Talanta 82 (2010) 1421–1425

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

The optimization of microwave digestion procedures and application to an evaluation of potentially toxic element contamination on a former industrial site

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ARTICLE INFO

Article history:
Received 9 April 2010
Received in revised form 1 July 2010
Accepted 3 July 2010
Available online 13 July 2010

Keywords:
Contaminated land
Potentially toxic elements
Former industrial site
Soil guideline values microwave digestion
ICP-MS

ABSTRACT

The optimization of a microwave dissolution procedure for potentially toxic elements in a contaminated soil sample has been evaluated using a central composite design approach. By considering the operating parameters of temperature, digestion time, microwave power and acid volume it was possible to identify the following optimum conditions: temperature, 160 °C; power, 750 W; digestion time, 25 min; and, an aqua regia volume of 13 mL. These microwave digestion conditions were then applied to 19 samples obtained from a former industrial site in Newcastle upon Tyne. Of the range of potentially toxic elements present at the site as a consequence of former industrial activity (As, Cd, Cr, Cu, Mo, Ni, Pb and Zn), the majority of topsoil samples indicated elevated concentrations of one or more of these elements. In particular, data obtained using either inductively coupled plasma mass spectrometry or flame atomic absorption spectroscopy indicates the high and wide concentration of Pb on the site (188–60300 mg/kg). Comparing the resulting potentially toxic elements data with UK soil guidelines values (SGVs) suggests at least parts of the site represent areas of potential human health risk. It was found that lead soil values exceeded the SGV on 17 out of the 19 sampling sites; similarly for As 6 out of 19 sampling sites exceeded the SGV. While for Cd, Cr and Ni the soil levels were below the stated SGVs.

1. Introduction

Data on potentially toxic element (PTE) pollution in urban soils has increased over the last few decades as their significance in human health related issues has gained wider public and media attention [1–3]. Of particular concern in this paper is the importance of a former industrial site and the legacy that remains with respect to its current use as a country park for recreational activity. The site of the former St. Anthony's Lead Works lies to the east of Newcastle upon Tyne City Centre with an area of 52,651 m^2 [4]. The factory which operated from around 1840 to the mid 1930s smelted lead ore imported from Europe, mainly Spain and processed this along with United Kingdom produced lead. The factory refined lead ore which was then manufactured locally into white and red lead, sheet metal, and lead pipe. Historical maps also confirm a range of other industrial activities on and adjacent to the site including a copper/arsenic works, railway and tram lines, St. Anthony's Chemical works/Tars works (to the east) and Northumbrian Chemical/Paint works (to the SW on the opposite banks of the River Tyne). Consequently, the range of contaminants potentially present in sufficient concentrations to pose a risk to humans and the wider environment includes As, Cd, Cr, Cu, Mo, Ni, Pb and Zn. The site was landscaped in the mid 1960s by Newcastle City Council and Newcastle University [4]. This involved a surface dressing of topsoil, tree planting on slopes and the establishment of grass on the flatter areas. The current uses of the site include: fishing on the riverside, ball games, walking, and dog exercise. The site is currently occupied by Walker Riverside Park, an area of public open space to the east of the city centre. Site surfaces include hard standing (footpath, road and car park) grassed and wooded areas. Although the majority of the site is vegetated, areas of bare ground are exposed, predominantly under the wooded slopes, where ash and clinker debris are evident.

Inductively coupled plasma mass spectrometry (ICP-MS) is a widely used analytical technique for the analysis of trace metals in samples whereas flame atomic absorption spectroscopy (FAAS) is often used for major elements. Prior to elemental analysis however, the soil samples must first be converted into a liquid form by acid digestion. Acid digestion procedures are often employed for the determination of elements in solid samples in order to transfer the analytes into solution prior to the determination step (e.g. ICP-MS, AAS) [5–12]. Acid digestion involves the use of acid and heat to destroy the matrix of a sample to liberate the metal content. It measures the (pseudo) total concentration of the metal present in the sample matrix. The goal of every digestion process is (a) dissolution of the sample matrix (but the totality can depend on the

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doi:10.1016/j.talanta.2010.07.008

Table 1
Site description of St. Anthony's Lead Works [4].

Site name	The former St Anthony's Lead Works
Description of location	The site is situated next to both Felling View and Pottery Bank in the Walker area of Newcastle. (Grid reference: 428685E 562987E)
Site boundaries	North – disused railway track, east – Pottery Bank, south – River Tyne, west – open ground
Site setting	The site is situated on the banks of the River Tyne in a predominantly recreational area and consists of public open space
Adjacent land uses	Adjacent land uses includes educational, recreational and residential
Site shape	The site is roughly rectangular in shape
Site surfaces	This include hard standing (footpaths, car park and road) grassed, landscaped and planted areas
Vegetation	Vegetation present on the site includes grassed areas, shrubs and trees
Subsurface structures	This may include foundations, structures and various tanks associated with the sites former land uses
Relevant features	The River Tyne is located to the south of the site

choice/combination of acid), (b) avoidance of element losses and minimisation of contamination risk, and (c) reduction of handling and process times [11]. There are different approaches to heating the acid and sample in the digestion procedure including use of a hot plate/sample digestion block, and a microwave oven. The choice of acid and their combination is an important aspect. In this study acid digestion using aqua regia (HNO_3:HCl) (1:3, v/v) in combination with a microwave oven was used to extract the metals of interest from topsoils collected at the St. Anthony's Lead Work site (SAL) prior to determination.

The work presented in this paper proposed to (a) optimize the influence of microwave oven operating parameters on PTE recovery: acid volume (V), digestion time (t), microwave power input (P) and temperature (T) and (b) use the optimized microwave operating conditions and apply the approach to a range of soil samples from the former industrial site.

2. Experimental

2.1. Chemicals and apparatus

All chemicals used were of analytical grade. Concentrated hydrochloric acid and concentrated nitric acid were obtained from Fisher Scientific UK Ltd. (Loughborough, Leicestershire). A multi-element standard for As, Cd, Cr, Cu, Mo, Ni, Pb and Zn and an internal standard solution containing Sc, In, and Tb were purchased from SPEXCertPrep (Middlesex, UK). Ultra pure water of resistivity 18.2 MΩ cm was produced by a Direct Q^{TM} Millipore System (Molsheim, France). Soil samples were collected from the former St. Anthony's Lead Works in Newcastle upon Tyne (Table 1). Two soil certified reference materials were used (GBW 07041 and SRM 2711) obtained from LGC-Promochem Ltd., London; SRM 2711 was originally sourced from agricultural soils close to a former smelting plant in Montana, USA. ICP-MS measurements were carried out with an ICP mass spectrometer X series II (Thermo Electron Corporation, Cheshire, UK). Flame atomic absorption spectroscopy (FAAS) measurements were carried out using an A. Analyst model 100 supplied by Perkin-Elmer Corporation, Norwalk, CT, USA. All digestions were carried out using a Start D Multiprep 42 High Throughput Rotor microwave digestion system supplied by Milestone Microwave Laboratory Systems UK.

3. Methodology

3.1. Sample collection and sample handling

Samples of soil were collected from 19 sample points on the site by digging a rectangular hole of about 10 cm deep to collect the topsoil. The sample points were selected to provide wide geographical coverage both within the known boundaries of the former site and its immediate periphery. The soil was put inside a sample bag, closed and labelled to include the sample point, date of collection and sample location (Fig. 1). During sampling, sample handling and sample preparation polyethylene gloves were worn. The soil samples in the sample bag were dried in an oven at a temperature of 37 °C for 6 days.

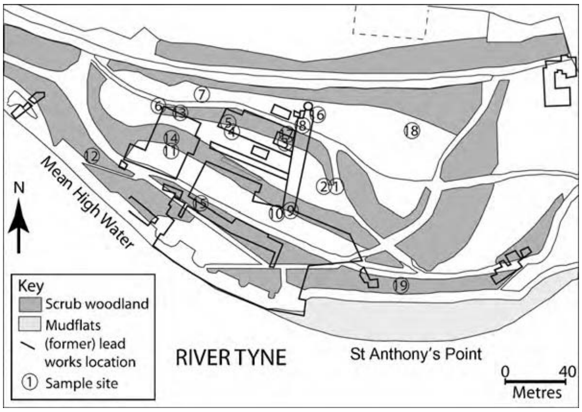

Fig. 1. Site map of St. Anthony's Lead Works (The map highlights the current surface topology. In addition, the historic position of the former Lead Works is highlighted. Sampling points are identified via the numerical key).

3.2. Sample preparation

The dried soil samples were first passed through a plastic sieve of mesh size <2 mm and stored. Sub-samples of the <2 mm fraction were powdered in a rotating ball mill and powdered aliquots were digested using the microwave digestion technique and then stored in a fridge (4 °C) prior to metal analysis using either ICP-MS or FAAS.

3.3. Microwave digestion protocol

Central composite design (CCD) is required in order to establish the optimum conditions and also to obtain information about the inter-relationships between the variables [13]. A randomised central composite design was set up to obtain the various experimental conditions for each run. A total of 28 standard runs were obtained from the CCD. A maximum and minimum limit was chosen for each of the variables i.e. temperature, time, power and volume (Table 2). The use of a CCD allows all operating parameters to be investigated individually, as quadratic effects, and to consider interaction effects. The results of the CCD were evaluated using multilinear regression. The range of PTEs for which this technique has been applied are Cr, Cu, Mo, Ni, Pb and Zn.

A soil sample (0.5 g) was accurately weighed into a PFA (65 mL) vessel pre-cleaned with concentrated HNO_3. Then aqua regia (HCl:HNO_3, 3:1, v/v) was added to the soil. The vessel was sealed with the TFM cover and placed inside a rotor of the microwave digestion system and submitted to a microwave dissolution program. The microwave oven was operated with a nominal capacity of 4 vessels per run. A ventilation (cooling) time of 30 min was allowed while the vessels were still in the oven. After cooling, the digest

Table 2
Upper and lower limit of the microwave variables.

Coded levels	Temperature (*T*) (°C)	Time (*t*) (min)	Microwave power (*P*) (W)	Volume (*V*) (ml)
+2.27	80	10	550	10
0	130	20	675	13
−2.27	180	30	800	16
−1	160	24	730	14
+1	110	16	620	12

was filtered using a Whatman filter paper into a 50 mL volumetric flask and diluted to the mark with Milli-Q water of conductivity 18.2 MΩ cm at 25 °C. For each digestion, reagent blanks were also prepared. The filtrate obtained from the digestion was stored in the fridge (4 °C) prior to PTE analysis.

3.4. ICP-MS protocol

The X series II ICP-MS was tuned using a 10 ppb solution of Li, Be, Bi, Ce, Co, In, Ba, Pb, Tl, U in 2% HNO_3 to verify mass resolution and maximise sensitivity. The tuning was done in standard and CCT (collision cell technology) mode. The CCT mode is used for the determination of first transition row elements. The conditions for standard mode and CCT mode are shown in Table 3. A calibration standard of 0–400 ppb prepared from the 100 ppm of the multielement mixture was used to calibrate the instrument; eight separate concentrations were prepared to construct the calibration graph. The soil samples were diluted with an appropriate dilution factor. A mixed internal standard (Sc, In and Tb) was added to the diluted soil samples, calibration standards, blanks and CRM and analysed using ICP-MS. Calibration curves for metals (As, Cd, Cr, Cu, Mo and Ni) based on a concentration range of 0–400 ppb with eight calibration data points were done on ICP-MS; typical correlation coefficient data was >0.999 (in either standard or CCT mode).

3.5. Atomic absorption spectroscopy (AAS)

The instrument was calibrated using standard solutions of 0–10 ppm of Pb and Zn. The digested samples were diluted to fall within the calibration range. A certified reference material was also analysed. The concentration of Pb and Zn was determined at wavelengths of 217 and 213.9 nm, respectively. Lead and Zn were determined using FAAS over a concentration range of 0–10 ppm with six calibration points; typical correlation coefficient data was >0.999.

Table 3
Operating conditions for ICP-MS.

ICP-MS conditions	Standard mode	CCT mode
Extraction	−152.9	−156.9
Forward power (W)	1400	1400
D1	−40	−40
D2	−140	−110
Quadrupole bias (V)	0.2	−14.0
Hexapole bias (V)	−2.0	−18.0
Nebuliser gas flow (L/min)	0.83	0.83
Count rate	^{7}Li > 40,000, ^{115}In > 200,000, ^{238}U > 300,000	^{59}Co > 10,000, ^{115}In > 50,000, ^{238}U > 100,000
Ratio limit	^{156}CeO/^{140}Ce < 0.0200	^{156}CeO/^{140}Ce < 0.0200
Collision cell gas (L/min)	N/A	H_2/He (3.50)
Cool gas flow (L/min)	13.0	13.0
Auxiliary gas flow (L/min)	0.90	0.90
Internal standards	^{45}Sc, ^{115}In, ^{159}Tb	^{45}Sc, ^{115}In, ^{159}Tb

4. Results and discussion

4.1. Microwave optimization

Microwave digestion was carried out using an experimental design approach. The variables considered were temperature, time, power and volume of solvent. To fully understand the way in which the microwave system affects digestion, individual operating variables were considered along with nonlinear effects and interaction terms. The operating variables were studied using a full second order central composite design [14]. The results from the central composite design have been assessed using multilinear regression represented by the equation:

$$Y = \beta_0 + \beta_1 T + \beta_2 t + \beta_3 P + \beta_4 V + \beta_5 T^2 + \beta_6 t^2 + \beta_7 P^2 + \beta_8 V^2 + \beta_9 T \cdot t + \beta_{10} T \cdot P + \beta_{11} T \cdot V + \beta_{12} t \cdot P + \beta_{13} t \cdot V + \beta_{14} P \cdot V \quad (1)$$

where T = temperature, t = time, P = power, V = volume, β_0 = intercept and $\beta_1 - \beta_{14}$ = parametric coefficients and Y = response.

The total PTE concentration was determined (see Supplementary Data). The PTEs considered were Cr, Cu, Mo, Ni, Pb and Zn. The individual metals were investigated using multilinear regression equation (Eq. (1)). The results of the individual PTEs were interrogated and statistical data treatment carried out (see Supplementary Data). It is clear (see Supplementary Information) that some individual elements have statistical significance at the 95% confidence level (p value <0.05) including for Cu the quadratic of volume and the interaction between temperature and pressure; for Mo the quadratic of temperature and the interaction of temperature and pressure were significant; while for Zn time of extraction was significant. This data implies that, in general terms, the key operating variables were temperature, volume of aqua regia and extraction time having the most significant role in the recovery of some elements using microwave digestion. By using surface response methodology (Fig. 2) it is possible to visualise the important operating parameters. Fig. 2(A) shows the influence of extraction time and aqua regia volume on the recovery of copper (mg/kg); it can be seen that a volume of 13 mL and an extraction time of 25 min lead to optimum recovery. Similarly in Fig. 2(B) the influence of operating power and extraction time on the recovery of molybdenum (mg/kg) is shown; it can be seen that a high operating power (750 W) leads to optimum recovery provided that the extraction time is between 10 and 26 min. Finally, in Fig. 2(C) the influence of aqua regia volume and temperature on the recovery of lead (mg/kg) is shown; it can be seen that a volume of 13 mL leads to optimum recovery irrespective of temperature. It was therefore concluded, based on an evaluation of the data, that the compromise microwave operating conditions were as follows: temperature, 160°C; power, 750 W; extraction time, 25 min; and, an aqua regia volume of 13 mL. These microwave operating conditions were therefore used for digestion of all soil samples.

Table 4
Elemental analysis of soil certified reference materials.

Element		GBW 07401 soil			SRM 2711 Montana soil			
Symbol	Isotope	Certificate value (μg/g) mean ± SD	Standard mode (μg/g) mean ± SD (n = 3)	CCT mode (μg/g) mean ± SD (n = 3)	Certificate value (μg/g) mean ± SD	Non-certified leachable concentration range (median) (μg/g)[a]	Standard mode (μg/g) mean ± SD (n = 3)	CCT mode (μg/g) mean ± SD (n = 3)
As	75	34 ± 5	27.8 ± 1.8	34.8 ± 5.4	105 ± 8	88–110 (90)		ND
Cd	111	4.3 ± 0.6	4.8 ± 1.2	N/A	41.70 ± 0.25	32–46 (40)	37.7 ± 0.77	
Cr	52	62 ± 6	62.9 ± 2.3	61.5 ± 0.5	(47)	15–25 (20)		32 ± 1.65
Cu	63	21 ± 2	14.9 ± 1.8	20.0 ± 2.3	114 ± 2	91–110 (100)		114.8 ± 0.9
Mo	98	1.4 ± 0.2	1.3 ± 1.3	N/A	(1.6)	(<2)	0.73 ± 1.9	
Ni	60	20.4 ± 2.7	15.7 ± 2	20.1 ± 2.9	20.6 ± 1.1	14–20 (16)		19.9 ± 1.4
Pb		98 ± 8	99.3 ± 0.1[b]		1162 ± 31	930–1500 (1100)	1150 ± 15[b]	
Zn		680 ± 39	682 ± 6.8[b]		350.4 ± 4.8	290–340 (310)	ND	

N/A, not applicable.
ND, not determined.
Values in parentheses are indicative values only.
[a] Based on Addendum to SRM 2711 Certificate of Analysis (Table 3) and determined using US EPA Method 3050 which used a HNO_3–HCl–H_2O_2 acid mixture.
[b] Measured by FAAS.

4.2. *Analysis of soil CRMs*

Analysis of two soil certified reference materials (GBW 07401 and SRM2711) after microwave digestion was done in order to assess the accuracy and precision of the approach. The obtained results for the PTE analysis are shown in Table 4. Initially, data from the analysis of GBW 07401 was used to evaluate the mode of operation of the ICP-MS i.e. standard and collision cell technology (CCT) modes. The CCT mode is used mainly for first order transition elements in order to reduce or eliminate polyatomic interferences encountered in ICP-MS. As far as measurement mode is concerned it is appropriate to consider elements with masses <80 amu in both standard and CCT mode. Therefore, As, Cr, Cu and Ni were measured in both modes.

It is noted (Table 4) that the measured values for As, Cr, Cu and Ni in CCT mode are closer to the certificate values (GBW 07401) than those for the standard mode. The percentage recovery obtained from CCT mode for these elements are all above 95% compared to the standard mode whose recoveries are <90%, except Cr. In the case of Cr it can be seen that it has a measured value of 62.9 mg/kg (102% recovery) in standard mode and 61.5 mg/kg (99% recovery) in CCT mode. The standard deviation for Cr in standard mode is ±2.3 and ±0.5 for CCT mode. The results in both modes are good but Cr has a smaller standard deviation when measured in CCT mode. On the basis of the elements determined in the soil CRM, the following operating modes were identified as the most appropriate: As, Cr, Cu and Ni would be determined in CCT mode while Cd and Mo were determined using standard mode. As a result all subsequent soil samples were measured using these experimentally determined ICP-MS operating mode conditions.

In the case of SRM 2711 certified and non-certified leachable concentration data is available. While the certified data is based on total element content the leachable values were obtained using US EPA Method 3050 (an approach that uses an acid combination of HNO_3–HCl–H_2O_2). In the case of Cr the leachable concentration is 43% of the total indicative value reported whereas for other elements investigated the difference between the total certified and leachable concentration is considerably less (typically in the range 78–96%, of the certificate values). So while it is not possible to directly compare the data generated in this paper using a microwave digestion approach based on aqua regia with the non-certified leachable concentration the inclusion of this data in Table 4 can be used as a guide.

The use of flame atomic absorption spectroscopy (FAAS) for the measurement of some elements is useful when their concentration in the sample would require extensive dilution if analysed by ICP-MS. Based on the certified values for GBW 07401 it was concluded that it was appropriate to measure Pb and Zn by FAAS. The digest of the CRM was analysed for Pb and Zn by FAAS and the results are shown in Table 4. Lead gave a measured value of 99.3 mg/kg (101% recovery) against the certificate value of 98 mg/kg while Zn gave 682 mg/kg (100% recovery) against the certificate value of 680 mg/kg. Subsequent soil samples were analysed for Pb and Zn using FAAS.

4.3. *Analysis of contaminated soil samples*

Powdered soil (<2 mm fraction) from St. Anthony's Lead Works was analysed by either ICP-MS or FAAS (see Supplementary Data). Fig. 1 identifies the 19 sampling points on the former site of St. Anthony's Lead Works. Also indicated on the plan of the site is an outline of the former lead works as well as the current layout of scrub woodland. In general terms the scrub woodland are located on raised and steep slopes that are interconnected by surfaced walkways leading to grassed areas. The levelled grassed areas now provide opportunities for recreation in the park.

By comparing the data with previously released UK soil guidelines values (SGV) for As (640 mg/kg, dry weight) [15], Cd (230 mg/kg, dry weight) [16] and Ni (1800 mg/kg, dry weight) [17] as well as more historic SGVs for Cr (5000 mg/kg) [18] and Pb (750 mg/kg) [19] based on specified land use (commercial) it can be seen that certain sampling sites (Fig. 1) within the area of investigation exceed these values (*Note*: In 2009, the Environment Agency published a paper called 'Using Soil Guideline Values' [20]. The new SGV reports, for metals, were published in summer 2009 for As, Cd, Hg, Ni and Se only. In this study 'commercial' was selected for reference in preference to the other two choices of residential with, or without, plant uptake).

Perhaps not surprisingly as the site under investigation is a former lead works the concentration of Pb within 17 out of 19 sampling sites exceeds the previously identified SGV for commercial sites. As sampling points 2, 6, 7, 8, 10, 16 and 18 have elevated lead levels from topsoil located in the levelled grassed areas they represent areas of potential human health risk (sampling sites 1 and 11 are also on grassed areas but have lead values below the SGV for commercial sites). In one case the Pb level exceeds the SGV by 80× (sampling point 14).

In the case of As, soil samples from sampling points 3, 6, 13, 15, 17 and 19 have values that exceed the SGVs for commercial sites (640 mg/kg). In each case while the As levels exceed the SGV (by a maximum of 10× in the case of sampling site 19) the potential risk to humans is more limited as the sampling sites are all located on steep, sloped scrub woodland that is partly fenced off and therefore not readily accessible.

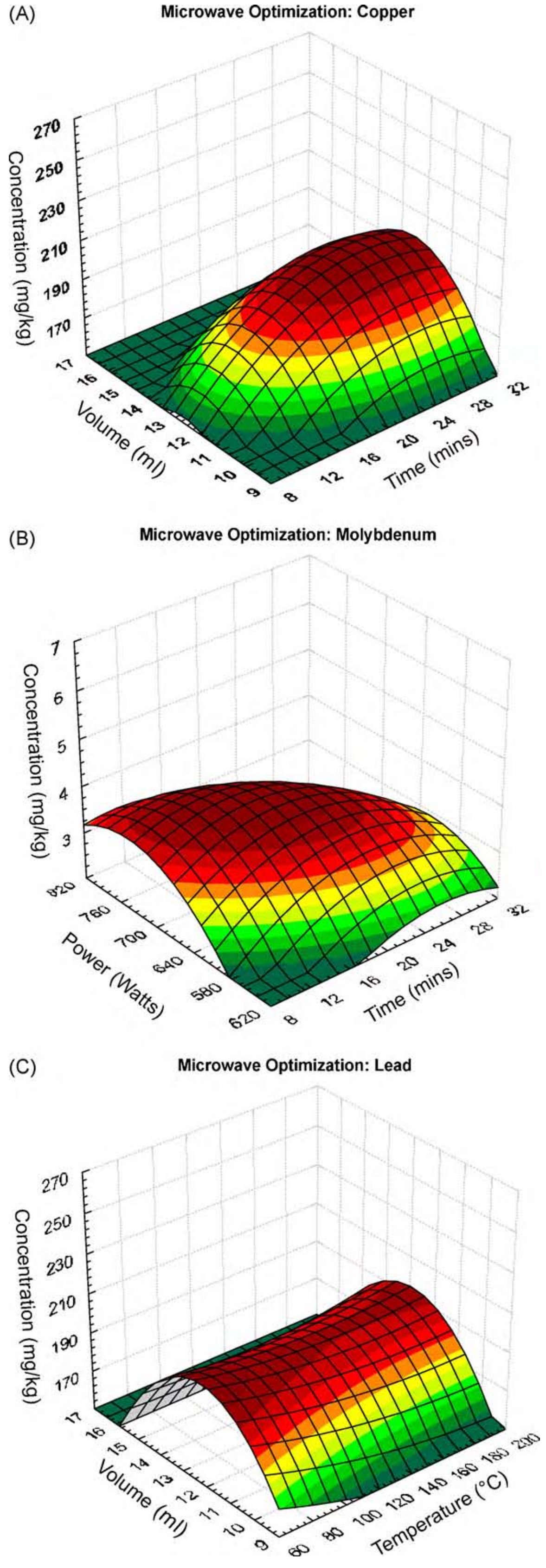

Fig. 2. Surface response methodology for microwave digestion of metals from contaminated soil. (A) Microwave optimization: copper, (B) microwave optimization: molybdenum, and (C) microwave optimization: lead.

In the case of Cd, Cr and Ni the determined values on the site are considerably below the SGVs for commercial sites and so the potential risk to humans is significantly reduced.

At the present time no other metals have SGVs for comparison, however, the Chartered Institute of Environmental Health (CIEH) and the Land Quality Management Ltd. (LQM) published generic assessment criteria for an additional range of metals, and this included Cu (71,700 mg/kg) and Zn (665,000 mg/kg) for commercial soil [21]. Further work is being undertaken to assess the potential risk to humans from this site using an oral bioaccessibility test based on a physiologically based extraction test (PBET) [22,23].

5. Conclusion

The paper reports data for selected potentially toxic elements on a contaminated land site in Newcastle upon Tyne. Potentially toxic element concentrations have been compared with previously released soil guideline values to assess the potential environmental risk. Further work is required to assess the potential risk to humans using an oral bioaccessibility test procedure.

Acknowledgements

Mr. P. Hartley and L. Bramwell (Newcastle City Council) are acknowledged for providing access to the site and valuable background information. Mr. Gary Askwith is acknowledged for his technical support in the operation of the ICP-MS.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2010.07.008.

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