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Contamination of soils with Cu, Na and Hg due to the highway and railway transport

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Abstract

Contamination of soils with three metals due to the highway and railway transport was studied. Copper was selected as a suitable indicator for both kinds of transportation. Sodium served to assess the level of contamination resulting from the road salting in winter. Mercury was determined in samples taken close to the railway in order to test its release from impregnated wooden ties. All analytes were determined using the methods of the trace element analysis; values are expressed as dry matter. The highest concentrations of copper, sodium and total mercury in soil samples were 52.7 mg/kg, 770 mg/kg and 0.181 mg/kg respectively. The highest copper content was observed in soils taken close to the railroad and the highway. Elevated sodium levels originated from winter road salting – the highest winter value was 770 mg/kg as compared with maximal summer value of 416 mg/kg. The concentration of total mercury in soils depended on the type of railway ties used – the highest values for location with wooden and concrete ties were 0.181 mg/kg and 0.145 mg/kg, respectively. Wooden railroad ties are considered as a potential source of mercury because of impregnation with antifungal mercury compounds.

Keywords: Copper, environment protection, mercury, salting of roads, trace element analysis.

Introduction

Soil is the basis of all agroecosystems; it is an important part of the Earth. Most of soils are endangered with various types of erosion and pollution. Heavy metals and hazardous elements play a significant role among the pollutants. The aim of the present study is to quantitatively characterise the contamination of soils taken close to the major highway and railway in South Bohemia with selected metals: copper, sodium and mercury. Copper was determined in samples taken close to the highway and railway as well. Sodium served as an indicator of the road salting. Mercury concentrations in soils were measured in order to test the possible release of this heavy metal from impregnated wooden railway ties. The study should assess the risk of the highway and railway transportation for the environment and for the agricultural production.

All observed metals occur in soil in their natural forms. Copper is a microelement essential for many organisms. It is present in soil in form of ions, organic compounds, complexes, chalcopyrite ($CuFeS_2$) and other sulphide ores. Sodium is a ubiquitous element, mainly present as a free ion Na^+ in capillary water, or bound into salts. In contrast, mercury is present in soil only in trace amounts and is considered as a polluting element with toxic effect on all organisms. Mercury is the volatile element; its ability to form toxic alkyl-mercury derivatives is well-known (Harley et al., 2015; King et al., 2002).

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The pollution of soils with metals due to the aerial transportation is a worldwide issue. Metals are released during various processes, such as combustion or component wearing. Lead, copper, zinc and cadmium are considered as major inorganic pollutants. Previous studies revealed that the highway traffic increased copper levels in soil close to the road up to 20 times. Copper concentration at the studied locations was usually higher in surface layers; it reached 565 mg kg^{-1} and decreased along with depth (Kluge and Wessolek, 2012). Brakes and sidings wear contribute to the total copper release in road runoff water more than by two thirds, most of it comes to nearby soils (Davis et al., 2001).

Concerning the railroad transport, the pollution depends on an engine type. Diesel locomotives use fuel combustion. Similarly to the road vehicles, they also release polycyclic aromatic hydrocarbons (Wiłkomirski et al., 2011). In contrary, electric locomotives are considered as environmentally friendly, however, the presence of the railroad itself could significantly increase metal concentrations in nearby soils (Zhang et al., 2012; 2013). In addition, particle abrasion from wheels, tracks and pantographs can get metals into aerosols and pollute the wider railway surroundings (Bukowiecki et al., 2007). Cleaning bays and railway sidings are also heavily polluted areas; concentrations of Pb, Cu, Zn, Fe, Cr and Hg in soils could be several times higher than at relatively clean control areas outside study sites (Malawska and Wiłkomirski, 2001).

The main anthropogenic sources of sodium are road salting and fertiliser usage. Concentration of sodium in road runoff water varied from 25 mg L^{-1} up to 10400 mg L^{-1} after consistent application of de-icing salt (Helmreich et al., 2010). Road salt helps to melt the snow and ice on the road surface; it is composed mainly of sodium chloride (NaCl), often with addition of calcium chloride ($CaCl_2$). Alternative compounds were used, for instance calcium-magnesium acetate (CMA), but the cost/efficiency ratio was not optimal in this case (Vitaliano, 1992). High sodium and chloride concentration originating from de-icing salt usage during winter could also increase the mobility of the mentioned metals (Tromp et al., 2012). Intensive use of road salt and consecutive excess of sodium in soil can also cause an ion imbalance and adverse effects on many plants (Moťková et al., 2014).

Material and Methods

Study sites

Soils were taken from two sampling sites. One site was situated 25km north-east from České Budějovice (South Bohemia, Czech Republic) near the České Budějovice – Prague highway "E55" (49°15'97.825"N, 14°64'29.089"E). The daily traffic density ranged between 7.000 and 10.000 vehicles in 2010 (Czech Traffic Survey, 2010). A meadow is located next to the road; the grass is usually mown up to six times per year. Five sampling points were designated at this sampling site in distances of 0, 5, 10, 80 and 100 m from the road. Six soil samples were taken at each point (three surface samples from the depth of 0-15 cm and three from the depth of 15-30 cm) three times in 2014 (April 4, August 8 and November 17). An additional sampling was conducted on February 15, 2015 in order to determine sodium in soil taken near the highway and to investigate the effect of road salting. Second sampling site was situated a few kilometres north-east (49°12'27.622"N, 14°45'6.194"E). It was located near the railway that connects České Budějovice and Brno cities. Four sampling points were designated at this site (at distances of 1.5, 3, 10 and 25 m from the railroad). Samples were taken three times throughout 2014 (April 29, August 10 and October 30) in 2-, 10-, 20- and 30-cm depths. There are two different types of railway ties used at this site: concrete and wooden. The wooden ties can be a potential source of mercury contamination due to their impregnation. Therefore, two batches of soil samples were taken: in the vicinity of concrete and wooden railway ties, respectively. The only possible pollution sources are traffic and agriculture. The sampling sites have not been industrially active.

Sampling and sample pre-treatment

All collected samples were transported to the laboratory, where larger particles, stones and roots were removed. Samples were further processed with slightly modified treatment according to Borůvka et al. (1996) and Száková et al. (2010). The soil was air-dried for 6 hours at 100 °C. From each sample, 8 g of dried soil was mixed with 40 ml of 2M nitric acid (Merck, Darmstadt, Germany) and shaken thoroughly for 24 hours. Mixtures were filtered through Whatman glass microfibre filters (pores size of 1.2 µm) and the extracts were diluted with deionised water to 50 ml volume. Samples were analysed by flame atomic absorption spectrometry (FAAS) and flame photometry in the case of copper and sodium, respectively. A fraction of each raw sample taken at the railway sampling site was dried at room temperature for 7 days. Samples treated in this way were used for direct total mercury determination by an advanced mercury analyser (AMA-254).

Instrumental and determination of analyses

Ultrapure (deionised) water was obtained from a Milli-Q® Gradient A 10 system (Millipore, Billerica, USA). All chemicals used were either of analytical reagent grade or of higher purity. Stock standard solutions (1000 mg/l) of individual metals (Merck, Darmstadt, Germany) were used to prepare calibrating solutions and validate the analytical methods. Quantitative data were obtained based on the calibration curve method. Two certified reference materials [Light Sandy Soil 7001 (Analytika, Prague, Czech Republic) and SPS-WW2 (Spectrapure standards, Oslo, Norway)] were used to determine the accuracy. Precision is expressed as repeatability. Limits of detection (LOD) and quantification (LOQ) were determined on the basis of 3σ and 10σ criteria, respectively. All characteristics of the analytical methods are summarised in Table 1.

Table 1. Characteristics of analytical methods used for determination of individual analytes

Characteristic	Cu	Na	Hg
Accuracy	105.2 %	99.1 %	96.6 %
Repeatability	0.36 %	0.26 %	1.95 %
Linear dynamic range	0.18–10.00 mg dm^{-3}	0.08–2.00 mg dm^{-3}	1.20–200.00 μg kg^{-1}
Limit of detection	0.054 mg dm^{-3}	0.024 mg dm^{-3}	0.360 μg kg^{-1}
Limit of quantification	0.182 mg dm^{-3}	0.080 mg dm^{-3}	1.200 μg kg^{-1}
Sensitivity	0.0540 dm^{-3} mg	0.4910 dm^{-3} mg	0.0022 kg $μg^{-1}$
Correlation coefficient	0.9994	0.9988	0.9975
Characteristic conc.	0.08 mg dm^{-3}	N/A	2.30 μg kg^{-1}

The analytical methods were always properly optimised and validated. A Thermo Scientific iCE 3500 spectrometer (Thermo Fisher Scientific, Cambridge, United Kingdom) was used for sodium and copper determination. It was operated in the flame atomic absorption spectrometry (an acetylene/air flame) and the flame photometry modes for Cu and Na determination, respectively. Mercury was determined using an advanced mercury analyser (AMA 254, Altec, Prague, Czech Republic).

Results and Discussion

Stagnosol (pseudogley) soil group dominates on the sampling site. The geochemical background concentrations in topsoils vary from 8.7 to 17.5 mg kg^{-1} for copper and from 0.05 to 0.09 mg kg^{-1} for mercury, according to the Geochemical Atlas of Europe. We measured somewhat lower values (20-100m from the highway and railway), because of the dissolving in nitric acid. The total content of metals and their availability heavily depend on many physical and chemical characteristics of soils (soil type, pH, redox potential, amount of minerals, organic material and water). pH of the soil is very important, it is well known that most metals are less available and less mobile in basic soils. And conversely, along with possible acidification of soils and thus with decreasing pH the mobility of metals increases. Measured pH (H_2O) values of our soil samples ranged from 6.48 to 8.46 with average value 7.56, they are not affected with acidification. All samples were dried before analytes determination, the content of water varied from 10.6 % to 14.1 %, Slightly wetter soil samples were found on the second sampling site, but the difference compared to the first sampling site is negligible just as the effect on availability of the Cu, Na and Hg. Different amounts of organic compounds affect the migration of metals and their solubility in water (Smičiklas et al., 2015). Some other studies mentioned positive correlation between organic matter and the sorption of metal cations (Kluge and Wessolek, 2012). Total organic carbon (TOC) determined in our samples was 1.35 ± 0.26 %. Measured values are usual for this soil type.

Determination of copper

All values mentioned in results are expressed as dry matter. The results obtained for copper in soil samples taken close to the highway are given in Figure 1 and 2. Individual lines in these figures show the concentrations obtained for respective sampling dates. The concentration changes in the course of the year bring significant information (the effect of the road salting), therefore mean values were not calculated in this case. According to the Ministry of the Environment of the Czech Republic (1994), the concentration limit of copper in agricultural soils is 50 mg kg^{-1}. The determined values did not exceed the limit. As expected, the highest content of copper was found near the road, most likely due to the traffic. Other authors obtained similar or even higher concentration of copper, especially near very frequent highways, and reported the same conclusions (Zehetner et al., 2009; Kluge and Wessolek, 2012; Zhang et al., 2012). The friction of brakes and moving engine parts as well as other vehicular components could release copper (Davis et al., 2001). The concentration of copper falled down rapidly with the distance from the highway. Back from the road (more than 5 meters), the determined content of copper varied between 4 and 8 mg kg^{-1}. Similar concentration levels were published in other studies as well (Sabiene et al., 2004; Zhang et al., 2012).

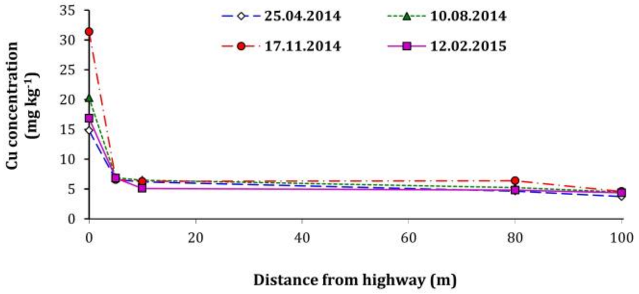

Figure 1. The influence of the distance from the highway on copper concentration in soil (surface samples).

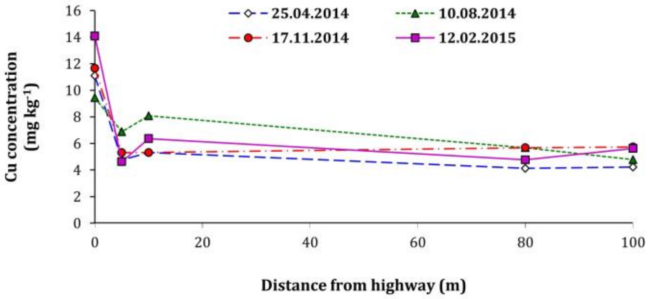

Figure 2. The influence of the distance from the highway on copper concentration in soil (samples from the depth of 15–30cm).

As it is evident from Figure 2, copper also migrates into the deeper (15-30 cm) layer of soil, however, its peak concentration is lower than in the respective surface layer. It supports the presumption that highway traffic has been the source of pollution. Copper content in soil samples taken near the railway reached 52.7 mg kg^{-1} and 25.0 mg kg^{-1} at locations with wooden and concrete ties, respectively. The determined concentrations were up to ten times higher in comparison with a background concentration value (the samples taken farthest from the railroad) and the difference between the highest and the lowest copper concentration measured was more than 50 mg kg^{-1}. The trend is similar to the results obtained for the first location: the concentration of copper decreased sharply with the distance from the railway (Figure 3 and 4). Individual lines in these figures show the average concentrations obtained for respective sampling depths in this case. Significantly higher copper concentration obtained for soil samples taken at the site with wooden ties can be explained as a consequence of the wood impregnation using copper compounds (Reinprecht, 2010).

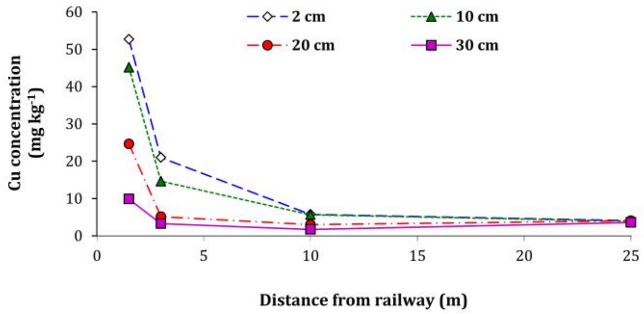

Figure 3. The influence of the distance from the railway on copper concentration (wooden ties used).

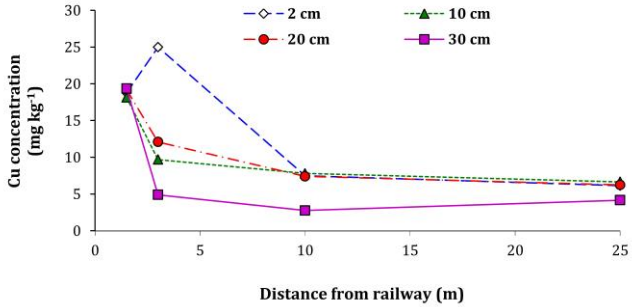

Figure 4. The influence of the distance from the railway on copper concentration (concrete ties used).

Determination of sodium

Sodium concentrations were also significantly higher in soil sampled close to the highway, as shown in Figure 5 and 6. The highest concentration was 770 mg kg^{-1}. The extraction efficiency depends on used extraction agent in the case of sodium as reported by Zehetner et al. (2009), who used the solution of NH_4NO_3 in order to extract sodium from soil sampled near the highway and obtained the maximum concentration of 48 mg/kg only. During winter months, the salt (NaCl) was applied in order to lower melting point of ice and to prevent ice forming on the road surface. Therefore, the sodium concentration in both soil layers was higher in winter and also in spring. During severe winters with extremely low temperatures, snowfalls and ice formation, elevated sodium level could be expected in soils close to the roads due to the extensive road salting. High concentration of sodium results in decreased bioavailability of potassium, calcium and magnesium for plants (Moťková et al., 2014). Sodium content in soils more distant from the road was lower, the determined values ranged from 28.5 to 165.0 mg kg^{-1}. According to the Czech Hydrometeorological Institute (CHMI), the precipitation during the winter period was below average (Czech Hydrometeorological Institute Data, 2014). It can be assumed that more sodium would be found in deeper soil layers in the case of more intensive precipitation. Sodium content in soil samples taken near the railroad was not determined since there is no salting effect in the vicinity of railroad.

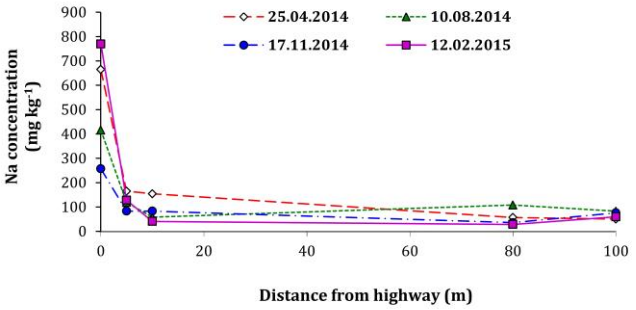

Figure 5. The influence of the distance from the highway on sodium concentration in soil (surface samples).

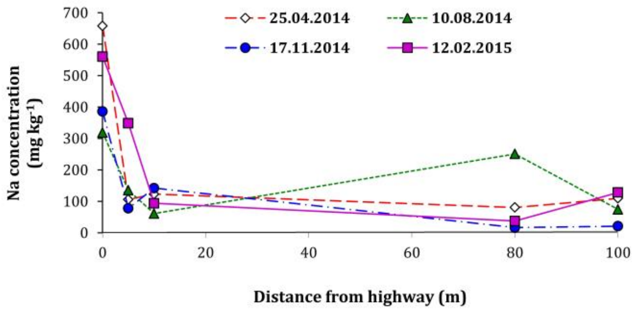

Figure 6. The influence of the distance from the highway on sodium concentration in soil (samples from the depth of 15–30cm)

Determination of mercury

Total mercury concentrations were determined in soil samples taken from the railroad location only. The results obtained for the sampling site situated close to the railway are shown in Figure 7. There is an evident correlation between distance from the railway and total content of mercury in soil. The highest Hg concentration reached 0.181 mg kg^{-1} at distance of 1.5 m from the railway, in the surface sample near the wooden ties. High concentrations of mercury near the railroad indicate that the track bed could be the source of pollution. It is known that railway wooden ties were impregnated using the mercury compounds in order to prevent fungal degradation (Reinprecht, 2010). The lowest mercury concentration (0.017 mg kg^{-1}) was found in the distance of 10 meters from railway, in the depth of 30 cm. The different results were obtained for the location with concrete railway ties (Figure 8). The concentration of mercury slowly increased with the distance from the railway with the highest value of 0.145 mg kg^{-1}. This supports the assumption that the main source of pollution is impregnation of wooden ties (Reinprecht, 2010).

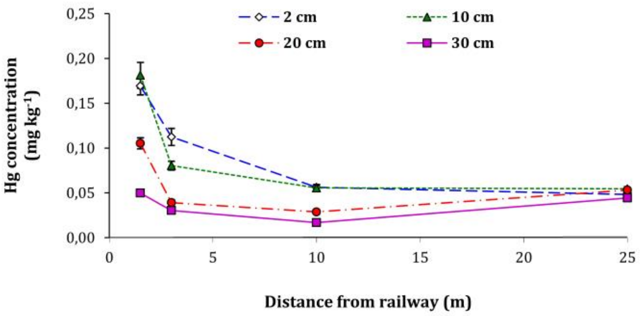

Figure 7. The influence of the distance from the railway on total mercury concentration (wooden ties used).

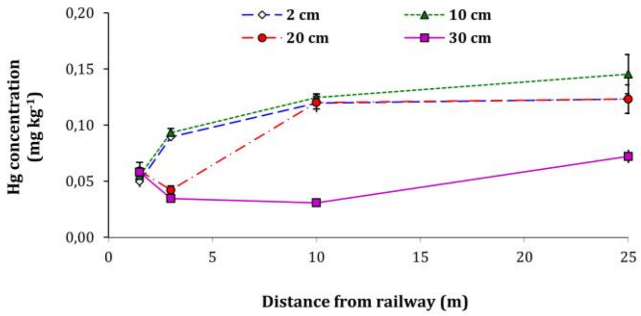

Figure 8. The influence of the distance from the railway on total mercury concentration (concrete ties used).

Conclusion

There is still a lack of available information dealing with concentration of metals in soils near highways and especially near railroads. This study revealed that the wooden railroad ties could be a source of mercury and copper in soils near older railroads since their wooden ties were impregnated with mercury and copper compounds. Another significant aspect of the study is the elucidation of the road salting effect on nearby soils. Along with the strong rise of traffic and road transport, surrounding soils are potentially endangered by increasing salinity. The level of copper concentration in soil depends on the distance of nearby railway or highway as trains, cars and trucks release copper into the environment as well. However, the relatively fast decrease in concentrations of individual contaminants with increasing distance from the highway and railway indicates that the safe distance, e.g. for agricultural production, is approximately 10 m from the source of pollution.

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