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THE ANALYSIS OF HEAVY METAL POLLUTANTS EMITTED BY RAILWAY TRANSPORT

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Abstract. Recently, concern for a rapid increase in heavy metal pollutants released by railway transport has been expressed. Most of pollutant emissions from combustion processes are related to fuel consumption in the internal combustion engines of traction rolling stock. The main pollutants released into the environment cover particulate matter, volatile non-methane organic compounds, sulphur dioxide and nitrogen oxides. In this way, it is likely that the biggest polluters of the environment are traction units with internal combustion engines. However, other types of pollution are possible, where polluters can be not only traction rolling stock with the internal combustion engines, but also electric locomotive. For example, when due to friction of metals and deterioration of rolling stock wheels, heavy metals such as aerosols are released into the atmosphere, soil, surface and ground water, etc. and severely pollute the railway environment. Along with an increase in the electrification of railways, local environmental pollution is likely to be increased in the future. High pollution by heavy metals can also occur near the track storing creosote-impregnated wooden railway sleepers. Having analysed railway transport intensity and in order to assess pollution level, the stations of three major cities of Lithuania (Vilnius, Kaunas and Klaipėda) were selected to investigate heavy metal pollutants (lead (Pb), cadmium (Cd), zinc (Zn)) acting as the most toxic and widespread elements. The highest concentrations of Pb (up to 50 mg/kg) were found at a distance of 5.0 m from railway sleepers in the upper (up to 10 cm) soil layer at Vilnius Railway Station. A comparison of the results of the investigated soil across the tested stations showed that Klaipėda Railway Station was the area most polluted with Cd. The highest concentrations of Cd (up to 1.5…1.8 mg/kg) were established at a varying distance of 5…10 m from the sleepers in the upper (up to 10 cm) soil layer of light loam. Among the investigated stations, the lowest pollution by heavy metals, including Zn, was found at Kaunas Railway Station where sandy loam dominated. A comparison of heavy metal pollutants deposited on the intact used and rotten wooden railway sleepers disclosed that the latter were more heavily contaminated with heavy metals and made from 8 to 13 mg/kg for Pb, from 0.3 to 1.2 mg/kg for Cd, from 13.8 to 66 mg/kg for Zn.

Keywords: railway transport, pollution, wooden railway sleepers, environmental protection, soil pollution, heavy metals, lead, cadmium, zinc.

Notations of chemical elements

Al – aluminium;
As – arsenic;
Ba – barium;
Ca – calcium;
Cd – cadmium;
Co – cobalt;
Cr – chromium;
Cu – copper;
Fe – iron;
Hg – mercury;
K – potassium;
Mn – manganese;
Mo – molybdenum;
Na – sodium;
Ni – nickel;
Pb – lead;
Pt – platinum;
Sb – antimony;
Se – selenium;
V – vanadium;
Zn – zinc.

Introduction

Railway transport appears as one of the major polluters of the environment. Most of pollutant emissions from combustion processes are related to fuel consumption in the internal combustion engines of traction rolling stock. The main pollutants released into the environment cover particulate matter, volatile non-methane organic compounds, sulphur dioxide and nitrogen oxides. In this way, it is likely that the biggest polluters of the environment are traction units with internal combustion engines. However, other types of pollution are possible, where polluters can be not only traction rolling stock with the internal combustion engines, but also electric locomotive. For example,

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when due to friction of metals and deterioration of rolling stock wheels, heavy metals such as aerosols are released into the atmosphere, soil, surface and ground water, etc. and severely pollute the railway environment. Along with an increase in the electrification of railways, local environmental pollution is likely to be increased in the future. High pollution by heavy metals can also occur near the track storing creosote-impregnated wooden railway sleepers. Thus, the concentrations of heavy metals (Pb, Cd, Cu, Zn, Fe, Cr, Hg, etc.) in the soil can be several times higher than those in the clean control sites outside the study. The pollutants accumulated in the soil can alter its pH thus destroying its natural chemical, physical and biological balance. Physiochemical changes in the environment may lead to the redistribution of the accumulated pollutants on the soil surface. A part of them migrate to deeper soil horizons. When entered groundwater, the pollutants tend to accumulate in the sludge of shaft wells (Christoforidis, Stamatis 2009; Bai *et al.* 2011; Hasselbach *et al.* 2005; Helmreich *et al.* 2010; Šeda *et al.* 2017; Paschke *et al.* 2000; Wierzbicka *et al.* 2015; Zhang *et al.* 2013).

The elements weighing more than 5 g/1 cm^3 are commonly referred to as heavy metals. As for biological classification, the elements with an atomic weight greater than 40 tend to be named as heavy metals. Some of these elements, including Fe, Co, Zn, Cu, Mn, etc. are simply given the name of microelements that are essential for living organisms. However, high concentrations are harmful to living organisms. 38 heavy metals are counted in nature but not all are unconditionally classified as toxic (Chen *et al.* 2014).

Element toxicity rises with an increase in atomic weight. Any element, subject to its concentration and form of a chemical compound, can become toxic. Heavy metals can cause endemic diseases related to a specific element, lead to growth and developmental abnormalities and weaken the immunity system. Some of more dangerous heavy metals embrace Cd, Pb, Zn, etc. (Chen *et al.* 2014).

There are no natural processes that destroy metals at the rate they have been artificially introduced into ecosystems. Some scientists, however, still believe that metals are slowly eliminated by leaching under erosion and deflation thus entering plants. Lysimetric research on the arable land of turf sandy loam and heavy clay loam demonstrated that the soil polluted with heavy metals (Cd, Zn and Pb) decontaminated very slowly during natural processes. It takes about 500 years for Zn, 500 for Cd and 1100 for Pb (Zhang *et al.* 2012) for the half-life of being eliminated from the soil (halving its initial concentration).

Since the late 1990s, some pollution investigations have found that air and soil alongside railway had higher heavy metal levels than control sites (Chen *et al.* 2014; Lorenzo *et al.* 2006). Chen *et al.* (2014) revealed that friction processes between wheel sets and rails during railway transportation make railways released heavy metals including Zn, Cd, Pb and other into the environment. With regard to the soil heavy metal pollution along railways, recent studies are primarily focus on the heavy metal pollution levels at different function areas (Chen *et al.* 2014), the concentration variation of soil heavy metals with the distance from track (Lorenzo *et al.* 2006) and the influence of environmental factors (topography, temperature and pH) on the distribution pattern of heavy metals sleepers (Liu *et al.* 2009; Zhang *et al.* 2012; Chen *et al.* 2010; Baumhardt *et al.* 2015; Blake, Goulding 2002; Blok, 2005; Dai *et al.* 2004; Fakayode, Olu-Owolabi 2003; Khan *et al.* 2011a; Li *et al.* 2007; Lee *et al.* 2009; Liu *et al.* 2009; Ma *et al.* 2009; Malawska, Wiołkomirski 2001; Morra *et al.* 2009; Plakhotnik *et al.* 2005; Saeedi *et al.* 2009; Stojic *et al.* 2017; Wiłkomirski *et al.* 2012).

Research has found that road transport affects levels of numerous heavy metals, including Pb, Cd, Cu, Zn, Cr, Ni, Fe, Mn, Al, Co, V, Sb, Ba, Pt, Mo, Hg, Se and As. Chinese scientists have only examined the relationship between railways and heavy metals for a limited number of elements, i.e., Ni, Pb, Mn, Cr, Zn, Cu and Cd. Scientists have directed greater attention to the soil environment near railways. Their research has shown that railway transportation can affect the surrounding environment, especially in urban areas. With respect to the soil environment along railways, recent studies have primarily shown: the differences of soil heavy metals across different sites, the horizontal distribution of soil heavy metals, and the influence of terrains on soil heavy metal distribution (Liu *et al.* 2009; Zhang *et al.* 2012).

For example, the studied by Chinese scientists Qinghai–Tibet railway provides favourable conditions for exploring the effects of railways on soil heavy metal enrichment. These results indicate that railway transport has a significant effect on the concentration of Zn, Cd and Pb in the soil, with levels of enrichment ranging from no pollution to significant pollution. The affected area was within 20 m of the railway. The soil at Delingha was the most contaminated soil with heavy metals, and the enrichment level of Cd in the soil was the highest along the Qinghai–Tibet railway. The horizontal distributions of the three heavy metals present different characteristics at different sampling sites, which may be due to discrepancies in terrain and vegetation types. Alkaline soils and guardrails along the railway might reduce the effect of soil pollution on local people and animals (Zhang *et al.* 2012).

The study other Chinese scientists investigated the effects of railway transportation on the enrichment of heavy metals in the artificial soil on railway cut slopes near Suining Railway Station (Sichuan Province, China). The results showed that the cut slopes were polluted by Cd and Pb. Cd exhibited remarkably higher levels compared to the results of other studies. Consequently, Cd contamination in the soils at the study sites was noteworthy. The contaminate levels increased with the operation time of the railway lines. Cd and Pb showed a moderate enrichment in the soils and all sampling locations showed considerable ecological risks. Railway traffic made a great contribution to elevated Pb and Cd in railway-side soils, but little influence on Cr, Cu and Fe (Chen *et al.* 2014).

The study of Czech scientists revealed that the wooden railway ties could be a source of Hg and Cu in soils near older railway s since their wooden ties were impregnated with Hg and Cu compounds. Wooden railway ties are considered as a potential source of Hg because of impregnation with antifungal Hg compounds. The level of Cu concentration in soil depends on the distance of nearby railway as trains release Cu into the environment as well. However, the relatively fast decrease in concentrations of individual contaminants with increasing distance from the railway indicates that the safe distance, e.g. for agricultural production, is approximately 10 m from the source of pollution (Šeda *et al.* 2017).

Recent research by Serbian scientists confirms that that surface soil (0…10 cm) samples from 60 sampling sites along the length of railway tracks on the territory of Srem (the western part of the Autonomous Province of Vojvodina, itself part of Serbia) were collected and analysed for ten heavy metals in order to see how the distance from the railway affects the concentration of some organic and inorganic pollutants in the soil. According to results of these studies Cu, Co, Zn and Ni were the most ubiquitous heavy metals in the area near railway. Based on these results, it can be said that railway transport is a potential source of these heavy metals. Despite the fact that in most of the samples pollutants do not exceed acceptable levels of pollution (except in the case of Co and Ni), there are indications that the current amount of inorganic pollutants is a potential threat to the environment, so routinely monitoring of soil in the area around the railway track and railway stations is justified (Stojic *et al.* 2017).

The purpose of this study is to assess heavy metal contamination levels (Pb, Cd, and Zn) in the stations of three major cities of Lithuania (Vilnius, Kaunas and Klaipėda) and to investigate the impact of railway operation on the enrichment of heavy metals n the intact used and rotten wooden railway.

1. Methodology

Having analysed railway transport intensity and in order to assess heavy metal pollutants – Pb, Cd, Zn – the stations of 3 major cities of Lithuania (Vilnius, Kaunas and Klaipėda) were selected (Figure 1).

Each soil sample was collected on the "envelope" basis from different points across the area of 100 m^2 (10×10 m). Thus, the samples were taken at the distances of 1, 5, 10, 15 and 25 m from the sleepers arranged in different soil layers (upper layer of up to 10 cm deep) and deeper (10…20 and 20…40 cm). Soil samples were obtained using standardized equipment with reference to standards: LST ISO 10381-1:2005, LST ISO 10381-2:2005, LST ISO 10381-3:2003, LST ISO 10381-4:2006, LST ISO 10381-5:2007. The collected samples (500 g in weight) were analysed on

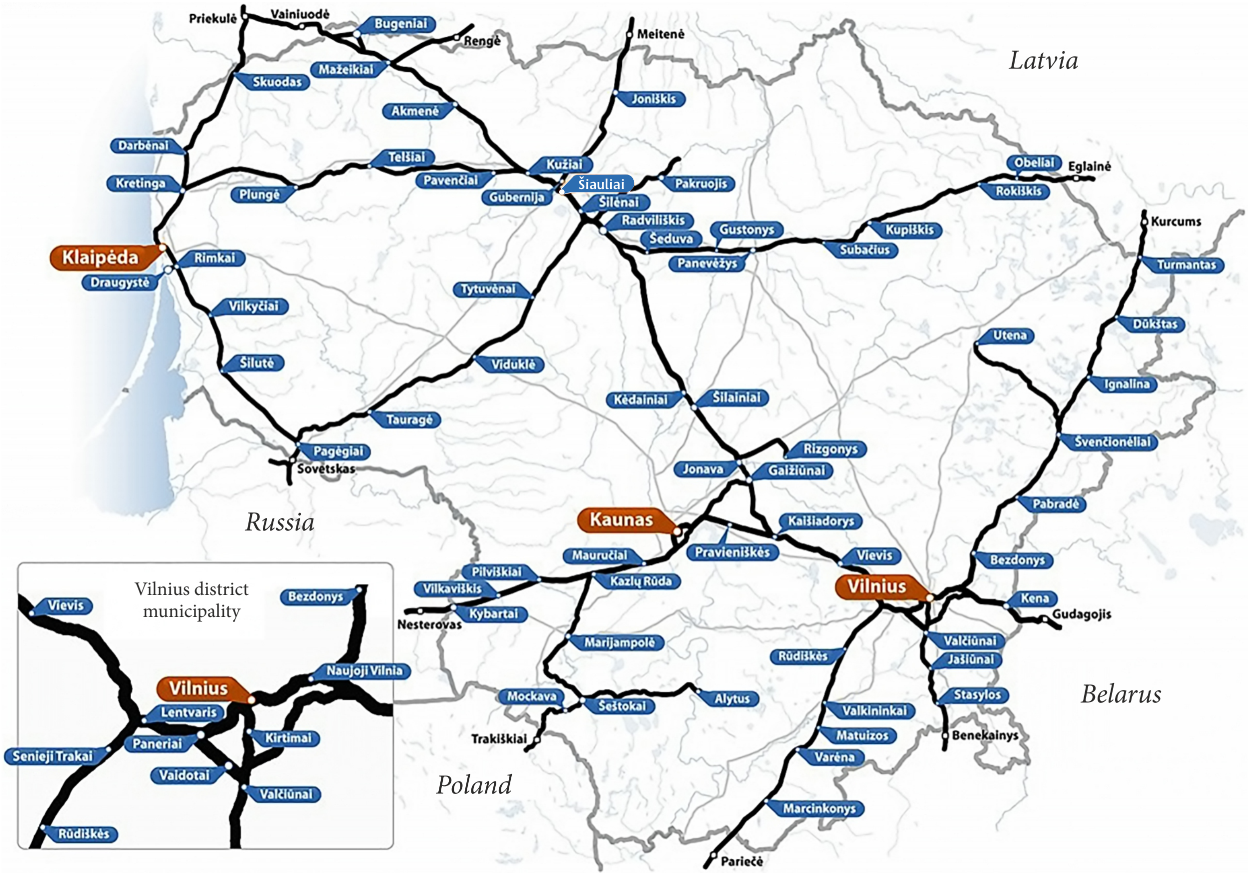


Figure 1. The stations of three major cities of Lithuania (Vilnius, Kaunas and Klaipėda)

the analytical basis. Heavy metals (Pb, Cd) were investigated according to standard LST CEN/TS 16172:2013 applying graphite furnace atomic absorption spectrometry. Heavy metal (Zn) analysis was performed following standard LST CEN/TS 16188:2012 employing flame atomic absorption spectrometry.

The carried out research involved the concentrations of heavy metals, including Pb, Cd and Zn, present in wooden railway sleepers. The samples were taken from the end of the intact used sleeper, the upper impregnated layer and the rotten sleeper. In order to assess the contamination of wooden railway sleepers, a new methodology for their collection and research has been adapted. The samples were collected from three railway stations (Vilnius, Kaunas and Klaipėda) and submitted for analytical analysis according to the aforementioned methods of atomic absorption spectrometry (Vilniškis, Vaiškūnaitė 2018). The novelty of this methodology consisted of complex studies of heavy metals (Pb, Cd, Zn) distribution in different soil profiles near railway stations, i.e. studies of soil morphological properties, studies of organic matter content and granulometric composition, studies and assessment of soil upper horizon contamination with heavy metals, studies of heavy metals mobile exchange distribution of concentrations in different soil profiles.

Based on Lithuanian Hygiene Norm on *Threshold Limit Value of Hazardous Substances in the Soil* (HN 60:2015), the specified threshold limit value of hazardous substances RV_p was established. This is the limit value of a hazardous chemical calculated according to the soil characteristics of a specific area.

Heavy metal pollutants found in the soil are determined with reference to RV_p equal to:

$$RV_p = RV \cdot \frac{A + B + M_{\%} + C \cdot OM_{\%}}{A + B \cdot 10 + C + 3},$$

where: RV_p – specified threshold limit value of hazardous substances in the soil; RV – threshold limit value of hazardous substances in the soil; $M_{\%}$ – content [%] of clay particles (less than 0.002 mm in diameter) in the examined soil. In the cases when the established content of clay soil particles exceeds 50% or is less than 10%, the values of 50 or 10% respectively shall be inserted in the formula; $OM_{\%}$ – content [%] of soil organic matter. In the cases when the established content of soil organic matter exceeds 10% or is less than 3%, the values of 10 or 3% respectively shall be inserted in the formula; A, B, C – coefficients the values of which are subject to heavy metals (Table).

Table. The coefficients used for establishing the specified threshold limit values RV_p of the investigated heavy metals (HN 60:2015)

Heavy metal	Coefficients the values of which are subject to heavy metals		
	A	B	C
Pb	50	1.0	1.0
Cd	0.4	0.007	0.021
Zn	50	3.0	1.5

The results of the conducted research were evaluated applying mathematical-statistical methods using the *Microsoft Excel* program. The accuracy of the averages of the obtained results was statistically evaluated from five replicates. Unreliable results were retested.

2. Research results

2.1. Determining Pb

Pb concentrations in the investigated soil of Vilnius, Kaunas and Klaipėda railway stations did not exceed the specified threshold limit value of hazardous substances (80 mg/kg). The highest concentrations of Pb (up to 50 mg/kg) in the upper (up to 10 cm) soil layer were found at a distance of 5.0 m from railway sleepers at Vilnius Railway Station (Figure 2). As for the application of statistical methods, recent research has demonstrated extremely high approximation coefficients (R^2) (up to 0.99). Such amounts of Pb were significantly affected by the content of physical clay particles, fine dispersion fraction (particles <0.002 mm), the origin of soil rock, the content of organic matter present in the soil and its acidity (pH). Fine sand (0.25…0.05 mm) fraction predominated in sandy and clay loam soils in the area of Kaunas Railway Station, and Pb concentration was 1.1 times less than that in the soil of heavier granulometric composition, that of limnoglacial origin (coarse dust fraction of 0.005…0.01 mm in diameter was prevailing) and that in the soil of higher organic matter content and lower pH (Vilnius Railway Station). As for deeper soil layers (10…20 and 20…40 cm), the concentrations of the above mentioned pollutant were evenly distributed within the limits of 10…20 and 8…12 mg/kg respectively, which was confirmed by statistical analysis ($R^2 = 0.95$). A comparison of the findings of Pb investigated at all railway stations demonstrated the remaining similar trend. The highest concentrations of Pb (up to 30…60 mg/kg) in the upper (up to 10 cm) soil layer was found at a distance of 5…10 m from railway sleepers at Klaipėda and Kaunas railway stations. Correspondingly, minor variations in Pb concentrations, i.e. from 10 to 18 mg/kg, were observed in the deeper soil layers (10…20 and 20…40 cm) of the above mentioned railway stations at a distance of 10…25 m from railway sleepers. Thus, under a negative anthropogenic effect, the mobility of metals can greatly alter and natural low-activity Pb can even become very mobile. In terms of the amount of mobile forms, heavy metals form the following order: Pb > Zn > Mn > Co > Ni > Cu > Cr (Chen *et al.* 2014). The results of the study showed that Pb had a relatively high level of mobility on the railway, which made 25 km from the track. Similarly, to the data provided by other scientists (Burkhardt *et al.* 2008; Christoforidis, Stamatis 2009; Davis *et al.* 2001; Fonseca *et al.* 2011; Guo *et al.* 2012; Ho, Tai 1988; Khan *et al.* 2011b; Kim, K.-H., Kim, S.-H. 1999; Langmi, Watt 2003; Saeedi *et al.* 2012; Nabulo *et al.* 2006; Sansalone, Buchberger 1997; Stojic *et al.* 2017; Tromp *et al.* 2012), these figures reaffirmed that Pb adsorption and desorption processes in the soil as well as their distribution in the solid and liquid phases of the soil were highly complex and subject to a number of factors, including an anthropogenic aspect.

Complex studies of the Pb pollution have shown that in order to reduce the negative impact on the environment, that the safe distance from the railway stations are up to 10…15 m. Therefore, based on the research of the scientists, it can be stated that it is necessary not only to monitor the distribution of Pb in different soil profiles, but also to monitor the morphological properties of the soil, its organic matter content and granulometric composition (Stojic *et al.* 2017; Šeda *et al.* 2017; Zhang *et al.* 2012; Chen *et al.* 2014).

2.2. Determining Cd

A comparison of the results of the investigated soil across the tested railway stations disclosed that Klaipėda Railway Station was the most polluted with Cd. The highest Cd concentrations (up to 1.5…1.8 mg/kg) were found in the upper (up to 10 cm) soil layer at a distance of 5…10 m from the railway sleepers placed in light clay loam (Figure 3).

Thus, the specified threshold limit value of hazardous substances (1.5 mg/kg) was exceeded. The site of technogenic pollution (10…25 m from the track) suffered from higher soil pollution. As for the application of statistical methods, recent research has demonstrated extremely high approximation coefficients (R^2) (up to 0.97). The results of the conducted study showed that the effect of railway transport on the roadside soil polluted with Cd was significant. Due to the higher concentration of humus, clay, minerals, phosphate and carbonate ions in the soil of Klaipėda Railway Station, insoluble and inorganic Cd compounds formed. The produced heavy metal-organic compounds may be of varying durability thus ranging from semi-persistent to fragile. The persistence of Cd compounds with humic substances is lower than that of Pb or Zn, and therefore Cd ions can move faster from organic complexes to the mobile state in the soil than the other metals (Chen *et al.* 2014). According to the mass fraction of mobile ions (as much as 56…70%), the other part of Cd enters minerals (hydroxides) or migrates in the form of true solutions (Stojic *et al.* 2017). The migration of Cd ions in the soil depends on adsorption-desorption processes involving Cd and other heavy metals. Like those of other heavy metals, Cd ions are absorbed in the soil by the sorbent complex and take part in ion exchange and other processes. The soil is a complex multicomponent system embracing the adsorption and desorption of metal ions, i.e. transition to soil solution (mobile state) is a reversible process. This equilibrium depends on a number of factors such as pH, soil sorption capacity, temperature, humidity, light, interaction with other cations, etc. (Huang *et al.* 2004; Koeleman *et al.* 1999; Kluge, Wessolek 2012; Lorenzo *et al.* 2006; Norrström 2005; Olajire, Ayodele 1997; Pagotto *et al.* 2001; Sezgin *et al.* 2004; Stojic *et al.* 2017; Wiłkomirski *et al.* 2011; Vitaliano 1992).

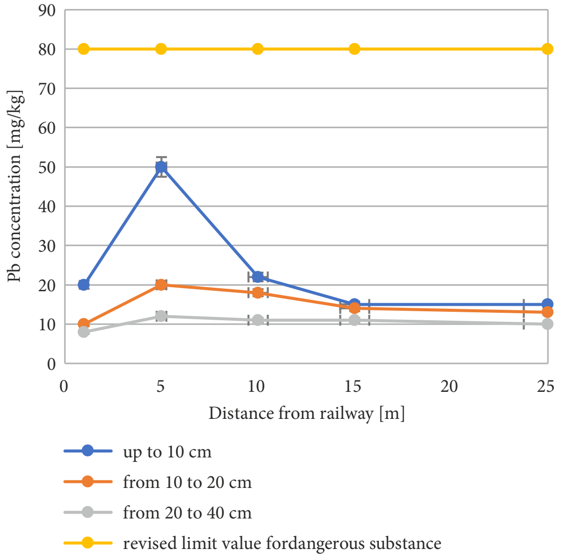


Figure 2. The influence of the distance from the railway on Pb concentration in the soil of Vilnius Railway Station (samples of up to 10 cm from the depth of 10…40 cm)

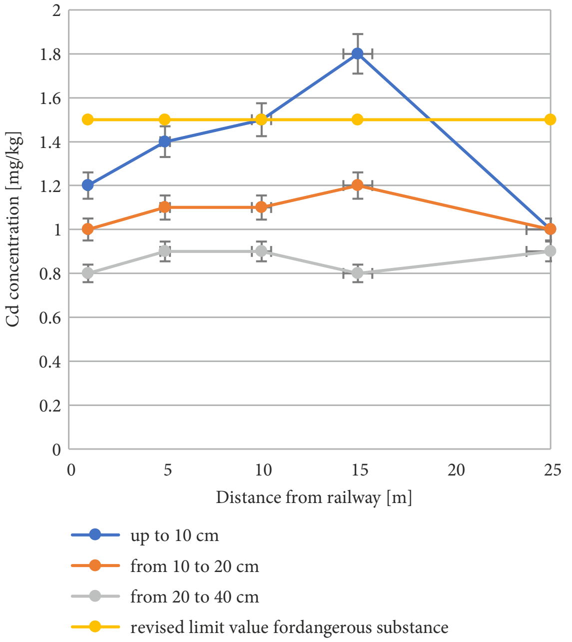


Figure 3. The influence of the distance from the railway on Cd concentration in the soil of Klaipėda Railway Station (samples of up to 10 cm from the depth of 10…40 cm)

The conducted study documented that the content of this heavy metal in the soil was mostly subject to its granulometric composition: a growth in the amount of physical clay particles (<0.01 mm) resulted in a rising content of Cd. An increasing distance from the road gradually decreased Cd concentrations from 0.8 to 1.8 mg/kg. As for the deeper layers of the soil (10…20 and 20…40 cm), Cd concentrations evenly distributed within the limits of 1…1.2 and 0.8…0.9 mg/kg respectively, which was confirmed by statistical analysis (R^2 = 0.95). Considering other railway stations situated in Vilnius and Kaunas, soil pollution with Cd was twice as low and distributed evenly in all soil layers, i.e. from 0.4 to 0.7 mg/kg. Hence, Cd ions dominated in the mobile state in the soils of the latter railway stations.

Complex studies of the Cd pollution have shown that in order to reduce the negative impact on the environment, that the safe distance from the railway stations are up to 15 m. Therefore, based on the research of the scientists, it can be stated that it is necessary not only to monitor the distribution of Cd in different soil profiles, but also to monitor the morphological properties of the soil, its granulometric composition and higher concentration of humus, clay, minerals, phosphate and carbonate ions in the soil. Complex studies have confirmed that the contaminate levels of Cd increased with the operation time of the railway lines (Stojic *et al.* 2017; Šeda *et al.* 2017; Zhang *et al.* 2012; Chen *et al.* 2014).

2.3. Determining Zn

Among the investigated stations, the lowest level of pollution by heavy metals, including Zn, was found at Kaunas Railway Station where sandy loams predominated. Maximum pollution with Zn (up to 130 mg/kg) was recorded at a distance of 10…20 m from railway sleepers; however, it did not exceed the specified threshold limit value of hazardous substances (300 mg/kg) (Figure 4).

As for the application of statistical methods, recent research has demonstrated extremely high approximation coefficients (R^2) (up to 0.98). Actually, more Zn may have accumulated in the upper layer due to a higher content of organic material where Zn was more likely to accumulate. As for deeper soil layers (10…20 and 20…40 cm), the concentrations of the tested pollutant evenly distributed within the limits of 50…70 and 30…50 mg/kg respectively. Organic matter is frequently flushed from the upper to the deeper layers of the soil. This fact is corroborated by other research findings (Zhang *et al.* 2012). For this reason, Zn in particular was found in considerable numbers in this layer. A comparison of the results of Zn tested at all investigated railway stations demonstrated the remaining similar trend. The highest concentrations of Pb (up to 180…200 mg/kg) were found in the upper (up to 10 cm) soil layer at a varying distance of 10…20 m from railway sleepers at Klaipėda and Vilnius railway stations. Correspondingly, fluctuations in the concentrations of Pb were minor and made from 50 to 78 mg/kg in the deeper soil layers (10…20 and 20…40 cm) of the above mentioned railway stations at a distance of 10…25 m from railway sleepers. This was confirmed by statistical analysis (R^2 = 0.96). It can be noted that pollution with Zn established in the soil at Klaipėda Railway Station was approximately twice as polluted as that of the other investigated stations where the soil of moderate granulometric composition dominated and where the solubility of Zn increased with a rise in the pH value thus forming zincates. In recent years, the soil has been adversely affected by acid rain containing sulphur, hydrochloric and nitric acids. When exposed to soil surface horizons, pollutants increase their acidity, intensify leaching alkaline biogenic cations (K, Na, Ca, Mn, Ba), Fe, Al and Mn and increase heavy metal (not only Zn, but also Cd, Pb and others) activity, mobility and toxicity (Stojic *et al.* 2017).

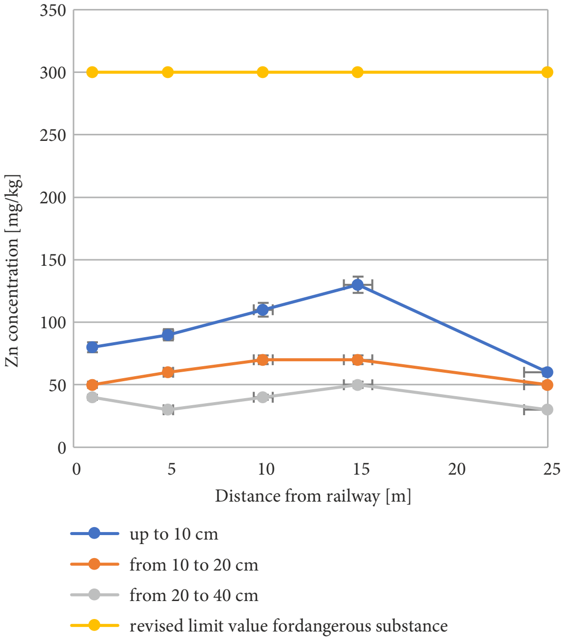


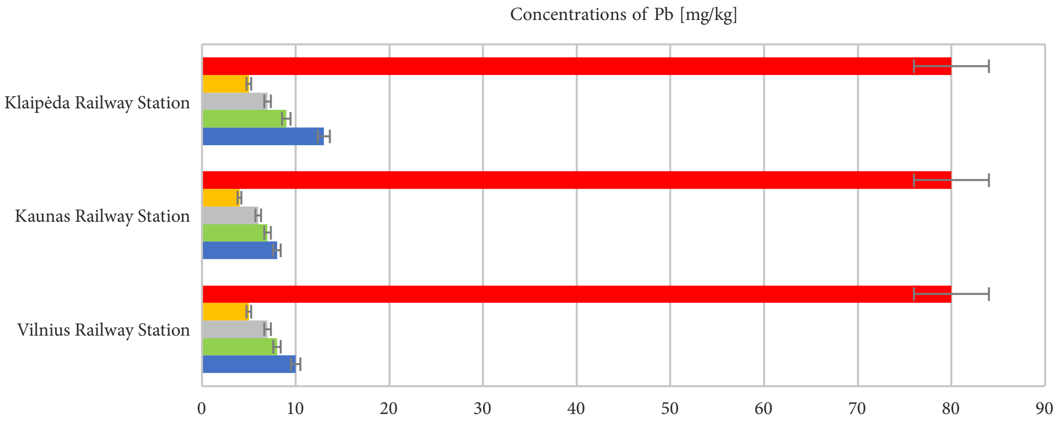
Figure 4. The influence of the distance from the railway on Zn concentration in the soil of Kaunas Railway Station (samples of up to 10 cm from the depth of 10…40 cm)

If the investigated heavy metals (Cd, Pb, Zn) form complex compounds with humic substances, their durability is arranged as Pb > Zn > Cd. In this case, the most easily absorbed Pb ions and the least easily absorbed Cd and Zn ions can be observed (Shi *et al.* 2008; Smičiklas *et al.* 2015; Stojić *et al.* 2014; Sun *et al.* 2010; Száková *et al.* 2010; Wei, Yang 2010; Zehetner *et al.* 2009; Vilniškis, Vaiškūnaitė 2018; Zhang *et al.* 2012).

Analogously performed and previously discussed Pb pollution studies, complex studies of the Zn pollution have shown that in order to reduce the negative impact on the environment, that the safe distance from the railway stations are up to 10…15 m. Therefore, based on the research of the scientists, it can be stated that it is necessary not only to monitor the distribution of Zn in different soil profiles, but also to monitor the morphological properties of the soil, its organic matter content and granulometric composition (Stojic *et al.* 2017; Šeda *et al.* 2017; Zhang *et al.* 2012; Chen *et al.* 2014).

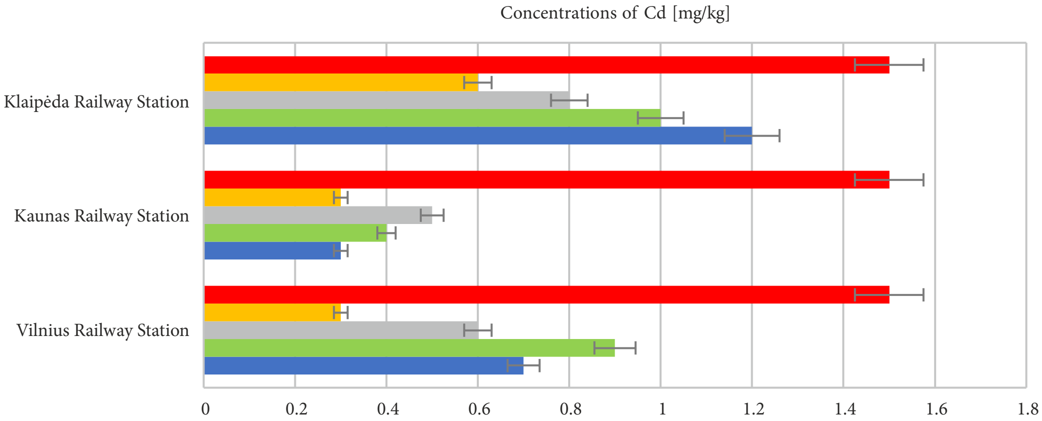
2.4. Concentrations of heavy metals (Pb, Cd, Zn) in the intact used and rotten wooden railway sleepers

A comparison of heavy metal pollutants found on the intact used and rotten wooden railway sleepers disclosed that the latter sleepers compared to the intact used ones, were more seriously polluted with heavy metals, which made from 8 to 13 mg/kg for Pb, from 0.3 to 1.2 mg/kg for Cd and from 13.8 to 66 mg/kg for Zn. The rotten sleepers contained a higher content of organic compounds involved in forming complex compounds of varying durability ranging from semi-persistent to fragile (Figures 5–7). This was confirmed by statistical analysis ($R^2 = 0.95$). Meanwhile, for examining the contamination of the intact used sleeper in different parts, the highest content of heavy metal pollutants was recorded in the upper layer of the sleeper, i.e. in the creosote impregnated layer (for example, from 8 to 59 mg/kg for Pb, from 0.9 to 1 mg/kg for Cd, from 26 to 59 mg/kg for Zn). Creosote is derived from coal and polycyclic aromatic hydrocarbons and from phenolic and heterocyclic aromatic compounds forming integrated compounds with heavy metals.



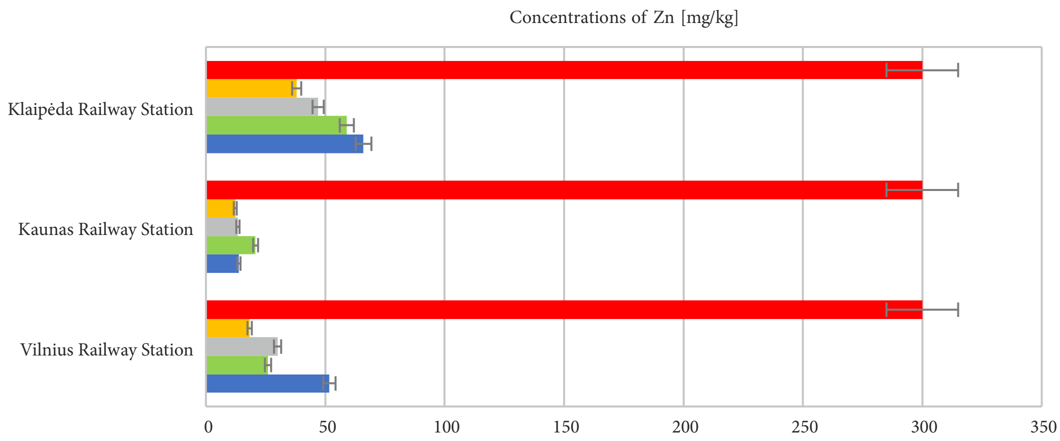
	Vilnius Railway Station	Kaunas Railway Station	Klaipėda Railway Station
🟥 Revised limit value for Pb	80	80	80
🟨 Intact used sleeper (middle of sleeper)	5	4	5
⬜ Intact used sleeper (end of sleeper)	7	6	7
🟩 Intact used sleeper (surface layer)	8	7	9
🟦 Rotten railway sleeper	10	8	13

Figure 5. The distribution of the concentrations of Pb in the intact used and rotten wooden railway sleepers at the biggest Lithuanian railway stations (Vilnius, Kaunas and Klaipėda)



	Vilnius Railway Station	Kaunas Railway Station	Klaipėda Railway Station
🟥 Revised limit value for Cd	1.5	1.5	1.5
🟨 Intact used sleeper (middle of sleeper)	0.3	0.3	0.6
⬜ Intact used sleeper (end of sleeper)	0.6	0.5	0.8
🟩 Intact used sleeper (surface layer)	0.9	0.4	1
🟦 Rotten railway sleeper	0.7	0.3	1.2

Figure 6. The distribution of the concentrations of Cd in the intact used and rotten wooden railway sleepers at the biggest Lithuanian railway stations (Vilnius, Kaunas and Klaipėda)



	Vilnius Railway Station	Kaunas Railway Station	Klaipėda Railway Station
🟥 Revised limit value for Zn	300	300	300
🟨 Intact used sleeper (middle of sleeper)	18.3	12.3	38
⬜ Intact used sleeper (end of sleeper)	30	13.4	47
🟩 Intact used sleeper (surface layer)	26	20.8	59
🟦 Rotten railway sleeper	51.7	13.8	66

Figure 7. The distribution of the concentrations of Zn in the intact used and rotten wooden railway sleepers at the biggest Lithuanian railway stations (Vilnius, Kaunas and Klaipėda)

As a result, heavy metal pollution was detected in the upper layer of the intact used sleeper rather than in the other parts of it. The highest concentrations of heavy metals (especially Pb and Zn) were found in both the intact used and rotten wooden sleepers taken from Vilnius and Klaipėda railway stations where rolling stock traffic was more intensive, loading operations were performed and traction rolling stock was stopped more frequently, which caused the friction of metals and resulted in the environmental pollution of the soil, surface and groundwater, etc. thus emitting heavy metals etc. The lowest level of pollution by heavy metals was established in the intact used and rotten wooden sleepers at Kaunas Railway Station. For example, the intact used railway sleepers contained from 4 to 7 mg/kg of Pb, from 0.3 to 0.5 mg/kg of Cd and from 12.3 to 20.8 mg/kg of Zn ($R^2 = 0.99$). Apparently, it was influenced by lower traction stock intensity compared to other railway stations (Klaipėda and Vilnius), which was supported by the research conducted by other scientists (Shi *et al.* 2008; Smičiklas *et al.* 2015; Stojić *et al.* 2014; Sun *et al.* 2010; Száková *et al.* 2010; Šeda *et al.* 2017; Wei, Yang 2010; Zehetner *et al.* 2009; Zhang *et al.* 2012, 2013).

Summarizing the obtained results according to the methods presented in the literature, we can say, that the investigated wooden railway sleepers are the most contaminated (up to 1.2 mg/kg) with Cd. In comparison, other researchers obtained similar research results with values from 0.35 to 1.19 mg/kg. Meanwhile, in wooden railway sleepers, the highest pollution of Pb was only 13 mg/kg. When other researchers recorded an average of three times higher contamination of Pb (about 34.4 mg/kg). Analogous research results were obtained with Zn. For example, in the investigated wooden railway sleepers, the maximum pollution of Zn was only up to 66 mg/kg, while other researchers recorded one and a half times higher pollution of Zn (on average up to 85 mg/kg). We are confident, that the investigated results will be confirmed by the further development of this study.

Consequently, in order to reduce the negative impact on the environment, creosote-impregnated sleepers should not be stored near the railway or at near railway stations (Stojic *et al.* 2017; Šeda *et al.* 2017; Zhang *et al.* 2012; Chen *et al.* 2014).

Conclusions

The highest Pb concentrations (up to 50 mg/kg) were found in the upper (up to 10 cm) soil layer at a distance of 5 m from railway sleepers at Vilnius Railway Station. As for deeper soil layers (10…20 and 20…40 cm), Pb concentrations evenly distributed within the limits of 10…20 and 8…12 mg/kg respectively. Such amounts of Pb were significantly influenced by the origin of soil rock, the content of organic matter in the soil and its acidity (pH).

A comparison of the results of the investigated soil across the tested railway stations disclosed that Klaipėda Railway Station was the most polluted with Cd. The highest Cd concentrations (up to 1.5…1.8 mg/kg) were found in the upper (up to 10 cm) soil layer at a distance of 5…10 m from the railway sleepers placed in light clay loam. Due to the higher concentration of humus, clay, minerals, phosphate and carbonate ions, insoluble and inorganic Cd compounds formed. As for the deeper layers of the soil (10…20 and 20…40 cm), Cd concentrations evenly distributed within the limits of 1…1.2 and 0.8…0.9 mg/kg respectively.

Among the investigated stations, the lowest level of pollution by heavy metals, including Zn, was found at Kaunas Railway Station where sandy loams predominated. Apparently, more Zn may have accumulated in the upper layer due to a higher content of organic material where Zn was more likely to accumulate. Considering deeper soil layers (10…20 and 20…40 cm), the concentrations of the tested pollutant evenly distributed within the limits of 50…70 and 30…50 mg/kg respectively.

A comparison of heavy metal pollutants found on the intact used and rotten wooden railway sleepers disclosed that the latter sleepers compared to the intact used ones, were more seriously polluted with heavy metals, which made from 8 to 13 mg/kg for Pb, from 0.3 to 1.2 mg/kg for Cd, from 13.8 to 66 mg/kg for Zn. The rotten sleepers contained a higher content of organic compounds involved in forming complex compounds of varying durability ranging from semi-persistent to fragile.

For examining the contamination of the intact used sleeper in different parts, the highest content of heavy metal pollutants was recorded in the upper layer of the sleeper, i.e. in the creosote impregnated layer (for example, from 8 to 59 mg/kg for Pb, from 0.9 to 1 mg/kg for Cd, from 26 to 59 mg/kg for Zn). Creosote is derived from coal and polycyclic aromatic hydrocarbons and from phenolic and heterocyclic aromatic compounds forming integrated compounds with heavy metals. As a result, heavy metal pollution was detected in the upper layer of the intact used sleeper rather than in the other parts of it.

The lowest level of pollution by heavy metals was established in the intact used and rotten wooden sleepers at Kaunas Railway Station. For example, the intact used railway sleepers contained from 4 to 7 mg/kg of Pb, from 0.3 to 0.5 mg/kg of Cd and from 12.3 to 20.8 mg/kg of Zn (R^2 = 0.99). In fact, it was influenced by lower traction stock intensity compared to other railway stations (Klaipėda and Vilnius).

Studies on the distribution of heavy metals (Pb, Cd, Zn) according to the new methodology have shown that railway transport can have an impact on the surrounding environment, especially in urban areas. These complex studies have shown that the safe distance from the railway stations is up to 10…15 m. Consequently, maintaining a safe distance from the railway in practice would reduce the negative impact of pollution on humans and the environment.

Disclosure statement

Authors do not have any competing financial, professional, or personal interests from other.

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