

Identification and mapping of heavy metal pollution in soils of a sports ground in Galway City, Ireland, using a portable XRF analyser and GIS

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Key words: urban soil, sports ground, heavy metal, portable XRF, GIS, hazard assessment

Heavy metals in urban soils continue to attract attention because of their potential long-term effects on human health. During a previous investigation of urban soils in Galway city, Ireland, a pollution hotspot of Pb, Cu, Zn and As was identified in the sports ground of South Park in the Claddagh. The sports ground was formerly a rubbish dumping site for both municipal and industrial wastes. In the present study, a portable X-ray fluorescence (PXRF) analyser was used to obtain rapid *in-situ* elemental analyses of topsoil (about 5 - 10 cm depth) at 200 locations on a 20 × 20 m grid in South Park. Extremely high values of the pollutants were found with the maximum values of Pb 10297 mg/kg, Zn 24716 mg/kg, Cu 2224 mg/kg and As 744 mg/kg. High values occur particularly where the topsoil cover is thin whereas lower values were found in areas where imported topsoil covers the polluted substrate. GIS techniques were applied to the dataset to create elemental spatial distribution maps, 3D images and interpretive hazard maps of the pollutants in the study area. Immediate action to remediate the contaminated topsoil is recommended to safeguard the health of children who play at the sports ground.

Introduction

Research into the distribution of potentially toxic elements (PTEs) in urban soils has increased in recent years (Yang et al., 2006; Lee et al., 2006) and their likely effects on the human population is gaining more attention in the media. PTEs such as lead and arsenic are known for their toxicity and persistence in soils (Sharma et al., 2007). Studies of human exposure to heavy metals (Nriagu, 1988; Waisberg et al., 2003) reveal that they accumulate in the fatty tissue of the body and may affect the central nervous system and the internal organs. Of particular concern is lead pollution of topsoil in parks and playground areas, as children are extremely vulnerable to lead which attacks the central nervous system and is a cause of decreased IQ levels (Mielke, 1999, Fuge et al., 2005). Historically, this problem tended to affect city areas due to traffic pollution attributed mainly to combustion of leaded petrol, but elevated lead concentrations may also derive from municipal rubbish and mine wastes. Lead is not the only element to have been the focus of many human exposure studies to date. Three more elements will be focused on

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in this paper, in varying degrees are As, Cu and Zn. These four elements are well known anthropogenic contaminants. Toxicological risks arise when soil arsenic concentrations exceed 40 mg/kg (Pendergrass et al., 2006). A study of a site in the USA contaminated by arsenic revealed that children between 1 and 6 years take up on average 117 mg/day and this increased to 277 mg/day in the 90th percentile with a maximum of 899 mg/day (Moller et al., 2005).

Sources of heavy metal pollution can be both natural and anthropogenic. Natural processes such as bioaccumulation in plants can result in significant differences in metal levels between the upper humus-rich layers and the deeper layers of a soil profile (Weber et al., 2004). Heavy metals tend to accumulate in topsoil which can then pose a risk to human health as a result of entering the food chain through direct ingestion of dust or ingestion of plants (Lu et al., 2005). When assessing the soil geochemistry of a given area, it is important to distinguish the natural background level for the area from the anomalous, anthropogenically enriched levels (Martin et al., 2006). The spatial variations of heavy metal enrichments in soils may be related to natural dispersion processes such as leaching by percolating rainwater or mechanical transport in runoff, anthropogenic dispersion processes such as ploughing and landscaping, or dilution of polluted soil by other materials such as imported soils. Therefore, when studying a contaminated land, it is important to understand the sources of soils which can be both natural and anthropogenic.

Modern field-portable X-ray fluorescence (PXRF) metal analysers enable rapid acquisition of *in-situ* metal concentrations, which is ideal for the assessment of metal-contaminated soil (Kalnicky and Singhvi, 2001). In a comparison of methods for investigating lead-contaminated land, Taylor et al. (2005) demonstrated that in-situ PXRF analysis is fit-for-purpose and can be three times more cost-effective than ex-situ sampling and laboratory analysis, despite generating higher uncertainty on individual measurements.

A recent study by Zhang (2006) on urban soils of Galway City showed a clear pollution hotspot of Pb, Zn, Cu and As in South Park of the Claddagh area. Due to its proximity to the urban area and the seafront, this is a popular recreation area and is used for various sporting activities such as Gaelic football. Originally a small fishing community of thatched cottages on the outskirts of the city, The Claddagh is now a built up area with a central location due to urban growth. An area of approximately 8 hectares of formerly swampy marshland between the residential area and the seafront was reclaimed in 1931 to form the South Park (O'Dowd, 1993). Prior to this date, the area had been used as an unregulated landfill site for various wastes. Although the majority of the ground is now covered by grasses, bare soil is exposed in several places such as around goalposts. On the north side of the park (adjacent to a docking quay) are exposed areas of reddish soil, thought to be industrial waste from a historical fertiliser plant.

Residents in the vicinity to South Park have attempted to highlight the polluted soils to the city council, but due to lack of understanding of the nature of this pollution, no action has been taken. This study was undertaken to provide scientific evidence for the local government to consider appropriate action. Therefore, the objectives of this research were (1) to investigate the extent and level of heavy metal pollution in topsoil of the sports ground of South Park; (2) to portray their spatial patterns using GIS mapping

techniques; (3) to define possible pollution sources and recommend remediation measures.

Methods

Ex-situ and in-situ analyses of South Park soils

A pilot study was first undertaken to assess whether or not the present study might be warranted. This consisted of the repeated analysis of a soil sample taken in November 2004 as part of the Galway City urban geochemistry study (Zhang, 2006) and the collection and analysis of 5 more samples within 2 to 3 meters of that location in May 2005 (Specific coordinates for the samples based on the Irish National Grid system are provided in Table 1). These samples were sent to OMAC Laboratories Limited in Loughrea, County Galway for inductively coupled plasma - atomic emission spectroscopy (ICP-AES) analysis for pseudo-total concentrations of the elements following a 4-acid digestion (HF, HClO₄, HCl, and HNO₃). Quality control was achieved using reference samples, and the results (presented below) confirmed the high levels of pollutants in the original (2004) sample, and it was decided that a detailed survey of topsoil geochemistry throughout the South Park sports ground was required.

As stated by Kalnicky et al. (2001) field-portable XRF (PXRF) spectrometry is now a common analytical technique that enables a much faster turnaround time than conventional methods of soil analysis. The PXRF survey was undertaken during a 5-day period in June 2006. At 200 locations on a 20×20 m grid (Fig. 1), a stainless steel spade was used to cut and temporarily remove the grass and uppermost layer of root-rich soil (the 'sod') to expose the mineral-rich topsoil at a depth of 5 to 10cm. Using the spade the exposed soil was mixed and compressed, and its elemental composition was analysed in-situ using an Innov-X Alpha Series™ 6500 portable XRF metal analyser. The instrument contains a miniature (1.6 kg in weight) energy dispersive spectrometer with a 35 kV Ag target excitation source. Fluorescence spectra are detected through a 3.5 mm² analysis window by a peltier-cooled-solid state Si (Li) photodiode detector. The instrument is equipped with a removable Personal Digital Assistant (PDA) containing the software used for running the different analysis modes. After data acquisition, results can be viewed on the PDA display and can be downloaded to a PC on a spreadsheet for further processing.

In order to ensure the accuracy of the sampling locations, a differential GPS was used to locate the positions of all sites. At each site, at least two readings were taken in areas with 'background' metal levels of Pb concentrations below 1000 mg/kg, and at least three readings where Pb concentrations were close to or exceeded this level. On the border areas when sampling positions on the grid were close to paths or walls, an alternative sampling position nearby was selected (Figure 1).

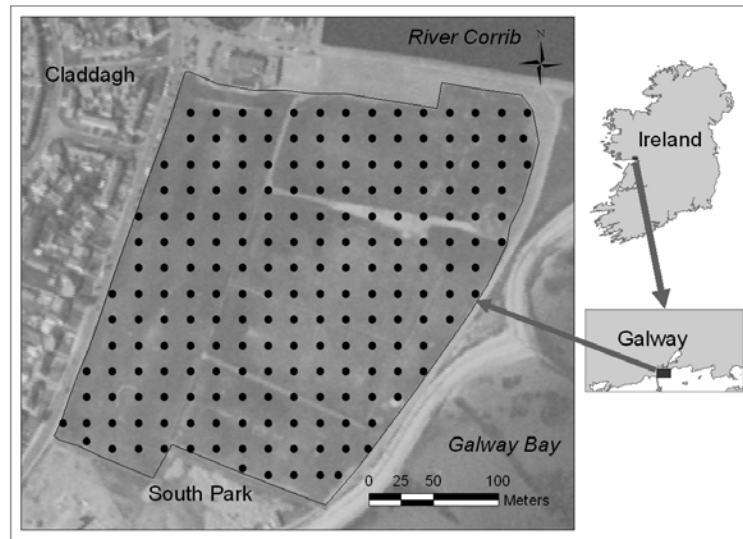


Fig. 1. Locations of *in-situ* soil analysis sites in South Park.

Data Analysis

The raw data was stored in a spreadsheet and an average value for the elements of interest was calculated for each site. Statistical parameters were then derived for the entire data set. The inverse distance weighted (IDW) method was applied to map the spatial distribution of the pollutants using ArcGIS[®] GIS software (v.9.1) to create maps and 3D graphics to display and interpret the data. Due to the significant pollution feature, the relatively easy method of IDW is sufficient enough to reveal the spatial distribution of pollutants in the study area. IDW uses a specific number of nearest points which are then weighted according to their distance from the point being interpolated. In this study, the power of 1 and the number of neighbouring samples of 12 were chosen to clearly show both spatial variation and spatial patterns of the pollutants. The interpolating surface is a weighted average of the neighboring sampling sites and the weight assigned to each point diminishes as the distance from the interpolation point to the sampling sites increases. When employing any spatial interpolation method it is important to note that, in theory, one can never be sure of reproducing the real value in the output plots. For this reason, results from specific locations should be taken as being the expected possible values and not the true values.

The 3D images were produced for better visualization and especially for non-experts (such as local government officials) to understand the spatial distribution of pollutants. Meanwhile, to aid decisions on site remediation, it is necessary to produce a hazard map showing the overall pollution status of the site. A pollution index (PI) for each pollutant at each sampling location was calculated based on the ratio with the Dutch intervention value (VROM, 2000). For calculation of PI values, the specific Dutch intervention values used were: Pb 530 mg/kg, Zn 720 mg/kg, Cu 190 mg/kg and As 55 mg/kg (VROM, 2000). The average and maximum of the PI values at each sampling location were calculated, and then subjected to IDW interpolation for creation of hazard maps.

Results and Discussions

Pilot study (confirmation of laboratory analyses)

Table 1 outlines the results of the pilot study. The ICP-AES data for samples collected in both 2004 and 2005 proved similar with the exceptions of two points, sample numbers L11-4 and L11-5, but they further confirmed the presence of elevated metal concentrations in the study area.

Table 1 Pilot study data (in mg/kg).

Sample No	Easting	Northing	Sampling Date	Pb	Zn	Cu	As
L11	129727	224374	07/11/2004	543	431	108	23
L11_Repeat	129727	224374	07/11/2004	512	418	106	21
L11_Repeat2	129727	224374	07/11/2004	531	421	108	23
L11-1	129725	224375	15/05/2005	537	436	112	21
L11-2	129727	224377	15/05/2005	569	463	126	20
L11-3	129728	224374	15/05/2005	542	432	106	19
L11-4	129725	224373	15/05/2005	2768	701	163	39
L11-5	129723	224377	15/05/2005	1001	610	133	29

Main study (in-situ PXRF): basic statistics and comparison

Table 2 shows the basic statistics for the raw PXRF elemental Pb, Zn, Cu, As concentration data obtained from the 200 sites. It can be observed by comparing the percentiles that there are large variations in the concentrations over the sample area, e.g., with Pb values varying from 17 mg/kg to 10297 mg/kg. More than 25% of the samples had Pb values higher than 1000 mg/kg. The highest value of Zn exceeded 2% (w/w). High values of Cu and As were also observed in the surface soils of South Park.

Table 2 Basic statistics of element concentrations in soils in South Park (in mg/kg).

	Min	5%	10%	25%	Median	75%	90%	95%	98%	Max
Pb	17	23	31	92	302	1016	2375	4056	5540	10297
Zn	31	44	57	126	328	809	1652	2996	4040	24716
Cu	<10	<10	<10	23	88	198	418	945	1660	2224
As	<3	4	5	7	18	60	167	225	333	744

Table 3 shows the median values obtained from the South Park in-situ survey in comparison to average levels of these elements in Galway City urban topsoil, average upper crust, and other Northern European countries. It is immediately obvious that the area of the Claddagh has atypically high levels of all four elements. Galway soils already exhibit elevated concentrations of these elements relative to Northern European agricultural soils (Zhang, 2006), and soils from South Park are further polluted.

Table 3 Comparison of median element concentrations in South Park soils with those for Galway urban soils, upper crust and Northern European agricultural soils (mg/kg)*.

Element	South Park Soils	Galway Soils	Upper Crust	N. Europe Soils
As	18	8	2	4
Cu	88	27	14	10
Pb	328	58	17	17
Zn	302	85	52	43

* Data sources: Galway Soil (Zhang, 2006), Upper crust (Wedepohl, 1995), Northern European agricultural soils (Reimann et al., 2003).

Spatial distribution patterns of the pollutants

As can be seen from Figure 2, all four elements considered here have elevated levels in over much of the study area. The highest levels of contamination occur on the north side where red-coloured industrial waste is exposed. On the north-east corner, pure industrial waste was observed exposed to the air, and extremely high concentrations of Zn (>2%) and very high concentrations of Pb, Cu and As were found there. Such a pollution feature is in line with the industrial waste from a fertiliser plant processing pyrite ores (U.S. EPA, 1997). Historically, a fertiliser plant existed adjacent to the study area, and the study area was used as municipal waste tip during this time. High levels of pollution were also observed in the main football pitch area on the west side of the park where a thin, dark brown to black topsoil covers other soil containing municipal waste such as broken glass, pottery, clinker, bones and metallic materials. All four elements tend to follow a similar spatial pattern with each showing the lowest levels of contamination close to the central and eastern areas of the maps. The areas with the relatively low concentration appear to be where imported topsoil (about 10-20 cm in thickness) has been laid over the contaminated substrate.

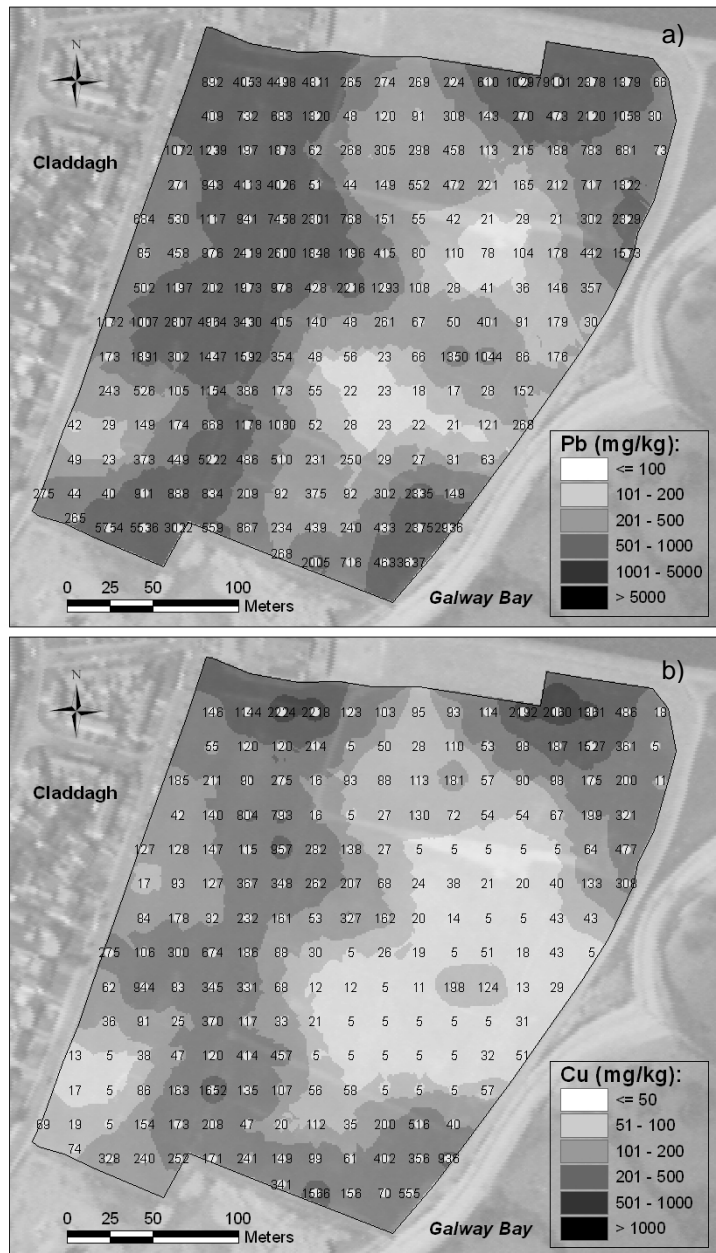


Fig. 2. Spatial distribution maps of a) Pb, b) Cu, c) Zn and d) As in soils of South Park, Galway City.

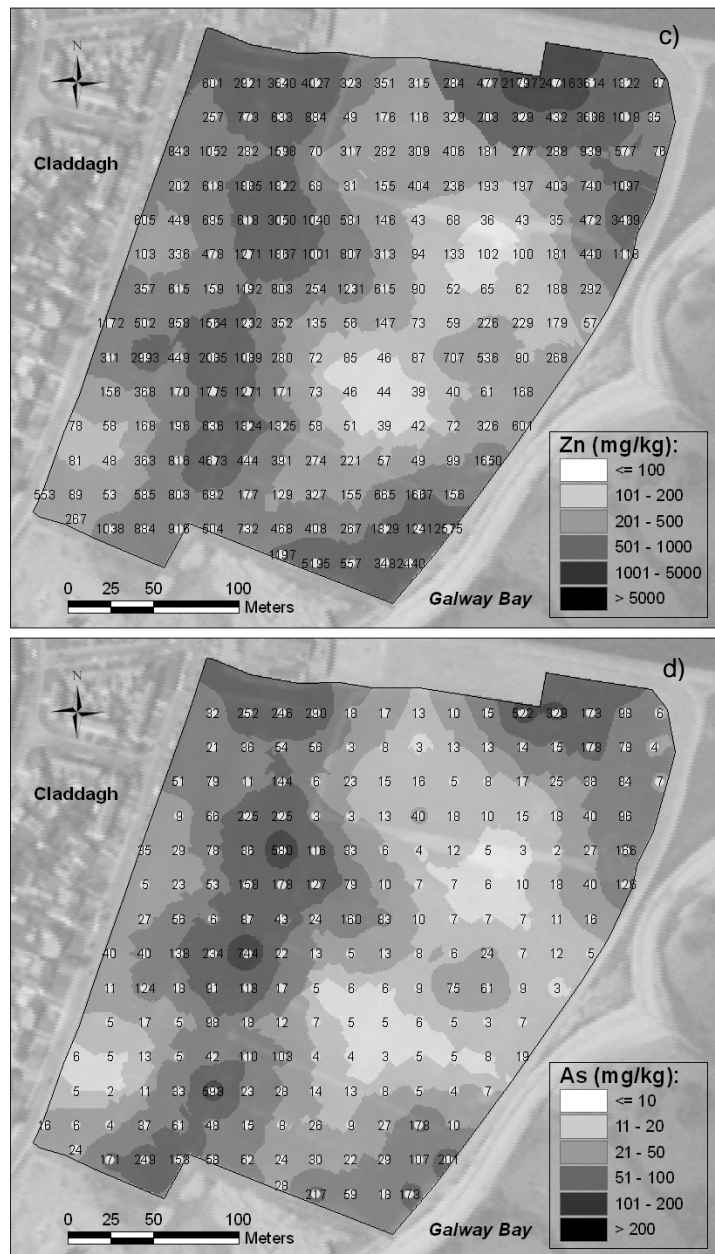


Fig. 2. Spatial distribution maps of a) Pb, b) Cu, c) Zn and d) As in soils of South Park, Galway City (cont.)

In order to more effectively display the distribution and levels of soil pollution in South Park, 3D views were created using the ArcGIS software. Figure 3 shows such a map for Pb, where the metal concentrations are shown as a drape over an oblique aerial photograph. It is immediately obvious that the concentrations of Pb in certain areas with the greatest spike occurring in the northeast of the area adjacent to the Quay, where the red-coloured metalliferous waste is exposed. It is also clear that most of the other hot

spots are along the sports pitches in the west side of the park. As lead is known to affect the health and intellectual abilities of children, its presence in greatest abundance in areas where children gather is clearly a matter of concern. It should be noted that the spikes are artificially caused by the IDW method, but they do visually depict the detected high values of those locations shown on the map. More sampling would be required to better model the areas with the spikes.



Fig. 3. 3D view of Pb concentrations in soils of South Park.

The hazard maps generated (Figure 4) show the average pollution index (Avg_PI) and maximum pollution index (Max_PI).

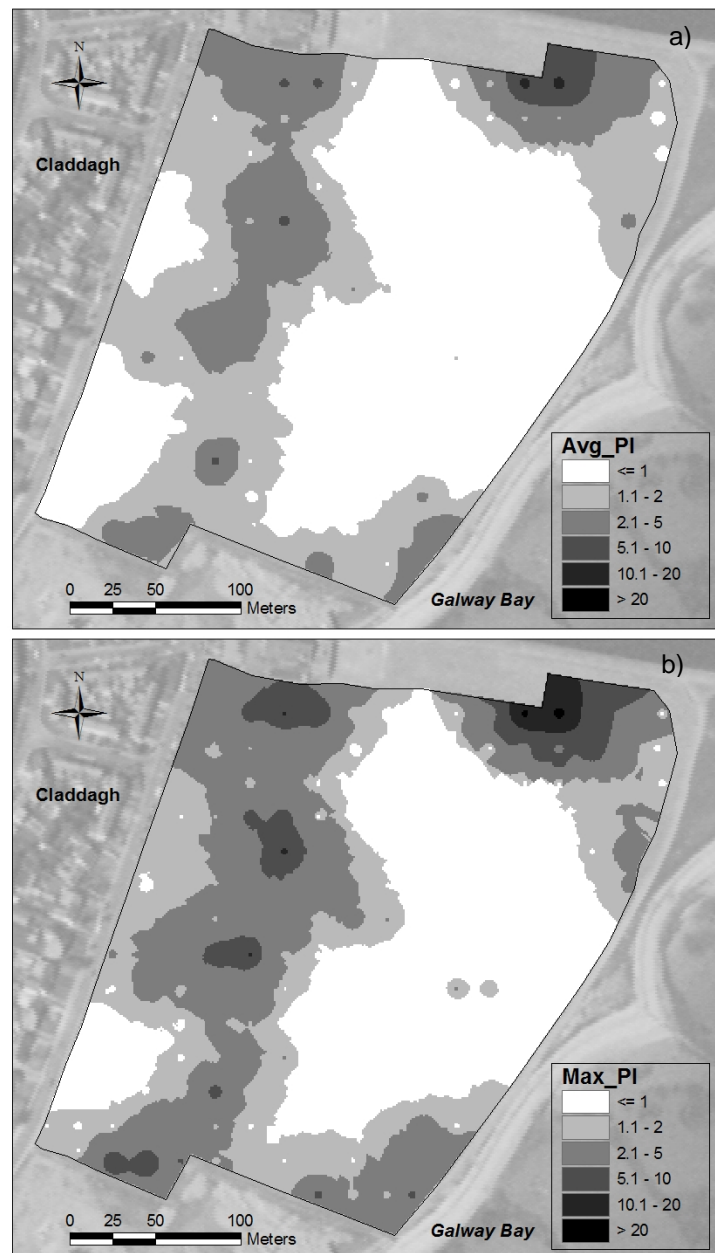


Fig. 4. Hazard maps of a) average and b) maximum pollution index in soils of South Park.

When the PI values are higher than 1, based on the Dutch criteria (VROM, 2000), soils should be subject to remediation. Areas with PI values higher than 1 in the “Avg_PI” map should be remedied when the 4 elements are equally considered. Areas with PI values higher than 1 in the “Max_PI” map are required to be remediated based on the criteria that concentrations of at least one of the pollutants were higher than its intervention value. Based on the hazard maps, the most hazardous areas are at the north

side of South Park with the average PI values reach the level of higher than 5. The west part is also very hazardous with the Maximum PI values generally higher than 2. Due to fairly good coverage of topsoil, the central-eastern part has the PI values lower than 1. It should be mentioned that there is uncertainty associated with the hazard maps, and the intervention values were for a Standard Dutch Soil (10% organic matter and 25% clay, in mg/kg dry matter), but the high PI values do demonstrate the high pollution levels. Even on the hazard maps of the surface soils, more than half of the South Park should be remediated.

Further studies are required to investigate the characteristics of the waste (municipal, industrial and mine ores) and the pollution history of the site, and more importantly the health of children who play regularly on the sports ground. Knowing the extent of contamination however is an important first step towards remediation of the problem. Clearly the past history of the site for the disposal of municipal and industrial waste has a continuing impact. From this study it is evident that the soil of the area is far too contaminated to remain as the topsoil of a sports ground and park area. To eliminate the health risk to children, local residents and tourists, as well as the surrounding environment, we advocate remediation of South Park as an immediate priority.

Conclusions

Serious soil pollution with Pb, Cu, Zn and As has been recorded in the sports ground of South Park in the Claddagh area of Galway City. The site is an historical waste disposal site containing both municipal and industrial wastes that are now variably mixed with soil. Extremely high concentrations of Pb, Cu, Zn and As in soil were found in the north side of the park where metalliferous industrial waste is present. High concentrations of these pollutants occur in the west part of the sports ground, a reclaimed marshy area with organic-rich soils where municipal waste is poorly covered by topsoil. These concentrations are orders of magnitude greater than the levels known to cause medical problems in children. Relatively low concentrations of pollutants occur in the central-eastern part of the park where the land is relatively well covered by imported topsoil. Since the whole sports ground is seriously polluted by municipal and industrial waste, immediate actions should be taken to remediate the site.

This study demonstrates the effectiveness of using a portable XRF metals analyser and GIS for mapping contaminated soils. A survey of 200 grid locations was completed within 5 days of fieldwork and the resultant data was immediately available for processing to create maps and 3D images.

Acknowledgements:

The pilot study in this paper was supported by the Millennium Research Fund of National University of Ireland, Galway (RM4005). Background air photo data were acquired from Ordnance Survey of Ireland. Helpful comments from the two reviewers and discussions with local residents, colleagues and government officials are acknowledged.

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