50 m from the intersection with Grojecka street and approx. 100 m from the Aviator Monument; green belt between traffic lanes; Urban buildings, compact. Six-lane roadway. 6 – Ochota, Wawelska street, approximately 50 m from the intersection with Grojecka street and approx. 100 m from the Aviator Monument; the area behind compact buildings adjacent to Wawelska street. A green area between residential buildings, adjacent to a car park intended for residents. 7 – Downtown, Saxon Garden, central part; park area. Samples from measuring points 2 and 7 were taken to determine the geochemical background of the elements studied. Three conscript series were made: in March, April and May 2019.

Fig. 1. Sampling points

Fig. 2a shows the collection point no. 2 and Fig. 2b its vicinity, i.e. Lazienkowska Route. On the other hand Fig. 3 shows the collection point no. 7.

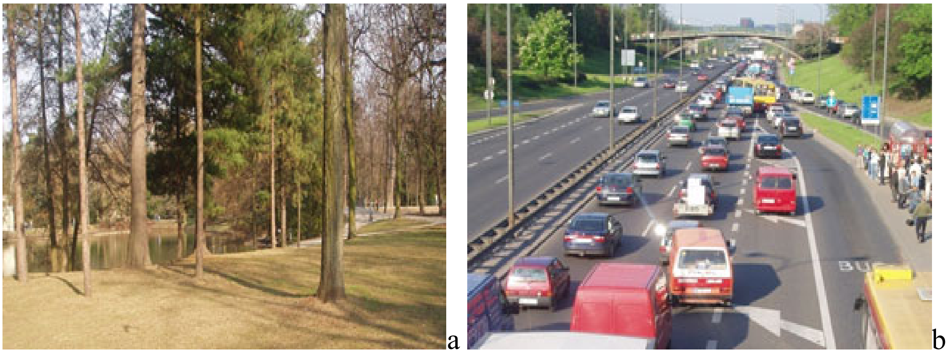

Fig. 2. a) Collection point no. 2; b) The vicinity of the Lazienkowska Route

Fig. 3. Collection point no. 7

2.2. Research methodology

In the laboratory scale spectrometer PU 9100X / 74 (Philips, England) was applied. The following reagents and solutions were applied: perchloric acid 70% (d = 1.67 g/ml), nitric acid 65% (d = 1.40 g/ml), acetic acid, glacial, part-d, deionized water as well as standard solutions: Zn: 1.5 mg/l, Pb: 5.0 mg/l, Ni: 5.0 mg/l.

Each time the sample of material was taken from the top (0-0.2 m), sodded soil layer. To obtain reliable results, each single sample weighing about 1 kg was a mixture of three smaller (about 300 grams) taken from a 1 m^2 measuring station. Soil samples were dried at room temperature. The airborne dry soil was thoroughly mixed and sieved through a 1 mm nylon sieve.

The wet clay mineralization variant based on concentrated nitric and perchloric acids was used to decompose the clay fraction of soil samples. Soil samples weighing 1 g were placed in 50 ml quartz flasks, to which 5 ml HNO_3 and 3 ml $HClO_4$ were added. Quartz coolers with a small amount of deionized water were placed in the neck of the flasks and heated on the burner until white fumes appeared. The mineralization time depend on the sample ranged from 40 to 90 minutes. The resulting solution was filtered on medium filters and then quantitatively transferred to 100 ml quartz volumetric flasks and made up to volume with deionized water. After wet mineralization, the content of zinc, lead and nickel in soil samples was determined directly by atomic absorption spectrometry with flame atomization. A 100 mm burner fed with a stoichiometric mixture of air and medical acetylene (acetylene A) was used. The flame temperature was 1200°C.

Hollow cathode lamps made by Philips were used as the radiation source. The spectrometer was program-controlled – Unicam Atomic Absorption – "Data Station ver. 1.7" from Unicam.

An attempt to assess the degree of toxicity was used according to the procedure recommended by the American Environmental Protection Agency (EPA), enabling the determination of toxicity and leaching potential of heavy metals from soils (TCLP). Soil samples were extracted with acetic acid solution.

The determined Corg content is the total amount of soil components that volatilize at 550°C during roasting. The dried soil sample with a mass was calcined in an electric furnace for 2 h. Then it was cooled in a desiccator and weighed.

3. Results and discussion

The highest concentration of lead (392 ±11.3 mg/kg s.m.) was recorded in samples taken near Lazienkowska Road, while the lowest (25.7 ±0.6 mg/kg s.m.) from the intersection area at Bankowy Square. The average lead concentration was observed in samples from the Lazienki Park and the Saxon Garden and was about 65 ±1.4 mg/kg s.m. While the highest value of zinc (728.2 ±22.1 mg/kg s.m.) were observed in samples from the area between residential buildings with the adjacent parking. Also, in this case, the metal concentration in the sample from Banking Square was lower than the concentration in the soil sample from control sites and reached the lowest value there. Relatively low concentrations were noted for nickel in all samples (Fig. 4-6). These Figures show the concentration of metals at the collection points.

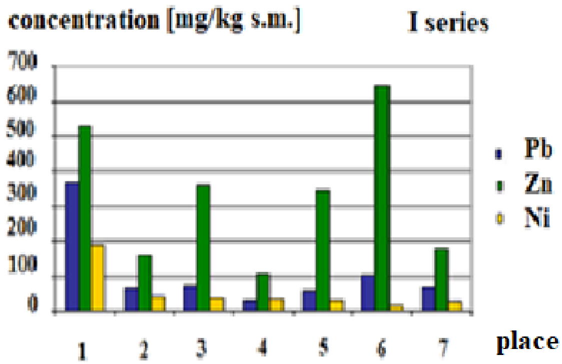

Fig. 4. Metal concentration in the soil for the first measurement series

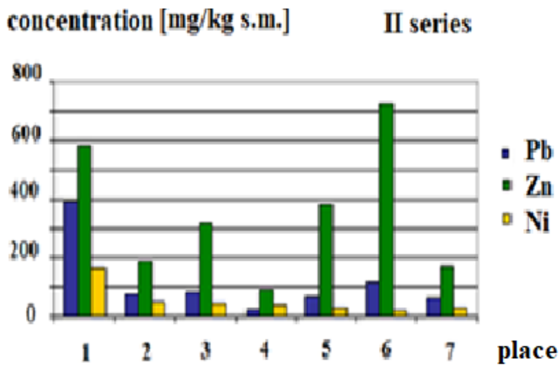

Fig. 5. Metal concentration in the soil for the second measurement series

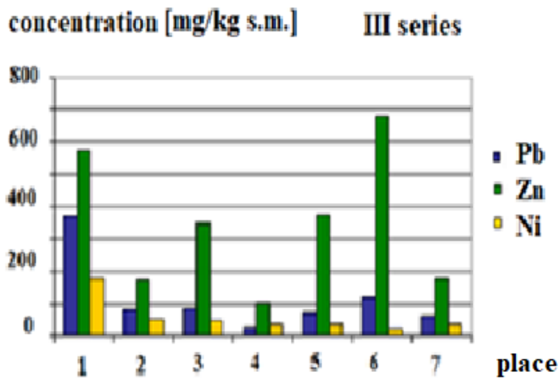

Fig. 6. Metal concentration in the soil for the third measurement series

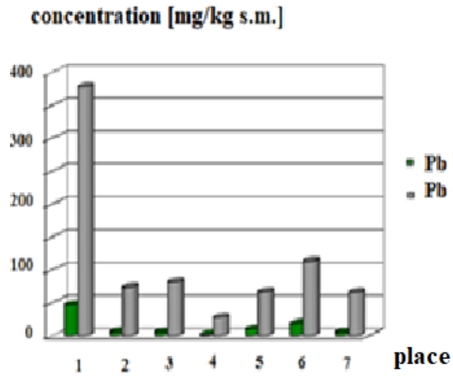

Fig. 7. Average content of lead in living organisms in relation to the average content of total lead (in mg/kg s.m)

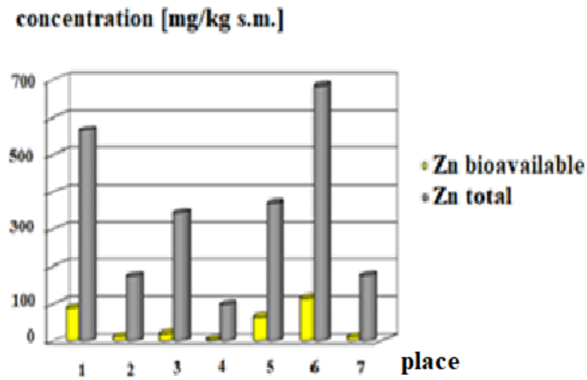

Fig. 8. Average content of zine in living organisms in relation to the average content of total zine (in mg/kg s.m)

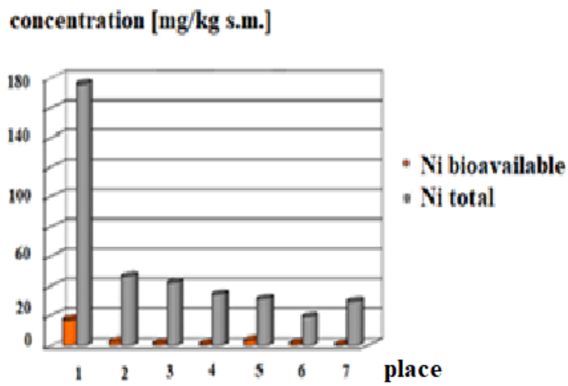

Fig. 9. Average content of nickel in living organisms in relation to the average content of total nickel (in mg/kg s.m.)

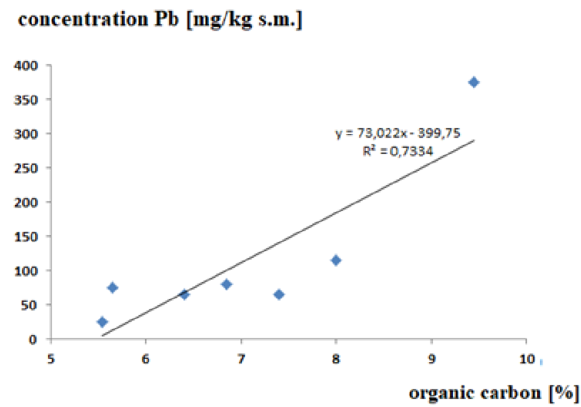

Fig. 10. Relationship between lead concentration and organic carbon content

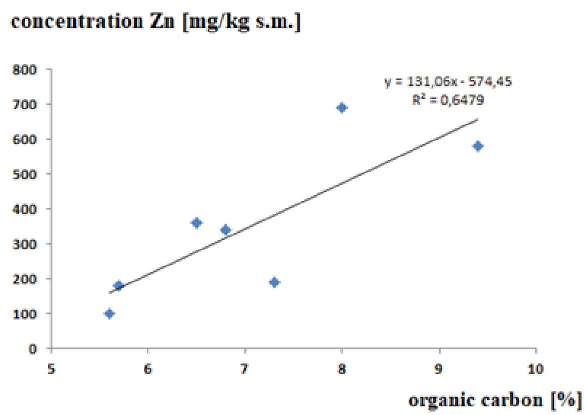

Fig. 11. Relationship between zinc concentration and organic carbon content

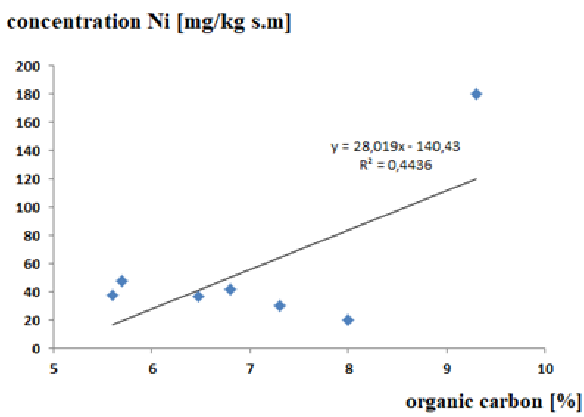

Fig. 12. Relationship between nickel concentration and organic carbon content

Analysis of concentration of selected metals in individual samples indicated that the highest concentrations of zinc are taken at place no. 1 with the highest traffic intensity and the strongest tendency to form traffic jams (Fig. 7 and Fig. 8). The values of lead emissions at the same site were in relation to the concentration of lead at site no. 5, which was at the same height as in station no. 6, but between lanes where lower Pb concentrations were recorded. At the same time, such a low (in comparison to no. 6) concentration of trace elements on a street with such a high traffic volume may indicate that along with the planting and care of greenery, the top layer of soil is replaced or mixed with its deeper layers, thus giving lower concentration values. A similar conclusion may be drawn when analyzing the results of samples taken from Banking Square. The determined concentrations are even lower than those in soil samples taken from areas recognized as reference points (background). Nickel soil pollution was negligible and oscillates within the range considered as a backdrop for urban areas. The general tendency indicates that in soils contaminated with one element, the content of other metals increased proportionally. The thesis that in the areas of anthropopressure, an increase in the concentration of one type of metals was in line with the general pollution of the soil environment. An analysis of the spatial arrangement of buildings gave grounds to conclude that in places where air traffic was restricted by buildings, the dust fall of heavy metals from motor vehicles was increased. The presented results of the reaction test showed that it did not have an impact on the level of soil pollution with heavy metals.

It was also observed that soil had limited capacity to absorb pollutant loads. It was investigated that the main problem of the automotive industry is the emission of zinc compounds. Moreover, the organic carbon content was in the range 5.0-10.3%, with the highest values obtained at place no. 1, and the lowest values in the Saxon Garden (control place). The soil organic carbon content was strongly correlated with the lead concentration (0.73), while the correlation coefficients for the other two metals were slightly lower and were: Zn (0.65) and Ni (0.44) (Fig. 10-12).

4. Conclusions

Dense network of communication routes and heavy traffic in Przyczolek Grochowski area caused that in the immediate vicinity elevated concentrations of the analyzed heavy metals were observed. This area has been identified as the most endangered among all measuring stations. However, due to the short-term scope of the analyzes, the test results may not be applicable to the long-term assessment of the degree of soil metal pollution. Moreover, heavy metals emitted to the ground layer of the atmosphere accumulate in the immediate vicinity of communication routes. Based on the analysis of interrelationships of zinc, lead, and nickel concentrations, it has been shown that there was a common source of their emission to soil.

Heavy metals are not biodegradable, they only change their forms under the influence of physical-chemical factors prevailing in soils. In areas exposed to anthropogenic pollution by heavy metals, the share of bioavailable forms of zinc, nickel and lead was higher than in control areas. While analysis of heavy metals in soils showed that road traffic was a common source of their emission.

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