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ORIGINAL PAPER

Mathematical models to predict soil heavy metal toxicity in the 2012 Olympic site

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Abstract Heavy metal concentrations in samples collected from the London 2012 Olympic Village were determined using a three-step sequential extraction and a rapid extraction method. Metal toxicity was measured by employing the Microtox® solid phase analysis. Both extraction methods produced comparable results ($p = 0.996$), but the rapid method produced higher readings. A number of heavy metals were detected using the two extraction methods, including aluminum, arsenic, cadmium, chromium, copper, iron, nickel, lead and zinc; beryllium, molybdenum, niobium and titanium were also found in low concentration ranging between 0.16 and 27.10 mg/kg in the total acid digestion. The total metal levels in all the soil samples were within the UK Soil Guideline Value (SGV) except for lead which ranged between 62.9 and 776.2 mg/kg. The 30 min EC_{50} of different soil fractions was 2–5.8 g/L. In the absence of any of heavy metals in the SGV, the Dutch Guideline values were referred. Mathematical models for a number of metals were generated based on the changes in EC_{50} values between each (F1, F2 and F3) soil fractions and the initial toxicity in the non-fractionated samples. The resulting models produced good R^2 values (>96%) for predicting the change in toxicity of lead, cadmium, zinc and copper by measuring their changes in concentrations. These models could substantially reduce the time requires to determine the toxicity in the samples; they would be a useful tool in the clean up process where monitoring of metal toxicity is required.

Keywords Heavy metals · Microtox · Rapid extraction · Toxicity prediction

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Introduction

The site designated as the Olympic Village for the 2012 Summer Olympic Games is situated in Stratford, East London, near the former Great Eastern Railway Works. It is approximately 2,000 m^2 in size. This site was first occupied in 1848 as a locomotive workshop to build railway engines, and in the past 150 years, provided maintenance and repair services (Burnby 1978). A pollution incident was recorded in the late 19th century, where oil from a plant to manufacture fuel for lights in the carriages was leaked into the river Lea (Lewis 1999). This site was also a target of aerial bombardments during the World War II (Poulsen 1976). The possible pollutants that may be present in the Olympic site is therefore of concern and importance to its development and also in the regeneration of the area.

A number of extraction techniques have been developed to study the bioavailability and toxicity of heavy metals in soil samples. The most established method was the five-step sequential extraction protocol developed by Tessier and the Commission of the European Bureau of Reference (Tessier et al. 1979), where selected reagents are used on a soil sample in series where the heavy metal concentrations are categorized according to the specific chemical form they are believed to be available such as loosely exchangeable, carbonated fraction, iron and manganese oxide bound, organically bound and residual. The sequential extraction methods focus on the extractable, organically bound and residual fractions only, have also been employed to study metal concentrations in soil and sediment (Pueyo et al. 2008; Mossop and Davidson 2003; Cid et al. 2001; Carapeto and Pruchase 2000). Heavy metals present in the exchangeable fraction (F1) are mostly available as the charged ions that could be easily adsorbed or desorbed; this fraction provides vital information of the bioavailability of the metals. The organically bound fraction (F2) represents the fraction under oxidizing conditions in natural water that may be released as soluble metals and transported into other media.

The residue fraction (F3) contains metals tightly bound to the soil matrix and thus not bioavailable. More recently, a rapid extraction method is gaining popularity in determining metal availability in soil and sediment (Arain et al. 2009; Ettler et al. 2007), sewage sludge (Jamali et al. 2009; Meers et al. 2007) and tannery waste (Gupta and Sinha 2007). The rapid method involves the same reagents and operating conditions as the three-step sequential method; instead of performing the extraction sequentially using a single sample, the rapid extraction procedures are carried out in parallel using different sub-samples from the main soil sample. The metals in each fraction are determined mathematically by subtracting the concentration of the previous fraction from the measured concentration.

Microtox® has been used globally as a standard test for aquatic toxicity testing (Park and Hee 2001). It has been widely employed in studies related to aquatic environment (Roig et al. 2007; Van der Schalie et al. 2006; Dizer et al. 2002). It is also available commercially for analysing solid matrices.

This study aims to evaluate the toxicity and bioavailability of heavy metals present in the sampling area using both the sequential and rapid extraction methods, and to develop mathematical models that can be used to predict the toxicity of heavy metals in soil. Soil samples were collected in the ground designated to be the Olympic Village (Fig. 1) and pooled together. Soil samples collected in December 2008 were labeled as the 'winter samples'. Similar amount of soil was gathered in August 2009 and identified as the 'summer samples'.

Materials and methods

Analysis of soil samples

Surface soil samples up to 0.5 m deep were collected randomly from five sampling points and pooled together to a final weight of 10 kg. The soil samples were stored at 4°C in darkness in sealed polyethylene terephthalate containers when not in use. Soil was air dried at room temperature, grounded and sieved via a 2 mm mesh prior to further analysis.

The pH of the soil suspension (soil:deionised water 1:2 w/v) was measured using a calibrated pH meter (Jenway, Model 3505). The organic matter content (OMC) was determined by the loss-on-ignition method (Nelson and Sommers 1996) and the determination of cation exchange capacity (CEC) was carried out using the ammonium acetate procedure of Chapman (1965).

Heavy metal analysis was performed using the inductively coupled plasma optical emission spectrometry (ICP-OES) from Thermo Fisher Scientific, Model iCAP6500 Duo. The ICP-OES operating conditions were as listed in Table 1.

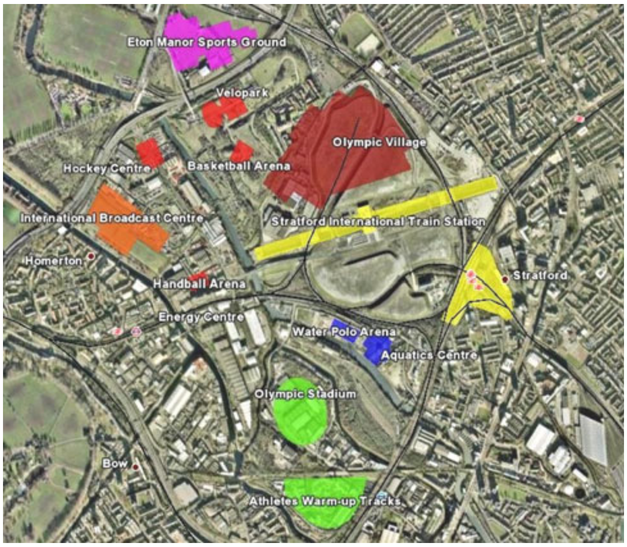

Fig. 1 Location of the Olympic village within the 2012 London Olympic Park in Strafford, London. (London Olympic Village 51°32′49.11″ N and 0°00′24.72″ W. Google Earth 5.0, viewed 10 August 2011, http://www.panoramio.com/photo/30450547?source=wapi&referrer=kh.google.com)

All the reagents used were of analytical grade (Sigma, UK; Fisher, UK) and metals standard at 1,000 µg m/L (Sigma, UK) were used as internal standard. Three samples from each of the winter and summer set were analysed and all the analysis was carried out in triplicates and the ICP-OES generated three readings per analysis.

Methodologies for metal extraction

The three-step sequential extraction method devised by Carapeto and Pruchase (2000) was used to determine the metal availability for exchangeable, organic and residual fraction. Briefly, for the F1, 15 g soil was extracted for 1 h with 1 M $MgCl_2$ at room temperature and a ratio of 1 g soil to 10 mL of $MgCl_2$. The F2 was obtained by mixing the remaining dried soil residue from F1 with 0.05 M EDTA for 2 h at room temperature, using the same v/w ratio as above. The F1 and F2 extractions were performed in an ultrasonic bath to ensure thorough mixing. All the mixture was filtered individually with filter paper (Whatman 2v), and the supernatant was analysed in ICP-OES. The residue was centrifuged twice in 30 mL of deionized water at 4,500 *g* for 5 min between each extraction step. The F3 was derived from the remaining dried soil residue from F2 digested with 30 mL of 70% HNO_3 in the microwave (CEM, Model MARS Xpress) using the USEPA SW-3051 method (USEPA 1986).

For the rapid extraction method, the soil sample was subdivided into 3 × 15 g subsamples; the subsamples were

Table 1 Instrumental details and operating conditions of ICP-OES

View	Axial
Power (W)	1,150
Auxiliary gas flow (L/min)	0.5
Nebuliser gas flow (L/min)	0.7
Coolant gas flow (L/min)	12
Analysis pump rate (rpm)	50
Flush pump rate (rpm)	100
Purge gas flow	Normal
Camera temperature (°C)	−47
Generator temperature (°C)	20
Optics temperature (°C)	38
Nebuliser	Concentric glass

extracted with reagents used in the sequential methods to produce the corresponding fractions (F1–3) in parallel (Fig. 2). Metal levels in the extractants were analysed using the ICP-OES as described above. Concentration of each fraction was obtained mathematically by subtracting the value obtained from the previous fraction. Hence, metal concentrations in F1 were obtained from subsample 1, and metal concentrations in F2 were calculated by subtracting the value in F1 from the result of subsample 2. Similarly, metal concentrations in F3 were derived by subtracting values of F2 from data obtained from subsample 3.

Microtox solid phase analysis

Toxicity of each soil sub-fraction was determined by the Microtox® solid phase analysis, using the Azur Environmental Microtox Photometer (Model 500 Analyser) and Microtox Omni software version 1.18. Residual soil samples (7 g) were retained after the extractions and they were air-dried for 24 h before the toxicity analysis. The default basic solid phase test was used with number of dilutions 9, dilution factor 2 and test time of 30 min, and the EC_{50} concentration reports of each test were generated.

Statistical analysis

All the data were analysed using the Minitab 15 statistical software package. The metal concentrations were normalized and logarithmically transformed before a two-sample *t* test was carried out to compare the two extraction methods. Correlation between heavy metal bioavailability and toxicity was analysed using the Pearson correlation analysis.

Results and discussion

General comparison between the sequential and rapid extraction methods

The mean pH, CEC and OMC for the winter soil samples (±standard error) were 7.52 ± 0.12, 90.46 ± 3.05 meq/100 g and 4.83% ± 0.17, respectively; for the summer samples, the values were 8.52 ± 0.15, 98.12 ± 4.57 meq/100 g and 3.86% ± 0.26, respectively. The mean metal concentrations obtained by the sequential extraction and the rapid extraction methods and the mean total metal concentrations are shown in Table 2.

Two-sample *t* test analysis was carried out to determine the significance of the differences observed using the two extraction methods. The equal variance analysis suggested that the two extraction methods are equal, but the data were not normally distributed. The data were transformed logarithmically and reanalysed using the two-sample *t* test, which showed that the difference was not statistically significant (the *p* values were 0.996 and 0.905 for the

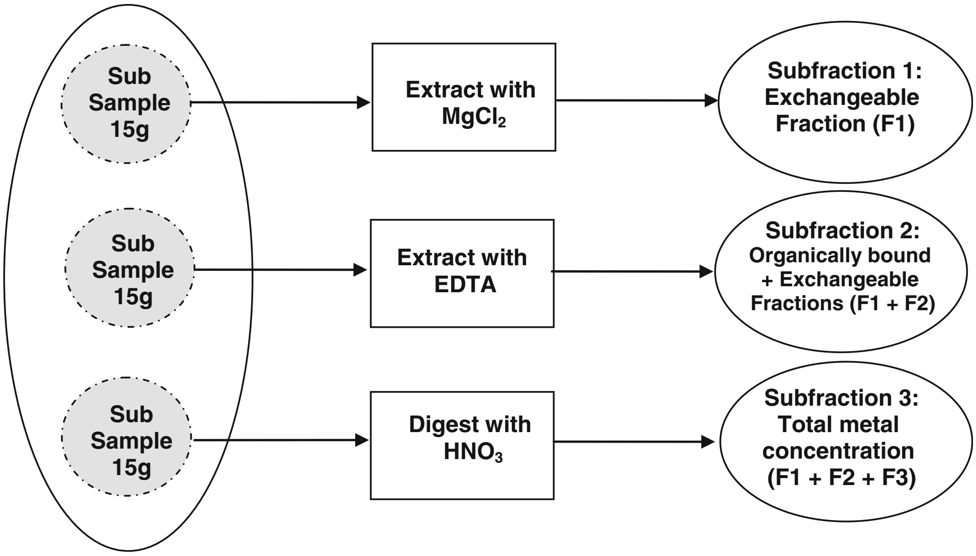

Fig. 2 A schematic diagram of the rapid extraction method

Table 2 The mean metal concentration (mg/kg ± standard error) of the soil samples from the Olympic Village obtained by the sequential extraction and the rapid extraction method

Element	Sequential extraction				Rapid extraction			
	F1	F2	F3	Σ F1, F2, F3	F1	F2	F3	Total metal
Winter samples								
Al	ND	157.14 ± 16.45	678.92 ± 35.18	836.06	ND	163.78	652.22	816.00 ± 13.52
As	0.03 ± 0.01	0.40 ± 0.06	9.93 ± 0.05	10.36	0.03	0.47	13.17	13.68 ± 0.59
Cd	0.06 ± 0.01	0.33 ± 0.03	0.38 ± 0.06	0.78	0.06	0.28	0.22	0.78 ± 0.06
Cr	ND	0.24 ± 0.04	20.65 ± 2.31	20.88	ND	0.25	19.32	19.57 ± 0.72
Cu	0.25 ± 0.06	56.75 ± 3.87	75.58 ± 5.41	132.58	0.25	65.27	80.26	**145.78 ± 12.67****
Fe	0.27 ± 0.14	348.97 ± 9.20	7,356.00 ± 416.77	7,705.24	0.27	386.80	8,277.00	8,665.00 ± 143.13
Ni	ND	ND	6.52 ± 0.12	6.52	ND	ND	7.83	7.83 ± 0.24
Pb	2.37 ± 0.91	479.27 ± 54.41	330.38 ± 50.29	812.02	2.37	463.16	310.64	**776.17 ± 35.42***
Zn	0.52 ± 0.42	284.27 ± 15.02	328.38 ± 31.03	613.17	0.522	317.56	326.76	**644.83 ± 31.69****
Summer samples								
Al	ND	215.22 ± 8.19	1,085.83 ± 59.53	1,301.05	ND	235.03	981.13	1,216.17 ± 12.82
As	ND	0.37 ± 0.06	2.97 ± 0.05	3.34	ND	0.44	3.52	3.337 ± 0.49
Cd	ND	0.04 ± 0.00	0.03 ± 0.00	0.08	ND	0.06	0.03	0.09 ± 0.00
Cr	ND	0.18 ± 0.02	8.53 ± 0.69	8.71	ND	0.23	11.44	11.67 ± 0.74
Cu	0.07 ± 0.01	12.07 ± 0.70	22.65 ± 0.65	34.79	0.07	15.36	25.26	40.69 ± 0.19
Fe	0.02 ± 0.00	325.23 ± 41.68	5,245.00 ± 40.05	5,570.26	0.02	366.19	5,825.00	6,191.67 ± 298.88
Ni	ND	ND	4.35 ± 0.12	4.35	ND	ND	6.59	6.59 ± 0.41
Pb	0.06 ± 0.00	53.02 ± 1.21	12.39 ± 1.22	65.47	0.06	51.26	11.61	62.93 ± 13.18
Zn	0.03 ± 0.00	18.60 ± 0.81	32.60 ± 2.28	51.23	0.03	21.32	34.88	56.23 ± 4.92

Bold values indicate concentration above guideline values

F1 Fraction 1 (exchangeable fraction), *F2* Fraction 2 (organically bound fraction), *F3* Fraction 3 (residual fraction), *ND* not detected

* Indicates exceeded the SGV limit

** Indicates exceeded the optimum Dutch Guideline but not exceeding its action threshold limit

winter and summer samples, respectively), suggesting the results obtained by these two methods were comparable.

In general, recovery obtained by the sequential extraction was lower than the rapid method, which was also observed by Alvarez-Valero et al. (2009), Arain et al. (2009) and Jamali et al. (2009). The percentage recovery using the sequential method (sum of all three fractions) compared to acid digestion is presented in Fig. 3. All the sequential extraction samples achieved over 83% recovery with the exception of As in the winter samples (75.7%), Cr and Ni in the summer samples (74.6 and 66%, respectively).

Fraction F1 (exchangeable) generated by both types of extraction methods were basically identical, and would be in agreement with each other; they were not included in the study of the relationship between the two techniques. Fractions F2 (organically bound) and F3 (residual) produced a significant homogeneity, and furthermore, the similarities within the methods were also reproducible between the two sampling periods, suggesting the rapid method is a quick alternative for metal determination. The rapid extraction method was also less error-prone as each sample was only treated with a reagent once, which significantly reduced the margins of error. The rapid method also minimized the loss of metals resulting from the washing process between each fraction (Carapeto and Pruchase 2000) and adhesion of metals to the filter paper (Peijnenburg et al. 2007). Hence, unsurprisingly, the rapid

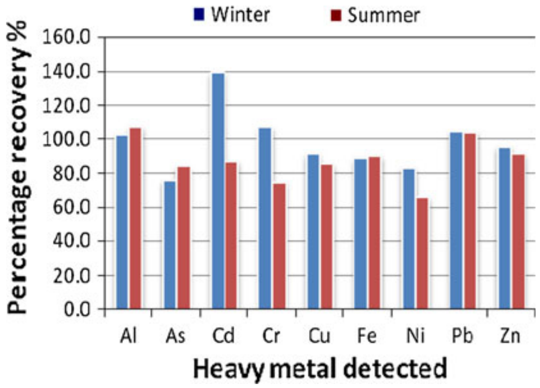

Fig. 3 Heavy metal percentage recovery of the sequential extraction (the sum of the metal concentrations of all three fractions, F1–3) compared to the total metal concentrations determined by the rapid extraction method

method gave imperceptibly higher F2 values for a number of metals (Al, As, Cu, Cr, Fe, and Zn) than the sequential method; similar trend was observed on F3 values for the above metals (except for Al, Cr and As).

Results obtained from the sequential method have often been used as a reference to calculate the percentage recovered by the rapid extraction method (Arain et al. 2009; Jamali et al. 2009; Rao et al. 2010). Figure 4 is constructed to present the overall view of metal recovery in F2 and F3 from both the winter and summer samples for rapid extraction method where the linear line denotes the theoretical relationship when same recovery percentage for each element at each fraction is observed. The dotted elliptical line indicates the proximity of the points towards the linear line, whereas the top right quadrant region indicates recovery above 100% and the lower left quadrant shows recovery lower than 100%. The distribution of the data points suggests that the recovery for the rapid extraction method was generally reliable, except for Cd, Cr and Ni. The F2 and F3 values for Pb obtained from the rapid extraction method were consistently lower compared to the sequential method. However, the differences obtained by these two methods were relatively small (between 3 and 6%). The variability in Cd, Cr and Ni concentrations probably resulting from the low total metal levels (0.09–19.57 mg/kg) present in the site, which exaggerates the effects of small differences.

Heavy metal concentration in the soil samples

For both sets of samples, the total concentrations of metal detected in the acid digestion were consistent: Fe > Al > Pb > Zn > Cu > Cr as shown in Table 2. In the winter samples, As appeared to be at a higher concentration than Ni, but this trend was reversed in the summer samples. Cd was present in the lowest concentration in all soil samples. Traces of Be (0.24–0.25 mg/kg), Mo (0.16–0.17 mg/kg), Nb (1.73–3.02 mg/kg) and Ti (12.27–27.10 mg/kg) were also detected in the acid digest (total metal) of soil samples. The level of Hg or Se was below the detection limit in all of the soil samples. With the exception of Pb, the concentrations in F1 were the lowest, followed by F2 and F3 in the sequential and rapid extraction results. The highest concentration of Pb distribution was found in F2 followed by F3 then F1 which was also observed by Carapeto and Pruchase (2000). F3 contained the highest metal levels in the sequential and rapid extraction result.

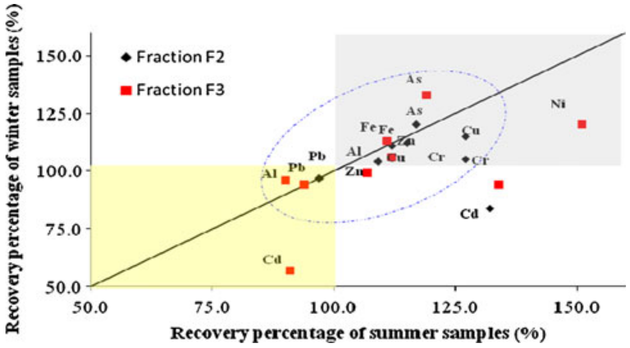

Fig. 4 Comparison of rapid extraction recovery for each metal in Fractions 2 and 3 of both the winter and summer samples

When comparing the winter and summer samples, with the exception of Al, the total metal concentration results of the winter samples were higher than those of the summer samples. Reductions between 15.8 and 91.9% were recorded, the highest reduction was observed in Pb and Zn (>91%), and the lowest reduction was Ni. It is noted that the percentage recovery of Cr and Ni in the summer samples was below 80% (Fig. 3), therefore, the reduction may not be an accurate representation. The overall trend suggests a reduction in metal levels in the summer samples. The decrease in metal levels observed during the summer season may result from natural bioremediation that took place in the soil. It is well established that the soil microorganisms are able to remediate high level of metal contamination in soil (Bruins et al. 2000), microbial activities increase with increase of temperature (Barja et al. 1997), and the heavy metals may be more actively sequestered or biotransformed by microbes in summer, resulting in a significant reduction in the metal levels.

Currently, the UK Environment Agency has published Soil Guideline Value (SGV) reports and associated toxicological (TOX) reports for 11 substances. Of heavy metals and other inorganic compounds, only reports for As, Ni, Hg, Se and Cd are available. In order to ascertain whether the metal levels detected in this study were within the acceptable limits, the Dutch Guideline values (Dutch Environment Ministry 2000) were also used. In the winter samples, total Cu (146 mg/kg), Pb (776 mg/kg) and Zn (645 mg/kg) were present in concentration and exceeded the optimal Dutch Guideline values. Lead exceeded the action limit (530 mg/kg dry wt), and it was found mainly in the organically bound fraction, which may be released as soluble metals under oxidizing conditions. However, in general, metal present in this fraction is not bioavailable (Zhao et al. 2009). Magrisso et al. (2009) demonstrated 1% of organic matter could complex up to 200 ppm Pb. Hence, most of the metals will be strongly held within the mineral matrixes and therefore not readily available.

The experience in employing the UK SGV as the initial tool to gauge the contamination revealed certain pros and cons. The SGV provides the 'fit for purpose' categories with specific cut-off point for each pollutant. However, the preciseness of the trigger value is also one of its drawbacks. The SGV is not recommended if they are not representative of the site under evaluation, and the SGV list is not extensive. As seen above, a number of heavy metals trigger values are not available. This study refers to the Dutch Guideline where the SGV is absent, as it presents a more comprehensive list of contaminants; it also provides the optimum and action values for each pollutant in soil as well as in groundwater. It should be noted that the Dutch Guideline is designed for a 'multi-purpose' approach; the values are more strict and stringent, nevertheless, the metals present in the sampling area appear to be within an acceptable limit.

Toxicity of heavy metals

Although a number of metals were detected using the total acid digestion method in both set of samples, results showed that the majority was bound to the organic and residual fractions, which rendered them less bioavailable. This was further supported by the EC_{50} values (Table 3).

The order of EC_{50} values as Fraction 3 was: (least toxic) > Fraction 2 > Fraction 1 > non-fractionated soil samples (most toxic) for both the winter and summer samples. The Pearson correlation coefficients for the EC_{50} and the metals present in the three fractions using the rapid extraction method were 0.850 and 0.763 for the winter and summer samples, respectively, suggesting the concentration of EC_{50} may be proportionally correlated to the total concentration of metals removed from the soil samples. The changes in EC_{50} (ΔEC_{50}) of each (F1, F2 and F3) of the rapid extraction fractions (the difference between the particular fractions and the initial toxicity in the non-fractioned samples), and the total metal removed were analysed. A Pearson correlation coefficient of 0.737 was obtained, indicating a positive correlation between the two values. Further analysis showed that there were strong correlations between ΔEC_{50} with the individual metals removed (Table 4).

Interestingly, the Microtox® analysis results show that the winter sample was less toxic ($EC_{50} = 5.9$ g/L) than the summer samples ($EC_{50} = 2.1$ g/L), even though the heavy metal contaminations were generally higher in the former. The finding of metal concentrations within the limits of both SGV and Dutch Guideline Values in the summer samples could be misleading and misinterpreted by not recognizing the potential toxicity effect from other pollutants. Activities related to the use of fuel (coal and oil) close to these sites have been documented (Burnby 1978; Refaat 2009), and an oil leakage incident that polluted the river Lea was recorded at the Great Eastern Rail Works (Lewis 1999). Organic pollutant such as polycyclic aromatic hydrocarbons (PAHs) which occur in oil, coal and fuel combustions may also present in this site. Some of the PAHs such as azaarenes and intermediate products such as benzo[a]pyrene are known to be carcinogenic, mutagenic and teratogenic (Pickering 2000; Bleeker et al. 2002). The higher toxicity detected in the summer samples could be attributed to these compounds.

Mathematical models to predict change in metal content and bioavailability

Employing the rapid extraction method's results, regression analysis of removed metal concentration and the change in toxicity have been carried out for each of the metals (Fig. 5). It unfolds the multiple hidden trends in association of each metal which instantly identify the metals that actually contributed to the toxicity and predictable. Moreover, the predictions of change in toxicity were supported with high reliable coefficient of determination (R^2) which is included in the graphs.

The R^2 percentage of Al, Fe and Ni is too low (<46%) to produce reliable predictable models, therefore they are not included further. The final individual metal regression models that could be used in predicting the toxicity concentration which R^2 values are greater than 50% are listed below.

'y' represents the change in EC_{50} concentration (g/L) and the metal symbols represent the concentration of the metal removed in mg/kg.

Table 3 EC_{50} Microtox analysis of soil samples after each fraction (g/L) ± standard deviation

Sample	Non-fractionated	Fraction 1	Fraction 2	Fraction 3
Winter samples	5.859 ± 0.46	7.678 ± 1.98	6.163 ± 5.31	21.09*
	$R^2 > 0.72$	$R^2 > 0.82$	$R^2 > 0.80$	$R^2 = 0.89$
Summer samples	2.083 ± 0.91	4.327 ± 0.54	5.882 ± 0.76	7.293*
	$R^2 > 0.81$	$R^2 > 0.82$	$R^2 > 0.86$	$R^2 = 0.99$

* SD not available

Table 4 Pearson correlation coefficient (*r*) of each metals and the change in EC_{50} concentration (ΔEC_{50})

	Al	As	Cd	Cr	Cu	Fe	Pb	Ni	Zn
Correlation coefficient	0.433	0.815	0.984	0.714	0.982	0.672	0.988	0.615	0.983
p value	0.391	0.048	0	0.111	0	0.143	0	0.194	0

ΔEC_{50} is the difference between the particular fractions and the initial toxicity in the non-fractioned samples

Cd, Cu, Pb and Zn showed the strongest correlation ($p > 0.98$)

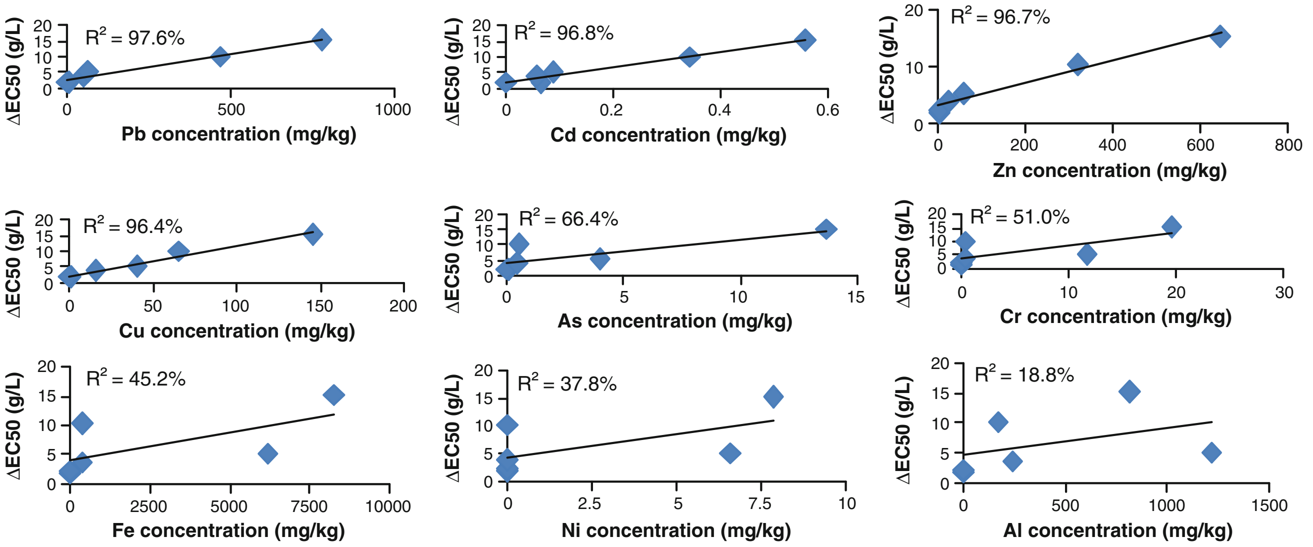

Fig. 5 Regression analysis of change in EC_{50} concentration (ΔEC_{50}, g/L) with each metal removal concentration

Table 5 Comparison between actual and predicted ΔEC_{50} with each model

Sample	Fraction	Observed ΔEC_{50} (g/L)	Predicted ΔEC_{50} (g/L) using the regression models (R^2)					
			Model 1 (66.4%)	Model 2 (96.8%)	Model 3 (51.0%)	Model 4 (96.4%)	Model 5 (97.6%)	Model 6 (96.7%)
Winter	1	1.819	3.98	3.56	4.06	2.30	2.80	2.99
	2	10.30	4.36	10.18	4.17	8.38	10.31	9.32
	3	15.23	14.88	15.32	12.86	15.86	15.35	15.83
Summer	1	2.24	3.96	2.03	4.06	2.28	2.76	2.98
	2	3.80	4.30	3.41	4.16	3.71	3.59	3.40
	3	5.21	7.12	4.10	9.31	6.07	3.78	4.10

$$\text{Model 1}: y = 3.96 + (0.798)\text{As} \tag{1}$$

$$\text{Model 2}: y = 2.03 + (23.8)\text{Cd} \tag{2}$$

$$\text{Model 3}: y = 4.06 + (0.45)\text{Cr} \tag{3}$$

$$\text{Model 4}: y = 2.28 + (0.0932)\text{Cu} \tag{4}$$

$$\text{Model 5}: y = 2.76 + (0.0162)\text{Pb} \tag{5}$$

$$\text{Model 6}: y = 2.98 + (0.0199)\text{Zn} \tag{6}$$

The predicted results from each metal were compared with the actual concentration and are presented in Table 5.

The equations for Cd, Cu, Pb and Zn gave similar values in the predicted and observed ΔEC_{50}. These equations should therefore provide reliable estimates in the changes in toxicity of the samples by just knowing the concentration of the particular metal that has been removed. The high reliability regression equations of Pb, Cd, Zn and Cu show that about 96% out of the predicted EC_{50} concentration could be accounted as the true value. Prediction of changes in toxicity contributed by Al, As, Fe. Cr and Ni was not reliable ($R^2 < 66\%$). This may be influenced by the low recovery percentage (Fig. 3), which underestimated the levels of metal present.

It should be noted that there are likelihood of other pollutants (besides heavy metal) could affect the overall toxicity and they are not accounted for by the above models. As the toxicity analysis is only able to reveal an overall effect as a whole, identifying the contribution of each metal is also complicated. However, these equations are the closest estimations that could be established from the current study, which may form the initial steps in quantifying estimated toxicity related to the metal being removed.

Conclusion

It is recognized that the current investigation only examined samples from a very limited area. The metal concentration and toxicity should not be over-interpreted. A more extensive sampling regime should be undertaken to provide a comprehensive view of the whole site. Nevertheless, heavy metals were detected in this study, although none of the concentrations except for Pb was a cause for concentration based on the UK SGV and the Dutch Guideline values. It is evident that heavy metals are not the only pollutant responsible for the toxicity observed in the summer samples. The

Microtox® analysis is a clear and simple procedure which provides quick and crucial information of toxicity. Girotti et al. (2008) suggested it could be used as a decision making tool that prevents further pollution impact to a site. This study presents an example to the capability of this analysis. The higher metal contamination sample had a lower toxicity and vice versa, by incorporating the Microtox® analysis, it enables vital toxicological information to be capture which may not be gleaned from chemical analysis alone. For example, the finding of metal concentrations within the guideline limits in the summer samples could be misleading and underrepresented the potential toxic effects from other pollutants.

The models generated to predict the ΔEC_{50} for Cd, Cu, Pb and Zn using the rapid extraction method could expedite the monitoring process by reduce substantially the analysis time required to determine the EC_{50}, and yet able to track the toxicity effectively.

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References

Alvarez-Valero AM, Saez R, Perez-Lopez R, Delgado J, Nieto JM (2009) Evaluation of heavy metal bio-availability from Almagrera pyrite-rich tailings dam (Iberian Pyrite Belt, SW Spain) based on a sequential extraction procedure. J Geochem Explor 102(2):87–94

Arain MB, Kazi TG, Jamali MK, Baig JA, Afridi HI, Jalbani N, Sarfraz RA (2009) Comparison of different extraction approaches for heavy metal partitioning in sediment samples. Pedosphere 19(4):476–485

Barja MI, Proupin J, Núnez L (1997) Microcalorimetric study of the effect of temperature on microbial activity in soils. Thermochim Acta 303(2):155–159

Bleeker EAJ, Wiegman S, de Voogt P, Kraak M, Leslie HA, de Haas E, Admiraal W (2002) Toxicity of azaarenes: a review. Rev Environ Contam Toxicol 173(1):39–84

Bruins MR, Kapil S, Oehme FW (2000) Microbial resistance to metals in the environment. Ecotoxicol Environ Safety 45(3):198–207

Burnby JGL (1978) The navigation of the River Lee (1190–1790). Edmonton Hundred Historical Society, London

Carapeto C, Pruchase D (2000) Use of sequential extraction procedures for the analysis of cadmium and lead in sediment samples from a constructed wetland. B Environ Contam Toxicol 64(1):51–58

Chapman HD (1965) Cation exchange capacity. In: Black CA (ed) Methods of soil analysis, Part 1. (1st edn). Methods of soil analysis. Chemical and microbiological properties, Part 2, American Society of Agronomy, Madison, pp 891–901

Cid BP, Albores AF, Gomez EF, Lppez EF (2001) Use of microwave single extractions for metal fractionation in sewage sludge samples. Anal Chim Acta 431(2):209–218

Dizer H, Wittekindt E, Fischer B, Hansen PD (2002) The cytotoxic and genotoxic potential of surface water and wastewater effluents as determined by bioluminescence, umu-assays and selected biomarkers. Chemosphere 46(2):225–233

Dutch Environment Ministry (2000). Circular on target values and intervention values for soil remediation. Dutch National Institute of Public Health & the Environment (RIVM), Holland

Ettler V, Mihaljevic M, Sebek O, Nechutny Z (2007) Antimony availability in highly polluted soils and sediments: a comparison of single extractions. Chemosphere 68(3):455–463

Girotti S, Ferri EN, Fumo MG, Maiolini E (2008) Monitoring of environmental pollutants by bioluminescent bacteria. Anal Chim Acta 608(1):2–29

Gupta AK, Sinha S (2007) Assessment of single extraction methods for the prediction of bioavailability of metals to *Brassica juncea* L. Czern. (var. Vaibhav) grown on tannery waste contaminated soil. J Hazard Mater 149(1):144–150

Jamali MK, Kazi TG, Arain MB, Affidi HI, Jalbani N, Kandhro GA, Shah AQ, Baig JA (2009) Speciation of heavy metals in untreated sewage sludge by using microwave assisted sequential extraction procedure. J Haz Mat 163(2–3):1157–1164

Lewis J (1999) London's Lea Valley: Britain's best kept secret. Phillimore and Co., Ltd., UK

Magrisso S, Belkin S, Erel Y (2009) Lead bioavailability in soil and soil components. Wat Air Soil Poll 202(1–4):315–323

Meers E, Laing GD, Unamuno V, Ruttens A, Vangronsveld J, Tack FMG, Verloo MG (2007) Comparison of cadmium extractability from soils by commonly used single extraction protocols. Geoderma 141(3–4):247–259

Mossop KF, Davidson CM (2003) Comparison of original and modified BCR sequential extraction procedures for the fractionation of copper, iron, lead, manganese and zinc in soils and sediments. Anal Chim Acta 478(1):111–118

Nelson DW, Sommers LE (1996) Total carbon, organic carbon, and organic matter. In: Sparks DL, Page AL, Helmke PA, Loeppert RH, Soltanpour PN, Tabatabai MA, Johnston CT, Sumner ME (eds) Methods of soil analysis, Part 3. Chemical methods. Soil Science Society of America Book Series, Number 5, Madison, pp 961–1010

Park K, Hee SQ (2001) Effect of dust on the viability of *Vibrio fischeri* in the Microtox test. Ecotoxicol Environ Safety 50(3):189–195

Peijnenburg WJGM, Zablotskaja M, Vijver MG (2007) Monitoring metals in terrestrial environments within a bioavailability framework and a focus on soil extraction. Ecotoxicol Environ Safety 67(2):163–179

Pickering RW (2000) Toxicity of polyaromatic hydrocarbons other than benzo(a)pyrene: a review. J Toxicol Cutaneous Ocul Toxicol 19(1):55–67

Poulsen C (1976) Victoria Park: a study in the history of East London. Stepney Books & The Journeyman Press

Pueyo M, Mateu J, Rgol A, Vidal M, Lopez-Sanchez JF, Rauret G (2008) Use of the modified BCR three-step sequential extraction procedure for the study of trace element dynamics in contaminated soils. Environ Poll 152(2):330–341

Rao CRM, Sahuquillo A, Lopez-Sanchez JF (2010) Comparison of single and sequential extraction procedures for the study of rare earth elements remobilisation in different types of soils. Anal Chim Acta 662(2):128–136

Refaat AA (2009) Correlation between the chemical structure of biodiesel and its physical properties. Int J Environ Sci Tech 6(4):677–694

Roig B, Valat C, Berho C, Allan IJ, Guigues N, Mills GA, Ulitzur N, Greenwood R (2007) The use of field studies to establish the performance of a range of tools for monitoring water quality. Trend Anal Chem 26(4):274–282

Tessier A, Campbell PGC, Bisson M (1979) Sequential extraction procedure for the speciation of particulate trace metals. Anal Chem 51(7):844–851

USEPA (1986) Test methods for evaluating solid waste. Volume IA (3rd edn) EPA/SW-846. National Technical Information Service. Springfield

van der Schalie WH, James RR, Gargan TP II (2006) Selection of a battery of rapid toxicity sensors for drinking water evaluation. Biosen Bioelectron 22(1):18–27

Zhao XM, Dong DM, Hua XY, Dong SF (2009) Investigation of the transport and fate of Pb, Cd, Cr(VI) and As(V) in soil zones derived from moderately contaminated farmland in Northeast. China J Hazard Mater 170(2–3):570–577