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Spatial distribution of potentially bioavailable metals in surface soils of a contaminated sports ground in Galway, Ireland

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Abstract Assessing the environmental risk of metal contamination in soils requires the determination of both total (TCs) and bioavailable (BCs) element concentrations. A total of 200 surface (0–10 cm) soil samples were collected from an urban sports ground (South Park) in Galway, Ireland, a former landfill and dumping site, which is currently under remediation. The potential BCs of metals were measured using ethylene-diamine-tetra-acetic acid (EDTA) extraction followed by inductively coupled plasma-optical emission spectrometry analysis, while the TCs were determined using portable X-ray fluorescence spectrometry. It was found that Zn was primarily present in the insoluble residue (EDTA un-extractable) fraction in soils, with the median ratio of BCs/TCs 0.27.

However, Pb and Cu had higher ratios of BCs/TCs (median values of 0.60 and 0.39, respectively) suggesting that they are potentially more bioavailable in the soils. The spatial distribution maps showed that both TCs and BCs for Cu, Pb and Zn in the study area were spatially heterogeneous. It was found that the BCs exhibited generally similar spatial patterns as their TCs of Cu, Pb and Zn: high values were mainly located in the west, north-east and south-east portions of the study area, where only a thin layer of topsoil existed. It was recommended that the current remediation action for this site needs to be carried out on an urgent basis.

Keywords Spatial distribution · Urban soil · EDTA · Bioavailability · Portable XRF · Metals

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Introduction

The distribution and abundance of total metal concentrations are useful indicators of the extent of soil contamination (Tokalioglu et al. 2000; Xiao et al. 2011), but as the risk from metals depends on their bioavailability (Prokop et al. 2003; van Gestel 2008), total concentrations fail to provide sufficient information regarding the potential environmental impact (Hobbelen et al. 2004; Bhattacharyya et al. 2008).

The bioavailable fraction is defined as the proportion of the total quantity of an element present in a

specific compartment of the environment, that within a given time span, is either available or can become available for uptake and accumulation by organisms either directly from the surrounding environment or by ingestion (e.g., dust) (Peijnenburg and Jager 2003; Peijnenburg et al. 2007). The assessment of the environmental risk requires the determination of not only total metal concentrations in soils but also the bioavailable fraction. In practice, the evaluation of metal bioavailability in soil samples is primarily based on the use of leaching or extraction techniques (e.g., single or sequential procedures) (Kim et al. 2005). This facilitates the measurement of labile or bioavailable forms of elements that are essential for establishing appropriate environmental policies (Quevauviller 1998; U.S. National Research Council 2003). Ethylene-diamine-tetra-acetic acid (EDTA) has been recommended by the “Measurement and Testing Program” of the European Community (EC) for determining the extractable or mobile fraction of metals from soils and sediments (Ure et al. 1993; Cajuste and Laird 2000) and as a result has been extensively used as an extractant for potentially bioavailable metals (Manouchehri et al. 2006; Jamali et al. 2009; Lee and Kim 2010).

In urban environments, soils that are heavily polluted with metals not only directly affect environmental quality, but also pose a potential threat to public health (Dudka and Miller 1999; García et al. 2004; Wong et al. 2006). Therefore, the monitoring of soil quality in parks and other green spaces used by the public in urban areas is of great importance. There are numerous urban parks in Ireland. The site of interest in this study, South Park, Galway is currently an urban public park (sports ground), and it was used as an unregulated landfill site for various wastes prior to the 1970s. The soils in the sports ground have recently been reported as severely polluted with respect to Pb, Cu, Zn and As (Zhang 2006; Carr et al. 2008). As more than half of the site contained metal concentrations in excess of levels deemed a health hazard and associated with potential medical problems in children (Carr et al. 2008), remediation was undertaken, but is currently delayed. However, these previous studies focused on total metal concentrations. The incorporation of site-specific bioavailability into the risk assessment process may help to reduce the uncertainty in determining contaminant risk and to better understand the sources and nature of the pollution.

In addition, many studies have shown the necessity of determining the spatial distribution of metals when assessing the current status of contamination in soils (Cattle et al. 2002; Jung et al. 2006; Wang et al. 2012). Such spatial data can help decision and policy makers in identifying locations where remediation efforts should be focused on (Maas et al. 2010). Despite this, previous studies on the evaluation of metal bioavailability have seldom considered spatial distribution. Mapping based on GIS and geostatistical techniques are useful approaches for the assessment of such spatial patterns (Liu et al. 2006; Tiwari and Rushton 2010).

The present study was conducted to determine both total (TCs) and bioavailable (BCs) concentrations of some metals, for example, Cu, Pb and Zn, in soils of the site, followed by the subsequent production of spatial distribution maps for the identification of patterns of pollution and possible pollution sources. Furthermore, this approach will establish whether the BCs of metals display similar spatial patterns with their corresponding TCs. The information and methodologies in this study will be useful for local government and others in the risk assessment of metals in urban soils.

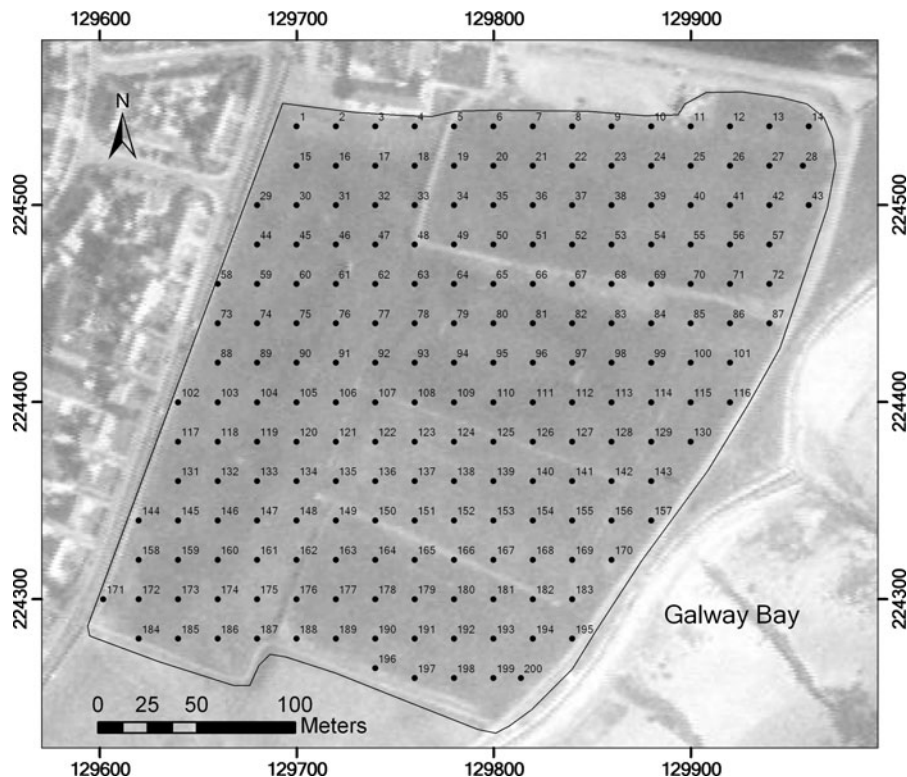
Materials and methods

Study area

The study site (South Park sports ground) is located in Galway City (population approximately 80,000), along the west coast of Ireland. Average annual rainfall is about 1,200 mm in the city. The bedrock on the west of the city is comprised of metamorphic and igneous rocks, with carboniferous limestone to the east (Zhang 2006).

The soil in South Park is comprised of shallow brown earths and rendzina. This park was originally the site of an old landfill that was converted into a sports field for public use in the 1970s (Carr et al. 2008). Numerous wastes were deposited in this dumping site, including municipal, hospital and industrial waste (Carr et al. 2008). The sampling site that covers an area of approximately 10 ha extends 290 m in the E–W direction and 330 m in the N–S direction (Fig. 1).

Fig. 1 Soil-sampling locations in South Park, Galway (background air photograph from Ordnance Survey Ireland)



Soil sampling

An intensive investigation of the site was conducted in April 2009. A total of 200 soil samples were collected on a grid system at intervals of 20 m (Fig. 1). The samples were collected using a stainless steel sampler from the surface (0–10 cm). Each sample was a composite sample, consisting of 4–6 soil cores (approximately 1 kg), taken randomly from 1×1 m areas.

Extraction, digestion and metal determination

Soil samples were placed in clear polythene bags and dried at room temperature (20 °C) in the laboratory. The samples were then homogenized with a wooden roller, sieved through a 2-mm stainless steel mesh in order to remove any stones and plant debris and finally mixed thoroughly to obtain a representative sample. All samples were subjected to the classical cone and quarter technique to split the soil samples.

The bioavailable metal fraction was extracted using the addition of 25 ml of 0.05 M EDTA to a 5-g aliquot of each sample, covered and mechanically shaken for 1 h (Quevauviller 1998). The bioavailable metal

concentrations were determined by ICP-OES (Varian Vista 735). Details of the process for determining metal bioavailability using the EDTA extractant are available in Quevauviller (1998).

Total metal concentrations were determined on the remainder of the sample using a portable X-ray fluorescence spectrometry (P-XRF) analyzer in the laboratory (model INNOV-X-SYSYEMS Alpha-6500). The equipment features a miniature X-ray tube and high-resolution detector that is pointed at the surface of the soil sample contained in a transparent plastic bag. The analysis time was set to 2 min for every reading. The equipment was standardized after every 30 readings using a standardization plate provided by the manufacturer. The P-XRF analysis was carried out in the laboratory for the processed samples so as to avoid variations and uncertainty in metal concentration associated with both soil moisture contents and differences in grain size. For comparison with the total element determination by P-XRF, a total of 30 sub-samples (0.2 g each) were acid digested (10 ml HF, 5 ml HClO₄, 2.5 ml HCl and 2.5 ml HNO₃) and analyzed using inductively coupled plasma-optical emission spectrometry (ICP-OES).

Quality assurance

Quality control assessment of the data included the use of soil certified reference materials (CRMs): Montana I (SRM2710), Montana II (SRM2711) and San Joaquin (SRM2709) from NIST (National Institute of Standards and Technology, USA) in the analytical procedure for both P-XRF and ICP-OES, as detailed in Dao et al. (2012). The results were in good agreement with the certified values and demonstrated the suitability of P-XRF and ICP-OES for determination of metal concentrations in soil samples, especially for contaminated soils.

Data analyses

This study focused on Cu, Pb and Zn. While both Zn and Cu are bio-essential elements, they are potentially toxic at elevated concentrations (Fatoki 1996). Lead, which is not considered to have any known biological function, can cause toxic effects and severe poisoning (George Cherian and Goyer 1978). The TCs, BCs and the ratios (BCs/TCs) of these metals are represented by TC_Cu, TC_Pb, TC_Zn, BC_Cu, BC_Pb, BC_Zn and Ratio_Cu, Ratio_Pb and Ratio_Zn, respectively. Basic statistical analysis was carried out for these variables, and correlation analysis was also employed to reveal the relationship between these variables.

Probability distribution

Prior to the production of the spatial distribution maps for the metals, the data were initially tested to establish whether it conformed to a normal distribution as a serious violation of normality, such as high skewness and outliers, can impair the variogram structure and the kriging results (Helesl 1987; McGrath and Zhang, 2003), and thus, data transformation is necessary to normalize such data sets. The log-transformation is the most popular method for data transformation in soil science (Hengl et al. 2004; Reimann and Filzmoser 2000) and was considered in this study.

Spatial structure

Geostatistics uses the techniques of variogram (or semi-variogram) to measure the spatial variability of variables and provides the input parameters for the spatial interpolation of kriging (Webster and Oliver

2001). In order to properly model the theoretical variograms, directional features of a spatial correlation were initially investigated using variogram surfaces. None of the metals determined showed a clear anisotropic feature. Therefore, isotropic variograms were employed to model the spatial structures of metals as this is an effective tool for quantitatively highlighting spatial variability (Burgos et al. 2006).

The kriging interpolation method was employed in order to reveal the spatial distributions of BCs and TCs of Cu, Pb and Zn, as it is considered the most appropriate linear unbiased estimator (BLUE) (Isaaks and Srivastava 1989). In this study, ordinary kriging (OK) was used to produce the spatial distribution maps for the selected metals.

Software

The raw data were stored in Microsoft Excel, and the basic statistical parameters were calculated using this software. Scatter plots were utilized to visualize the differences between the results from the two analytical methods. Semi-variograms were modeled with the aid of VarioWin (version 2.2). All maps were produced, and spatial interpolation was performed using ArcGIS (version 9.3).

Results and discussion

Comparison between P-XRF and ICP-OES results

In order to assess the performance of the P-XRF technique, a scatter plot was used to compare its results with those from ICP-OES, using Pb as an example (Fig. 2). The results from the two methods were consistent with the Spearman's correlation coefficient value of 0.977. With a few exceptions, most samples were located closely along a diagonal line on the scatter plot in Fig. 2. Copper and Zn for P-XRF readings also showed very high correlations with their ICP-OES readings (Spearman's correlation coefficient 0.956 and 0.958, respectively). Similarly, Clark et al. (1999) reported a very good correlation between Flame AAS and P-XRF techniques. Overall, the above data demonstrated the suitability of P-XRF for analyses of Cu, Pb and Zn concentrations in soils in this study.

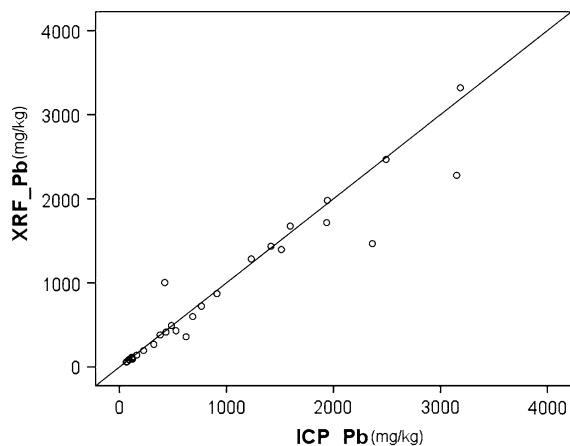


Fig. 2 Scatter plots between Pb values measured by P-XRF and ICP-OES methods

Basic statistics for total and potentially bioavailable concentrations

The basic statistical parameters (mean, median, minimum, maximum, skewness and kurtosis) for TCs and BCs of Cu, Pb and Zn in the soils are listed in Table 1. The median values of these elements in the surface soils of Ireland (Fay et al. 2007; Zhang et al. 2008), which can be regarded as background values in Ireland, are presented for comparative purposes.

Metal concentrations in soils of the study area were heterogeneous, as indicated by the large differences between the minimum and maximum values for both TCs and BCs. Overall, it was found that TC_Cu, TC_Pb and TC_Zn in all the samples were higher than the national background levels. The median TCs for Cu, Pb and Zn

were sevenfold, 15-fold and sixfold higher than their background values, respectively. Meanwhile, all mean values were significantly higher than the medians indicating the existence of outliers or extreme values which skewed the distribution of the data set. The high skewness and kurtosis statistics also provided evidence of disproportionate values at the upper tail of the distribution. Approximately 29, 42 and 30 % of the samples had TC_Cu, TC_Pb and TC_Zn concentrations exceeding the Dutch interventional values (Cu, 190 mg kg⁻¹; Pb, 530 mg kg⁻¹; Zn, 720 mg kg⁻¹) (VROM 2000). A TC value higher than the interventional value is an indication that the soils require remediation. These relatively high metal concentrations in the study area imply that the soils are contaminated.

The average abundance of metals in the extractable fraction of soils decreases in the following order: Pb > Cu > Zn. The result that Zn had the highest insoluble fraction in the residue form in the soil is in line with the previous reports (Adriano 2001; Li and Shuman 1996; Shuman 1985). The greater extractable values for Cu may be related to the highly stable soluble complex that Cu forms with EDTA (Madrid et al. 2008). Lead had the highest ratio suggesting a greater potential bioavailability in soils.

Relationship between metal concentrations and their bioavailable proportions

The Spearman correlation coefficients between metal concentrations (TCs and BCs) and their ratios were calculated, and the results are given in Table 2.

Table 1 Summary of total and bioavailable concentrations of Cu, Pb and Zn in soils of South Park, Galway

Variables	Minimum	Maximum	Mean	Median	StDev	Skewness	Kurtosis	Irish soil ^a
TC_Cu	18	2,168	190	116	268	4.36	24.7	16.2
TC_Pb	15	14,543	957	371	1,606	4.30	27.4	24.8
TC_Zn	30	4,883	689	380	803	2.20	5.77	62.6
BC_Cu	0.77	826	73.6	40.1	104.1	4.23	23.5	
BC_Pb	4.11	10,989	613	185	1,138	5.00	36.5	
BC_Zn	3.04	2,406	242	110	353	2.69	9.07	
Ratio Cu ^b	0.03	0.67	0.38	0.39	0.1	-0.32	1.08	
Ratio Pb ^b	0.11	0.93	0.59	0.60	0.13	-0.14	0.43	
Ratio Zn ^b	0.04	0.61	0.28	0.27	0.11	0.53	0.18	

n = 200, in mg kg⁻¹

^a Irish soil median values from Zhang et al. (2008)

^b Ratio = EDTA concentrations/P-XRF concentrations

Table 2 Spearman's correlation coefficients between metal concentrations and their bioavailable proportions

	TC_Cu	TC_Pb	TC_Zn	BC_Cu	BC_Pb	BC_Zn	Ratio_Cu	Ratio_Pb	Ratio_Zn
TC_Cu	1.00								
TC_Pb	0.95**	1.00							
TC_Zn	0.95**	0.94**	1.00						
BC_Cu	0.98**	0.93**	0.94**	1.00					
BC_Pb	0.93**	0.99**	0.92**	0.93**	1.00				
BC_Zn	0.93**	0.91**	0.98**	0.93**	0.90**	1.00			
Ratio_Cu	0.09	0.10	0.10	0.26**	0.17*	0.17*	1.00		
Ratio_Pb	0.03	0.11	0.02	0.13	0.23**	0.07	0.55**	1.00	
Ratio_Zn	0.59**	0.57**	0.64**	0.64**	0.58**	0.78**	0.32**	0.19**	1.00

Significant correlations are noted by: ** $P < 0.01$; * $P < 0.05$

Total concentrations of the individual metals in the study area were significantly correlated with each other (for example, the correlation coefficient of TC_Zn with TC_Cu and TC_Pb was 0.95 and 0.94, respectively). These correlations show that the variability of TCs is likely related to the same source of contamination. The correlations between TCs and BCs were also strongly correlated with respective values of 0.98 for Cu, 0.99 for Pb and 0.98 for Zn ($P < 0.01$ in all cases). Aslibekian and Moles (2003) also reported that EDTA-extractable metal concentrations correlated closely with total concentrations. In the case of the ratios of metals, it is more complex as both Ratio_Cu and Ratio_Pb were only weakly correlated with their corresponding TCs and BCs. However, Ratio_Zn showed a strong positive correlation with all variables except for Ratio_Cu and Ratio_Pb, which is potentially due to some common factors that influence Ratio_Zn and other related variables, such as TC and BC of Cu, Pb and Zn.

The comparison of spatial structures between total and potential bioavailable concentrations

In order to compare the spatial structures of the TCs and BCs, semi-variograms were produced for Cu, Pb

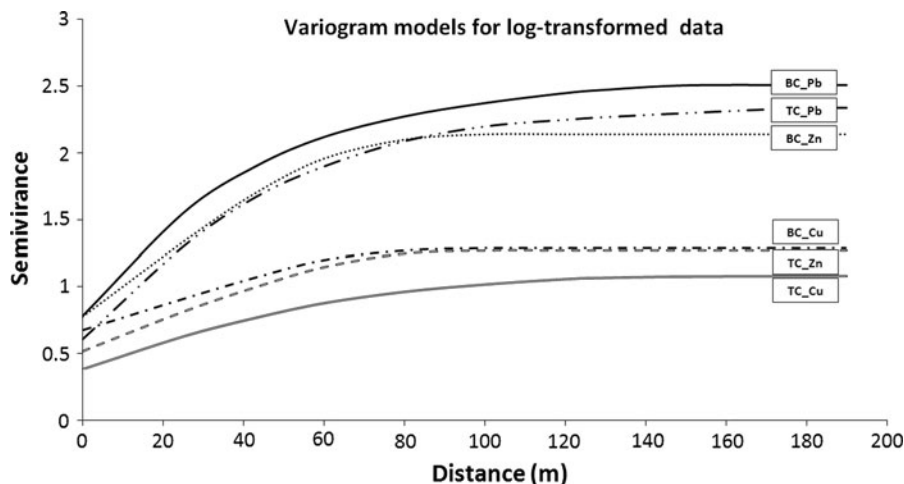
and Zn as these provide a clear representation of the spatial structure of variables and give some insight into the processes that are likely to affect their distributions (Wu and Zhang 2010). Prior to spatial analysis, the normality of metals was initially examined, and all the raw data for metals showed marked non-normal distributions. The Kolmogorov–Smirnov (K–S) test showed the normal distribution of the log-transformed data (all P values were above 0.05 for the three metals). Meanwhile, the data transformation toward normality is effective in reducing the effect of outliers (McGrath et al. 2004). Therefore, all subsequent spatial analyses were based on log-transformed data.

The parameters for isotropic semi-variogram models are listed in Table 3, and the fitted semi-variogram plots for all metals are shown in Fig. 3. An exponential model best characterized the structure of semi-variograms for Ln_TC_Cu, Ln_TC_Pb and Ln_BC_Pb and a spherical model for others. The existence of small positive nuggets in these models can be attributed to factors such as sampling errors, short-range variability and inherent unexplained variability (Bai et al. 2010). All semi-variograms are generally well structured

Table 3 Isotropic semi-variogram model parameters for the log-transformed data of Cu, Pb and Zn concentrations in soils and their standard deviations

Variable	Ln_TC_Cu	Ln_BC_Cu	Ln_TC_Pb	Ln_BC_Pb	Ln_TC_Zn	Ln_BC_Zn
Model	Exponential	Spherical	Exponential	Exponential	Spherical	Spherical
Nugget	0.39	0.68	0.61	0.78	0.52	0.78
Sill	1.08	1.29	2.33	2.51	1.27	2.14
Range	133	84	123.8	117.6	92.4	83.9
Nugget/sill (percentage)	35.65	52.4	26.2	31.2	40.9	36.3
SD	1.01	1.14	1.45	1.51	1.11	1.43

Fig. 3 Variograms for total and bioavailable metals in soils



with small nugget effects, in conjunction with the relatively long semi-variogram ranges (83.9–133 m) in comparison with the size of the study area, showing that the sampling density is adequate to reveal the spatial structures (McGrath et al. 2004). Generally, the nugget/sill ratio can be used to roughly classify the spatial autocorrelation of soil properties. In this study, the nugget/sill ratios for all models ranged from 26.2 to 52.4 %, indicating that these variables had a moderate spatial dependency. This spatial dependence is probably due to the distribution of patches of contaminated soils. The shape of the fitted variogram also provides information regarding the speed and intensity of the horizontal diffusion of metal concentrations in the environment (Romic et al. 2007). In this study, Pb diffuses relatively further than the other metals. It is worthwhile noting that the semi-variogram range for Ln_BC_Cu is two-thirds of that for Ln_TC_Cu and shows a higher nugget/sill ratio, which indicated its relatively weak spatial structure as compared to its correspondence. This finding is in line with several recent publications, which have shown the bioavailable fraction of metals had much higher spatio-temporal variability than the total concentration (Adamo and Zampella 2008; Mackey and Mackay 1996).

The most remarkable feature in Fig. 3 is the entire sill values of the models for BCs are higher than their corresponding TCs, and this feature is most apparent for Zn. Meanwhile, the standard deviation values for the log-transformed BCs were higher than the corresponding TCs, showing that BCs were more variable,

which should be related to the strong heterogeneity feature of pollution.

Spatial distribution of metal concentrations and their bioavailable proportions

Maps for all the total and bioavailable concentrations of the three metals showed similar spatial distribution patterns, indicating they may have been affected by the similar sources that may have been anthropogenic in origin in the study area. As an example, the maps for Pb are shown in Fig. 4.

The spatial patterns shown in this study concur with the findings of Carr et al. (2008), who previously studied this area using P-XRF in the field.

High concentrations of the metals were found in the main football pitch area on the west part of the park where a thin- and dark-brown topsoil covers the underlying soil that contains municipal and industrial waste such as broken glass, pottery, clinker, bones and metallic materials. The area close to the central and eastern sections of the site showed the lowest levels of contamination for all three elements, which were attributed to the relatively good coverage of topsoils. However, one clear exception was a region to the north of the study area, which contained very high TCs of Cu, Pb and Zn revealed by Carr et al. (2008) whose fieldwork was performed in summer 2006. In contrast, this area exhibited very low TCs in the present study. This was attributed to a new covering of topsoil as a preliminary immediate remediation by the local government in 2007.

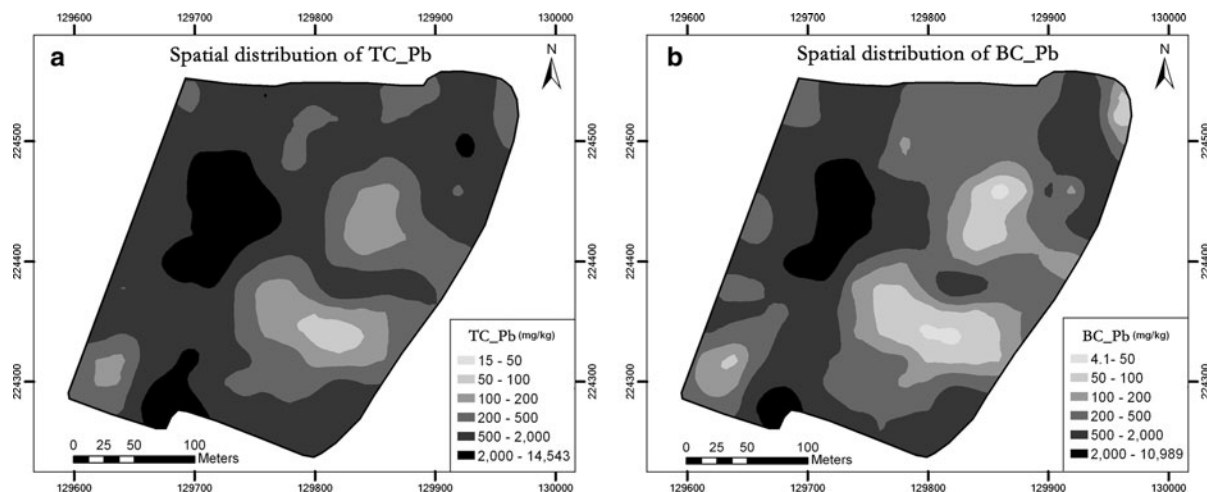


Fig. 4 Spatial distribution maps for total and bioavailable concentrations of Pb

Even though the overall spatial patterns of the bioavailable portions of the metals were similar to those of the total concentrations, the BC/TC ratio maps of the metals displayed some differences (Fig. 5). Ratio_Zn shows a distinctively different pattern from Ratio_Cu and Ratio_Pb, while the latter two share very similar distributions, indicating a similar EDTA-extraction capacity for these two metals. Interestingly, the Ratio_Zn displays a similar pattern to TC_Pb and BC_Pb, which lends some support to the previous finding that the Ratio_Zn exhibits a significant positive correlation with the TCs and BCs of Cu, Pb and Zn. The highest ratios for Zn occurred at the north-east corner of the site, while the ratios for Cu and Pb were elevated at the south-east corner, central and middle-upper part of the study area. Approximately 80 % of the area exhibited low ratios (0.10–0.35) for Zn, while 85 % of the area shows relatively high ratios for Pb (0.50–0.70). From these observations, it was clear that Zn was predominately bound to the residual (EDTA unextractable) phase of the soils. On the other hand, it demonstrated that EDTA has a strong chemical affinity for Pb. This finding is in agreement with other studies that frequently reported high EDTA-extractable Pb concentrations in urban soils (Kos and Leštan 2003; Stalikas et al. 1999). However, these relatively high ratios for Pb suggest that EDTA may be an aggressive extractant, and as a result, these values may reflect some of the total Pb concentration of the soil. This trend is similar to those reported by Madejón et al. (2009), as the BCs in some cases can be overestimated using

EDTA extraction due to the complex equilibrium involved. The U.S. Environmental Protection Agency (U.S. EPA 1990) has developed an uptake biokinetic model for estimating risks due to Pb exposure from soil. In the case of children, it is estimated that 30 % of the Pb concentration of soil may be bioavailable. In comparison with this model, the results in the current study may have overestimated the potential bioavailability of Pb. However, it should be noted that the elevated BCs for Pb in the study area (highest value for Pb is $10,989 \text{ mg kg}^{-1}$) indicate the high degree of pollution of these soils.

The bioavailability of metals in soils is complex as it is affected by numerous factors such as chemical properties, soil properties, elemental species exposed and climate (Burger et al. 2003; Clemente et al. 2003; Ernst 1999; Katayama et al. 2010). This location was historically used as municipal solid-waste landfill, which was most likely a source of many metals (including Cu, Pb, Zn, Cd and Sn) to the soil. Meanwhile, Mirlean et al. (2009) have reported that metals in heavily polluted soils are much more bioavailable than in the soils from uncontaminated areas. In addition, soil acidification and soil organic matter accumulation (SOC) can contribute to greater metal bioavailability, which in turn can increase the uptake and accumulation of metals by plants (Jin et al. 2005). According to the simplified Irish soil parameters distribution maps (Fay et al. 2007), the SOC and pH are estimated to fall in the range of 15.1–35 % and 5.01–6.0 %, respectively, in this area. These soil

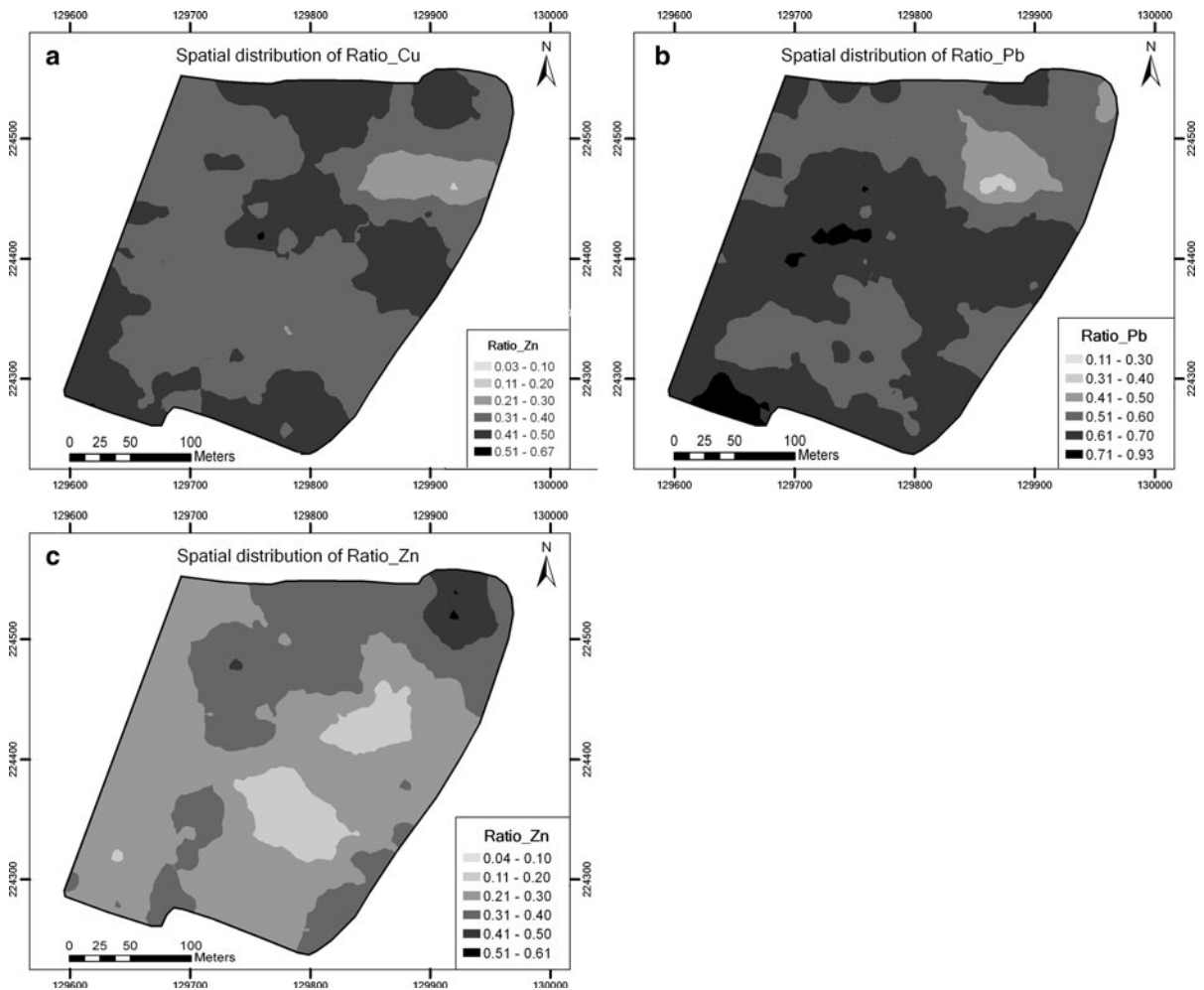


Fig. 5 Spatial distribution maps for BC/TC ratios of metals **a** Ratio_Cu, **b** Ratio_Pb, **c** Ratio_Zn

parameters, together with intense precipitation throughout the year ($\sim 1,200$ mm annually) combined with a high water table (close to the coastline), may predispose the area to a greater degree of metal mobility and toxicity, posing hazardous conditions. These results reinforce the necessity for immediate remediation of the contaminated topsoil in order to safeguard the health of children and others who use this amenity and are potentially exposed to metals.

Conclusions

The current status of metal contamination in an urban public park (sports ground), originally an old landfill,

in Galway, Ireland, was investigated based on a total of 200 soil samples. The total and bioavailable concentrations of the metals were determined and displayed wide ranges and asymmetrical probability distribution features, indicating the complexity of the study site. Elevated concentrations of Pb, Zn and Cu, which were observed in the surface soils, may pose a hazard to human and ecosystem health. High levels of bioavailable concentrations (BCs) of Pb, Cu and Zn were found in the study area. The BCs shared similar spatial patterns with the TCs for Cu, Pb and Zn, and elevated concentrations were predominately located on the western football field area and in both the north-east and south-east corners of the study area. The spatial distribution maps combined with the statistical

analysis results indicated soil contamination from the historical utilization of this site as a municipal solid-waste landfill. Therefore, the remediation actions should be implemented without delay to safeguard the users of this amenity, especially children.

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