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SCREENING OF THE SPATIAL DISTRIBUTION OF RISK METALS IN TOPSOIL FROM AN INDUSTRIAL COMPLEX

ROZKŁAD PRZESTRZENNY METALI TOKSYCZNYCH W GÓRNEJ WARSTWIE GLEBY TERENU PRZEMYSŁOWEGO

Abstract: For the sustainable development of urban areas, it is necessary to identify if environmental pollution exists and where hot spot pollution sources lie. In this study, 280 topsoil samples were collected from an industry estate in Zlin (the Czech Republic). In these samples, the presence of toxic metal was analyzed by wave dispersed X-Ray fluorescence (ED-XRF), and statistical analysis revealed that the major anthropogenic contaminants in the topsoil were Pb, Zn and Sn. Further contaminant analysis by atomic absorption spectrometry (AAS) determined the maximum contents of 28558.47 mg/kg for Pb, 1132.35 mg/kg for Sn and 2865.22 mg/kg for Zn in selected topsoil samples. According to soil pollution index results, the main proportion of topsoil is contaminated, with the possible sources of contamination being traffic and a nearby municipal heating plant. This study proves that the combination of preliminary ED-XRF topsoil analysis, a multivariative statistical approach, AAS analysis and the geographical information system (GIS) is effective and together form a powerful tool for mapping topsoil contamination and conducting an environmental risk assessment.

Keywords: industrial urban soil, pollution, heavy metals, multivariative statistics, cluster analysis, ED-XRF, AAS, GIS

Introduction

Soil has been perceived by human beings as a source of building materials and as the medium for farming, ergo the lowest component of the food chain. However, from an environmental point of view, soil should be perceived as an ecosystem, the quality of which is influenced positively or negatively by the mutual interaction of individual (animate and inanimate) components. For that reason, soil has to be considered an animate, dynamic and vitally important part of the ecosystem. Its quality should support the desirable development of plants and animals, as well as biological productivity, and should not be hazardous to human health [1-3].

According to the EU COM (2006) 232 directive proposal for soil protection, the member states of the EU have to identify localities where proven hazardous substances occur, as a consequence of human activities, in such quantities that represent a significant risk to human health or the environment. The risk must be quantified by taking present and future approved land use into consideration [3, 4]. Incidentally, a group of EU member states undertook the systematic monitoring of the quality of agricultural and forest soil in the past, which has been integrated into their legislation. However, the monitoring of urban soils has been neglected.

Even though the Czech Republic joined the European Union in 2004, soil quality monitoring was actually carried out in 1990-1993. Most attention was paid to risk elements

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(As, Cd, Cr, Ni, Pb) and persistent organic pollutants (PAH, PCDD/PCDF, DDT and styrene). It was found that only 2% of the total land mass of the Czech Republic (78,865 km^2) was contaminated. The pollution was limited to small areas and tended not to indicate diffuse sources. The areas in the northern part of the Czech Republic (municipal heating and power plants, surface mining, the chemical industry), northern Moravia (heavy industry), and Prague and its environs (traffic emissions) as well as fluvial soil in the alluvium of large rivers (the Labe, the Morava) were very affected by both pollutant groups [3, 5].

In the Czech Republic, Sanka [6] carried out a study to identify the sources of soil contamination and their impact on the health of the population of Brno. Soil and plant samples were analyzed for the presence of heavy metals (Cd, Cu, Cr, Ni, Pb, Zn) and PAH (*polyaromatic hydrocarbons*). The results displayed a significant difference between pollutant content in plants growing in an urban and suburban environment. Furthermore, it was discovered that the traffic in an urban environment is the major source of soil contamination by the elements of Zn, Cu, Pb. These conclusions corresponded with an earlier study of lead accumulation from petrol combustion on Californian roads, which was conducted between the years of 1976-1990. Due to the lead content of petrol being reduced from 0.4 to 0.15 g/dm^3 in 1986, the atmospheric deposition of lead fell by approximately 50% and no doubt there was a reduction in the deposition of airborne lead into soil.

The aim of this pilot study is to identify major inorganic hazardous metals which contribute to the heavy metal content in topsoil on an industrial estate. The employment of multivariate statistical techniques is used for determining the lithologic and anthropogenic origin of major inorganic pollutants, this in addition to visualizing their spatial distribution via GIS. The results of this study shall be the basis for topsoil monitoring over the long term and the environmental risk assessment support system used for area sustainability.

Methods

Site description

Sampling the 280 topsoil samples was carried out on an industrial estate that once served the SVIT shoe production company. This is located near the centre of Zlin (the Czech Republic) in a part of the city lying at the bottom of a valley, through which the Drevnice river flows. The industrial estate and its surroundings are in area formed from Paleogenic rocks - Maguras flysch of the Racans tectonic unit, where lime clay alternates with glauconitic sandstone. In the fluvial plain of the River Drevnice, the bedrocks are covered with alluvial sediment up to a thickness of 3-4 m. The terrain's surface contains various types of anthropogenic backfill, as well as tiled and concreted areas [7].

Soil sampling, analysis and data processing

The sampling points were all at accessible public places on the industrial estate. The points were located by a GPS. The 0.5 kg bulk samples were transferred into sealable polypropylene plastic sample boxes and transported to the laboratory for analysis. The screening analysis of inorganic contamination was carried out according to the European norm EN 15309:2007 for the characterization of waste and soil by XRF. According to the

XRF's measurement results, multivariative and cluster analysis was accomplished and samples containing potential contaminants were selected for analysis via AAS. Raw data (GPS coordinates, the intensity of XRF spectral lines, contaminant amounts in the leachates and the intensity of the photonic dose equivalent) were stored on the MS Access® database. The statistical evaluation was conducted by the Statistica 6® program, which is able to carry out the multivariative, correlation and cluster analysis that can assess the relationships between the soil contaminants found and their origin. Areal contaminant distribution was visualized by ArcGIS 9.3.1 software, which contains the extension for Inverse Distance Weighted interpolation.

Results and discussion

Pollutant identification

The identification of potential contaminants was conducted via cluster analysis. Four groups of elements are present in the dendrogram obtained (Fig. 1). It is supposed that, with a higher dendrogram position (from Sb to Ca), there is a decrease in the degree of anthropogenic origin and an increase in the degree of lithologic origin in topsoil. According to the geological map of the Czech Republic, the rocks belonging to the most recent geological era (Cenozoic middle Eocene - lower Oligocene) - glauconitic sandstone, calcareous claystone, sandstone, conglomerates and minor claystone exist in the study area. Therefore, it may be assumed that Ca, Mg, Fe, Si, Al, K and Na are the main lithologic elements of uncontaminated topsoil.

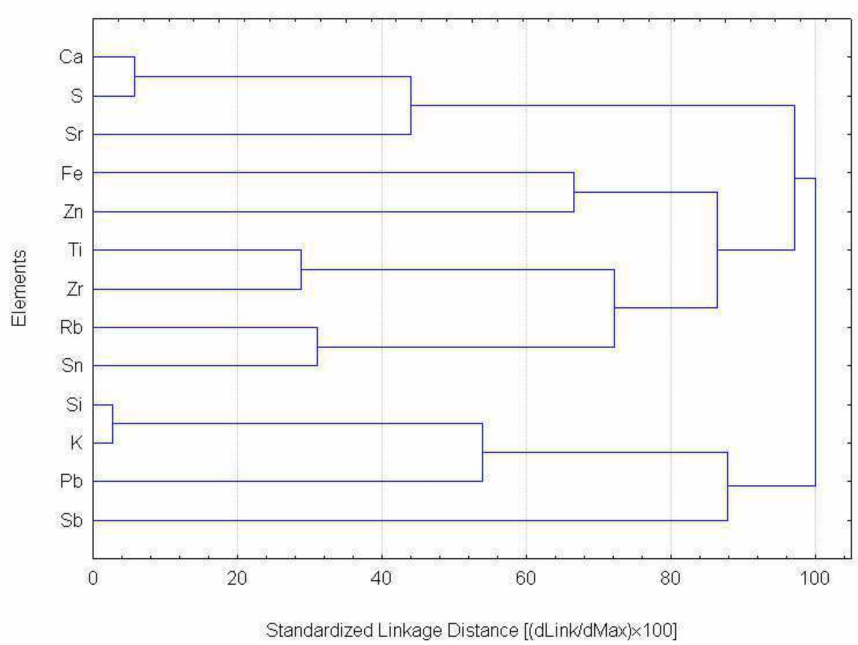

Fig. 1. Dendrogram of elements in soil samples based on ED-XRF spectral analysis

Taking into account the results of preliminary screening by XRF, the geological structure and mineralogical composition of rock in this particular environment, the foremost risk metals can be classified as Pb, Zn, Sn, Fe and Ca in the topsoil samples. However, for a qualified decision on whether the enumerated metals represent such topsoil contamination, it is necessary to compare the metal content of samples with the valid legislated regulatory levels of the country.

Spatial distribution of pollutants

The comparison of potential risk metals with regulatory levels from the Czech Ministry of the Environment - methodical directive No. 8/1996 [8] - is presented in Table 1. The topsoil limit levels for Pb, Sn and Zn were exceeded and, for that reason, attention shall now be focused on these metals.

Table 1

Czech regulatory levels and descriptive statistics of element content in soil samples and *soil pollution index* (SPI)

	Unit	**Minimum**	**Maximum**	**Median**	**SD**	**RL**
Pb	[mg/kg]	10.19	28558.47	38.56	2640.66	250
Sn	[mg/kg]	1.19	1132.35	20.50	14.63	200
Zn	[mg/kg]	16.73	2865.22	521.27	193.86	1500
SPI	[-]	0.02	39.83	0.52	2.38	< 1

As can be seen from Figure 2, the spatial distribution of Pb, Sn and Zn significantly differs. The highest topsoil content of Pb is concentrated in the southwest part between the road, railway and Building No. 122 (highest content = 28558.47 mg/kg), where the value of the limit has been exceeded more than hundredfold. It is more than probable that here the remediation of lead has to be conducted. A likely source of contamination can be found near Building No. 122, where a car repair workshop and a scrapyard firm are placed. It is there that used lead batteries from cars, containing PbO_2 and $PbSO_4$, are replaced or repurchased.

Nevertheless, the greater content of Sn and Zn occurred unevenly, distributed throughout the entire area. However, identifying the source proves difficult in the case of Sn. Figure 2 shows that highest content of Sn (1132.35 mg/kg) was discovered in front of Building No. 31 (a hospital car park), with increased concentration alongside roads. The amount of Sn oscillates around the mid value of 521.27 mg/kg in the study area, so it can be supposed that a sizeable source exists there. For that reason, thought was paid to the local heating plant. At present, a mixture of black and brown coal is combusted in a fluidized bed; for gaseous combustion products, a desulphurization process is applied. Nevertheless, until 1995, the products of combustion were freely released into the air. Danihelka et al [9] have found through analyzing the type of Czech coal used for combustion in heating plants that the Sn content in coal ranges between 0.9÷2.4 mg/kg. After combustion of the coal, and following product analysis, the content of Sn in particular emissions was 1÷85 mg/kg, in fly ash 2.5÷7.7 mg/kg, and in bottom ash 1.6÷3.7 mg/kg. Based on these results, it can be supposed that the Sn content in topsoil is probably residual, because the new technology now in place at the heating plant does not allow products of combustion to be dispersed in the air.

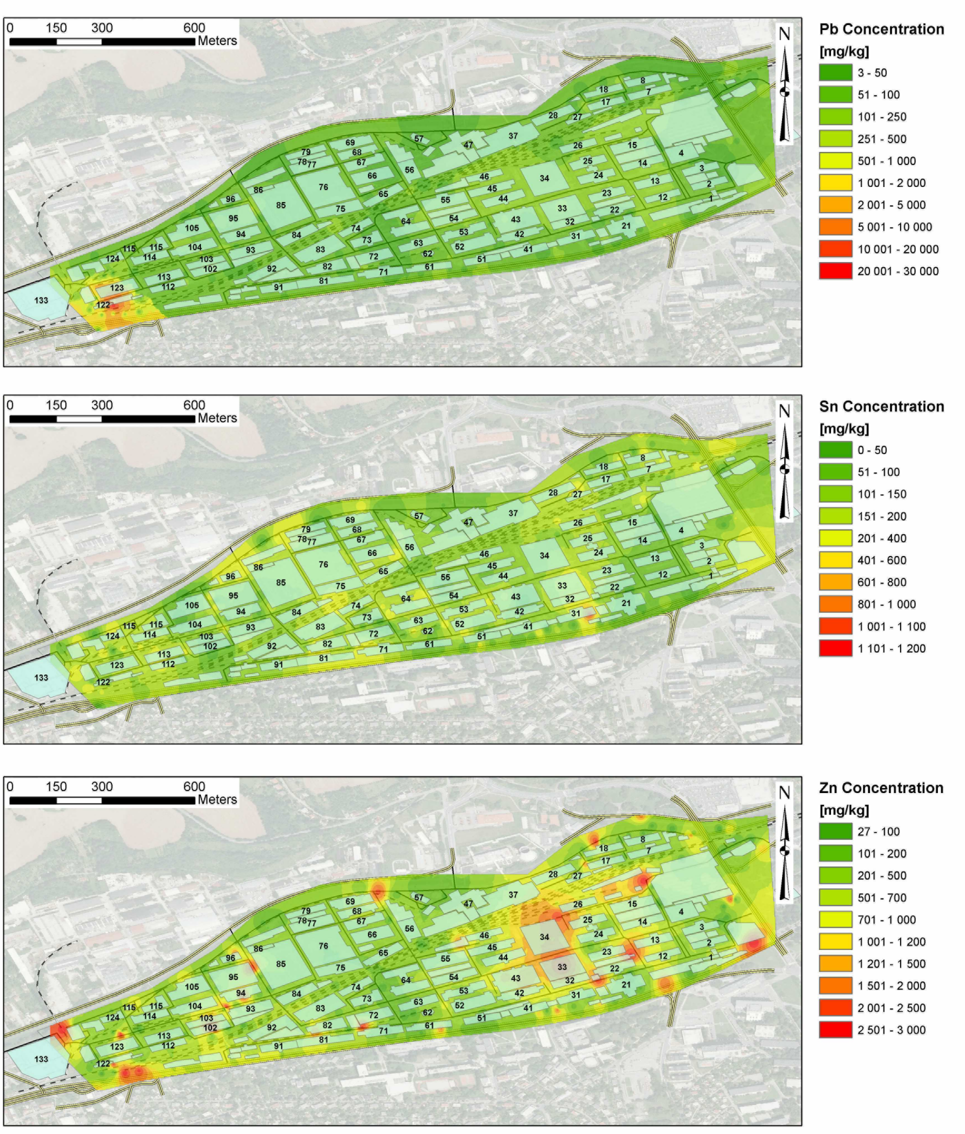

Fig. 2. Spatial distribution maps of Pb, Sn, and Zn

The last metal to be studied was Zn, of which higher concentrations have been found primarily beside roads and railways. The maximum Zn content of 2865.22 mg/kg was determined near Building No. 122 (a car repair workshop), but a high amount - as much as 2000 mg/kg - was discovered by many other buildings, as can be seen in Figure 2. Near to buildings number 122 and 34, a railway track traverses the roads and could cause the higher Zn content in topsoil found there. This assumption confirms the geochemistry study of urban surface soil by Anderson et al [10], or Pratt and Lottermoser [11], who investigated the mobilization of traffic derived trace metals. It has been discerned that the Zn in the sediments alongside roads orginates from tires, road signs and/or railings.

Another possible source of Zn can be shoe production, which took place at the SVIT industrial estate until 1990. A paper by Malik et al [12] focused on the study of soil contamination in the city of Sialkot (Pakistan) shows that a potential source of Zn was the zinc salts used for tanning. Another possible Zn source is rubber processing for tires and shoes, in which zinc oxide is used as an additive. Data from an archive revealed that plastic and rubber production for shoes was carried out in buildings numbered 43-46, 95 and 104. In shoe production technology, chromium tanning and various rubber types were utilized. Due to this, the possible major sources of Zn might be the railway lines and traffic, in association with a minor Zn source of past shoe production.

Conclusions

In the urban topsoil, a large amount of heavy metals, lithologic as well as anthropogenic in origin (traffic, industry, etc.), can be found. For that reason, knowledge of contaminated sites is necessary for their removal. The results of this work will be used as a basis for detailed and long-term monitoring of risk metals in the topsoil of the studied area.

The combination of multivariate statistical approaches, cluster analysis and GIS visualization seems to be very useful for interpreting soil environmental data sets. The use of multivariate analyses (CM and CA) by ED-XRF result processing helps to quickly identify the major anthropogenic elements (Pb, Sn and Zn) present in topsoil. In the selected samples, the exact content of risk elements was determined via the AAS method. It was found that in the western part of the industrial estate, the Pb content in topsoil reaches the extreme amount of 28558.47 mg/kg, whilst, in the opposite eastern side, the content of Zn was 2865.22 mg/kg and that of Sn was 1132.35 mg/kg, which indicates they were in excess of Czech regulatory limits. The visualization of spatial metal distribution and SPI was conducted by GIS. The maps created show that the distribution of contamination is not regular but depends on the kind of production process at specific sites. According to the SPI results, the places requiring immediate decontamination were identified, too.

Acknowledgements

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