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A new simple, low-cost approach for generation of the PM$_{10}$ fraction from soil and related materials: Application to human health risk assessment

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HIGHLIGHTS

- A simple, robust and low-cost approach for generation of PM$_{10}$ fraction is reported.
- Approach applied to soil and mine waste samples from Mitrovica, Kosovo.
- Fraction containing potentially harmful elements (PHEs) is applied in to a human risk assessment based on inhalation.
- Average daily dose for Cd from the inhalation of suspended soil particles is reported.

GRAPHICAL ABSTRACT
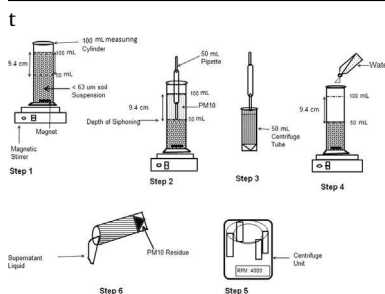
ABSTRACT

A new simple, robust and low-cost wet laboratory method for the generation of the $<10\,\mu m$ (PM$_{10}$) particle size fraction is reported. A sedimentation method is directly compared with a centrifugation method for generation of the PM$_{10}$ fraction. Both approaches are based on an integrated form of Stokes' law. Subsequently the sedimentation method was adopted. The results from the sedimentation method were corroborated using particle size distribution measurements. This approach for the generation of the PM$_{10}$ fraction was applied to soil and mine waste samples from Mitrovica, Kosovo as part of an investigation in to the human risk assessment from inhalation of the PM$_{10}$ fraction containing potentially harmful elements (PHEs). The average daily dose for Cd from the inhalation of suspended soil particles was calculated to be 0.021 and $0.010\,\mu g\,kg^{-1}{}_{BW}\,d^{-1}$ for a child and an adult, respectively. This corresponded to an inhalation dose of 0.50 and $0.70\,\mu g\,Cd\,d^{-1}$ for a child (20 kg) and an adult (70 kg), respectively.

1. Introduction

The PM$_{10}$ fraction represents the ambient particulate matter that enters the respiratory tract [1–4] and for this reason it is also the fraction of suspended particulate matter that is usually monitored as part of a human health exposure risk assessment. In addition, potentially harmful elements (PHEs) in the

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atmosphere are preferentially bound to the PM_{10} fraction [5]. This fraction has also been classed as a health-relevant fraction for inhalation exposure because it correlates to toxicity, respiratory diseases and mortality [6,7]. Mass contributions to ambient PM_{10} in several cities of the world have been traced to several sources including soil materials [8–19].

Whilst in the contaminated land exposure assessment (CLEA) model [20] for example, the inhalation contribution of soil-derived particulate matter is considered to be <1% for a number of elements (e.g. As, Cd and Se) across a range of land-uses, for other elements such as Ni the inhalation pathway is considered to be the most significant exposure pathway (50% or more) [21].

Ambient PM_{10} sampling methods though popular in exposure studies have some challenges. These challenges include small sample quantity and the bulk nature of many samples [22]. During ambient PM_{10} sampling volatile and semi-volatile chemicals can interchange with the gas phase and due to particle "bouncing" the sampled size fraction distribution may be distorted [22,23].

Sampling of the PM_{10} fraction from dust often involves sweeping the loose material present on surfaces into a clean dustpan with brushes [24–26], modified vacuum systems [27,28], the use of leaf blowers for the mobilization of dust from surfaces [29] or sampling surface soil [30–33]. However, the fractionation of bulk point source samples, to obtain the PM_{10} fraction, requires gravitation (fall through air), mechanical agitators (rotating cylinder entrained into airflow e.g. Portable In-Situ Wind ERosion lab, PI-SWERL) or pumps to simulate wind generated aerosol which allows the PM_{10} fraction to be extracted with cyclone or impactor units [34–36].

Most of the dry fluidization techniques require more laboratory space, experienced personnel to operate and are high in cost and maintenance [31]. During dry fluidization processes coarse particles can break apart into finer grains due to air pressure or high speed fine particles can collide and form larger particles [37]. In some cases after the sedimentation step the resultant wet particles are further sieved to obtain the PM_{10} fraction (e.g. Ljung et al. [31]). However, an assessment of the quality of these laboratory-scale PM_{10} sampling protocols is difficult since particle size distribution measurements were not reported. The application of the Na-hexametaphosphate may precipitate out some PHEs of interest during the suspension and sedimentation steps (e.g. Gallup [38]). The aim of this study was to investigate both sedimentation and centrifugation techniques for sampling of the PM_{10} fraction from bulk samples and to develop a simple, robust and low-cost laboratory-scale method applicable for soil and mine waste as part of a human health risk assessment on the potential risk from inhabitable suspended particulates. This is directly linked to previous research published by the group [39] on the development and application of a new inhalation bioaccessibility method for assessment of the human health risk based on the PM_{10} fraction.

1.1. The application of Stoke's law

Both sedimentation and centrifugation methods are based on Stoke's law. The law is a mathematical description of the force needed to move a sphere through a viscous fluid at a stated velocity. The equation (Stokes' law) describing the motion is written as [40]:

$$F_d = 6\pi\mu Vd \tag{1}$$

where F_d is drag force of the fluid on a suspended sphere; μ is the fluid viscosity; V is the velocity of the suspended sphere through the fluid; and, d is the diameter of the suspended sphere.

In a liquid suspension three forces are acting on the suspended sphere (i.e. the buoyancy effect of the displacing the fluid; the viscous drag on the sphere by the fluid; and, gravitational attraction). For a suspended solid in a liquid Eq. (1) is re-written [40] as:

$$V = \frac{gd^2\left(\rho_p - \rho_m\right)}{18\mu} \tag{2}$$

where g is the acceleration due to gravity; ρ_p is the average particle density for mineral soils; ρ_m is the density of water at a fixed temperature (20 °C); and, μ is the viscosity of water at a fixed temperature (20 °C) [41].

By substituting the velocity of sedimentation with the distance travelled (D) and the time required (T) for the PM_{10} fraction to reach a designated point in the liquid medium the re-arrangement of Eq. (2) gives the settling times for the sedimentation method. This can be expressed by an integrated form of Stokes' law as:

$$T = \frac{18D\mu}{gd^2\left(\rho_p - \rho_m\right)} \tag{3}$$

The settling times under the influence of centrifugal acceleration (used to speed up the separation) can then be expressed by an integrated form of Stokes' law originally developed by Svedberg and Nichols [42] and later modified by Jackson [40].

$$T_{min} = \frac{6.3 \times 10^9 \eta \log_{10}(R/S)}{N^2 D^2 \Delta s} \tag{4}$$

where T_{min} is the time for sedimentation in minutes; η is the viscosity at a fixed temperature; R is the distance (cm) from the centre point of the centrifuge head (axis of rotation) to the top of the sediment in the tube when the wall of the container is perpendicular to the rotation axis [43]; S is the distance from the axis of rotation to the top of the suspension; N is the number of revolutions per minute; D is the particle diameter (μm); and, Δs is the difference in specific gravity between the solvated particle and water.

2. Materials and methods

2.1. Chemicals/reagents

Concentrated nitric acid (HNO_3) and concentrated hydrochloric acid (HCl) were supplied by Fisher Scientific Ltd. (Loughborough, Leicestershire, UK). Standards (for As, Cd, Cr, Cu and Ni) and internal standard solutions (In, Sc and Tb) were obtained from SPEXCertPrep (Middlesex, UK). Ultra pure water of conductivity 18.2 MΩ cm^{-1} was produced by a direct Q^{TM} Millipore system (Molsheim, France). A certified reference material (BCR 143R, a sewage-sludge amended soil) was obtained from LGC-Promochem (London, UK).

An experimental test sample (topsoil) of approximately 300 g was collected from Cumbria, North West England. The soil was air dried, gently disaggregated and passed through a 2 mm plastic mesh sieve. A subsample of the <2 mm fraction was then further dry sieved to yield the <63 μm size fraction.

Soil and mine waste samples of approximately 250 g were obtained from Mitrovica, Kosovo. This is an area associated with uncontained mine waste dumps and metal/metalloid contaminated soil [44–47]. Surface (1–10 cm) soil samples ($n = 33$) included 4 smelter samples, 24 soil samples and 5 tailing samples were obtained [48],Table 1. The samples were sieved to the <63 μm size fraction.

2.2. Instrumentation

Microwave acid digestion was done using a Start D multiprep 42 high throughput rotor microwave system (Milestone

Table 1
Summary of sample details.

Sample ID	Origin	Matrix
RM6	Roma Mahalla	Soil
RM19	Roma Mahalla	Soil
RM27	Roma Mahalla	Soil
RM28	Roma Mahalla	Soil
RM42	Roma Mahalla	Soil
RM45	Roma Mahalla	Soil
RM49	Roma Mahalla	Soil
RM54	Roma Mahalla	Soil
RM66T1	Zharkov Potok	Tailings
RM66T2	Zharkov Potok	Tailings
RM66T3	Zharkov Potok	Tailings
RM67	Osterode	Soil
RM69	Osterode	Soil
RM70	Cesmin Lug	Soil
RM71	Cesmin Lug	Soil
RM72	Cesmin Lug	Soil
RM74	Cesmin Lug	Soil
RM76	Gornje Polje	Smelter waste
RM77(S/T)	Gornje Polje	Smelter waste
RM77(W)	Gornje Polje	Smelter waste
BM3	Bosniak Mahalla	Soil
BM5	Bosniak Mahalla	Soil
BM9	Bosniak Mahalla	Soil
BM11	Bosniak Mahalla	Soil
BM21	Mitrovica city centre	Soil
BM32	Zharkov Potok	Tailings
BM36	Zharkov Potok	Tailings
BM41	Mitrovica city centre	Soil
BM45	Mitrovica city centre	Soil
BM46	Mitrovica city centre	Soil
BM47	Mitrovica city centre	Soil
BM49	Mitrovica city centre	Smelter-public waste
BM50	Mitrovica city centre	Soil

Microwave Laboratory Systems) supplied by Analityx Ltd. (Peterlee, UK). Elemental concentrations were determined on an inductively coupled plasma mass spectrometer (ICP MS) X Series II (Thermo Electron Corp., Winsford, UK). A Mastersizer 2000 (Malvern Instruments Ltd., UK) was used for particle size analysis. A centrifuge (model Harrier 18/80) supplied by MSE (London, UK) was used for preparation of the samples.

2.3. Procedure for PM$_{10}$ fractionation by sedimentation

Before the PM$_{10}$ separation process the density of the <63 μm fraction was determined using a water displacement technique [49]. In to a 100 mL measuring cylinder an accurately weighed c. 2 g sample of the <63 μm fraction was suspended in 100 mL of deionised water and dispersed with the aid of a magnetic stirrer for 10 min (Fig. 1, step 1). Into each of the suspensions a pipette was placed at the 50 mL mark after the time required for particles >10 μm to sediment beyond that mark (Fig. 1, step 2) and 50 mL was siphoned off and transferred into a centrifuge tube (50 mL); this was then centrifuged for 10 min at 4000 rpm to obtain the <10 μm fraction (Fig. 1, steps 2, 3 and 5). To the remaining suspension (in the measuring cylinder) a fresh 50 mL of deionised water was added and the remaining solids re-suspended (Fig. 1, step 4), siphoned and centrifuged. After centrifugation the supernatant was decanted (Fig. 1, step 6) to obtain the particulate matter. The refilling, re-suspension, siphoning, centrifugation and decantation cycle was done at room temperature (20 °C) and repeated until the resulting suspension above the siphoning mark was visually interpreted to be clear. All extracted particulate matter in the centrifuge tubes were subsequently transferred into desiccators for drying and subsequent weighing.

2.4. Procedure for PM$_{10}$ fractionation by centrifugation

An accurately weighed approximate mass (0.3000 g) of the <63 μm fraction was transferred into a centrifuge tube (50 mL).
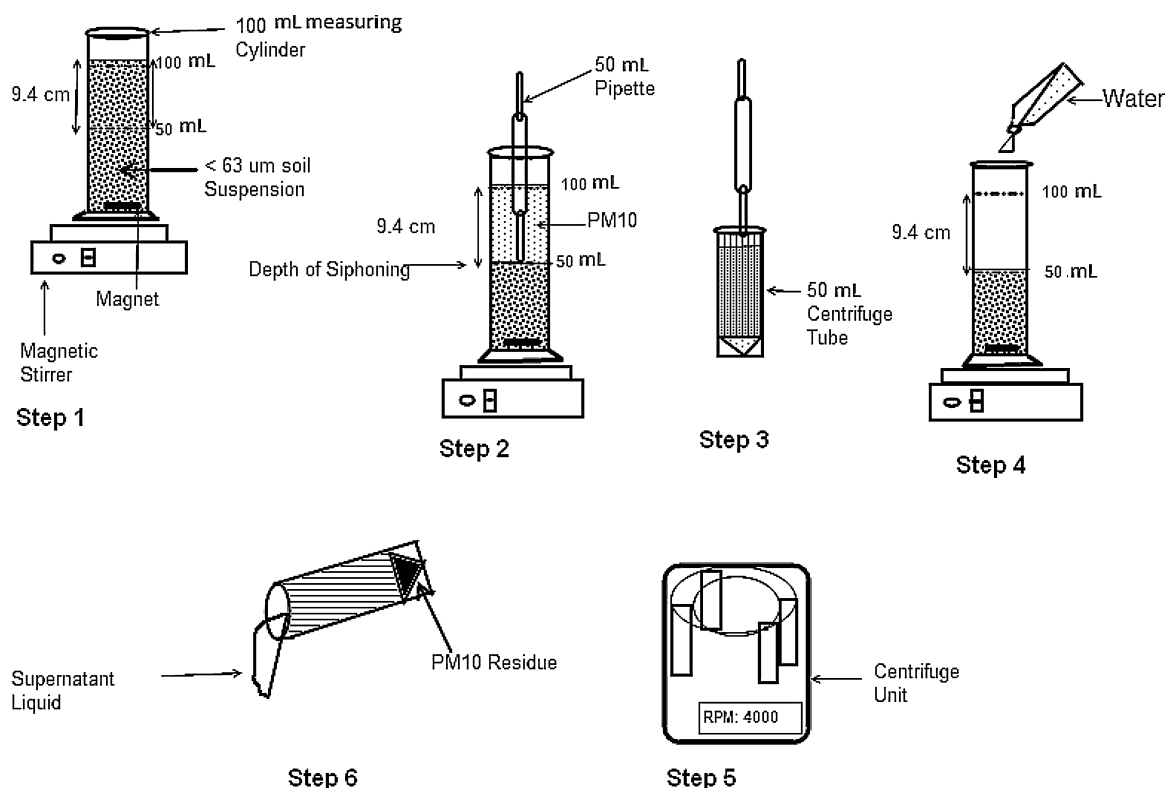

Fig. 1. Schematic diagram of the steps involved in the sedimentation method for extracting the PM$_{10}$ fraction from soil and related material.
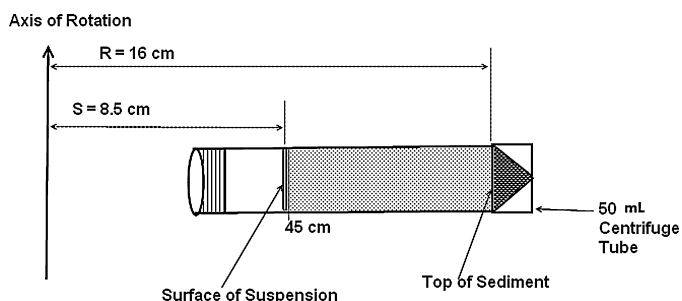
Fig. 2. Schematic diagram of the centrifugation method for extracting the PM_{10} fraction from soil.

Then, 45 mL of deionised water was added (i.e. $S = 8.5$ cm based on Eq. (4)) (Fig. 2) and the suspension stirred with a glass rod to allow wetting of the floating solids and to maintain the solids in suspension. The resulting suspension was placed in a centrifuge (at a position where $R = 16$ cm) and centrifuged for 2.57 min at 200 rpm to obtain the $<10\,\mu m$ fraction. The resulting supernatant was transferred into a fresh centrifuge tube and the PM_{10} sediment obtained as a semi-solid pellet following centrifugation at 4000 rpm for 10 min.

2.5. Procedure for digestion and analysis

Sub-samples of the PM_{10} fraction samples and the non-bioaccessible fractions were subjected to microwave-assisted aqua regia digestion according to the method by Okorie et al. [50] to obtain the PHEs aqua-regia soluble (pseudo-total) concentration. Briefly a sub-sample (0.5 g) was accurately weighed into a PFA (a perfluoroalkoxy resin) (65 mL) microwave vessel and 13 mL of aqua regia added (HNO_3:HCl; 3:1, v/v). Microwave-assisted digestion was then done under the following conditions: power, 750 W; temperature, room temperature to 160 °C (15 min) followed by a hold at 160 °C (10 min) and finally a 30 min cooling time prior to opening the vessels. The digestates were then filtered through a Whatman filter paper (grade 41, pore size 20 μm) and quantitatively transferred into volumetric flasks (50 mL) and made to volume with ultrapure water. For quality control the certified reference material (BCR 143R) was also prepared for analysis. All samples, the certified reference material and sample blanks were prepared in the same manner. Each sample/blank digestate was stored in the fridge (4 °C) prior to analysis.

Samples for analysis by ICP-MS were prepared by measuring 1 mL of either the sample or CRM digestate (and a blank) into a 10 mL Sarstedt tube; this was followed by addition of 30 μL of mixed internal standard (In, Sc and Tb) and 9 mL of water (1% HNO_3). Sample digestates were stored in the fridge (4 °C) for subsequent ICP-MS analysis. The use of the CRM was used to assess the precision and accuracy of the methodology whilst reagent blanks were included to check contamination. Eight calibration standards over the range 0–400 ppb were prepared from a 100 ppm multi-element standard with mixed internal standard; this was used to calibrate the instrument and also to construct the calibration graphs. The instrument was tuned to verify mass resolution and maximise sensitivity. The operating conditions were as follows: RF power, 1400 W; coolant gas flow rate, 13.0 L min^{-1}; auxiliary gas flow rate, 0.9 L min^{-1}; and a nebuliser gas flow rate, 0.83 L min^{-1}. Analysis was done in both standard mode (Cd) and collision cell technology (CCT) mode (As, Cr, Cu and Ni); collision cell mode was done using an additional gas flow i.e. 4.75 L min^{-1} of a 7% H_2:93% He mixture. The calibration curves produced linear graphs over the determined range with regression coefficient (R^2) data of at least 0.999.

2.6. Quality control of the separated PM_{10} fraction

For validation of the PM_{10} extraction efficiency and the percentage PM_{10} yield, portions of the siphoned suspensions from both the sedimentation and the centrifugation method were analysed with a laser light scattering particle size analyser (Mastersizer 2000). Prior to particle size analysis in the Mastersizer the samples were air dried for 4 days. Then, representative extracted dried samples (0.250 g) from the two different methods and four Kosovo sample (RM19, RM69, RM71 and RM77 W) were dispersed in 50 mL deionized water in a capped centrifuge tube. All samples to be analysed by this approach were prepared in triplicate. For the test soil the Mastersizer was programmed to determine the % total volume of PM_{10} and the mean particle diameter for suspensions resulting from the different extraction methods. For the selected Kosovo samples the Mastersizer was programmed to measure the % volume of $<1.00\,\mu m$, $<2.50\,\mu m$, $<5.00\,\mu m$, $<7.50\,\mu m$ and $<10.0\,\mu m$ in the suspensions resulting from the PM_{10} extraction process. Mastersizer obscuration and pump rate were set at 10% and 2300 rpm, respectively. Before dispersions were pumped through the path of the laser light they were homogenized by manual agitation. In addition, to compare the PM_{10} extraction efficiency of each of the two separation methods the resultant extracted solids were transferred into desiccators for drying and subsequent mass determination.

3. Results and discussion

3.1. Experimental test soil

The mass of particulate matter extracted using the sedimentation and centrifugation methods after initial suspensions were 0.0978 ± 0.0063 g and 0.0082 ± 0.0015 g, respectively. This corresponded to the fraction of the bulk sample extracted as PM_{10} as 4.6–5.2% and 2.2–3.2% for the sedimentation and centrifugation methods, respectively. Although both methods selectively extracted PM_{10} from the $<63\,\mu m$ fraction the centrifugation method consistently yielded a smaller quantity of the desired PM_{10} fraction from each sample. The percentage yield of the PM_{10} fraction sampled and the particle diameter from the sedimentation and centrifugation techniques investigated in this study are $89.52 \pm 0.11\%$, $10.15 \pm 0.11\,\mu m$ and $85.89 \pm 3.02\%$, $11.04 \pm 0.72\,\mu m$, respectively. Comparison of the mass, yield and particle diameter of the sampled PM_{10} fraction from both techniques indicated that the sedimentation technique gave the desired results. Given the slightly higher PM_{10} yield, the sedimentation technique was adopted and applied to the Mitrovica samples.

3.2. Sample particle size distribution

For a typical metallurgic (smelter) waste sample (RM 77W) 99.9% of the extracted particles can be classified as $<10\,\mu m$ (PM_{10}) (Table 2). However, for the 3 topsoil samples analysed only between 84.7 and 87.3% of the extracted particles were $<10\,\mu m$ (PM_{10}) (Table 2). The range obtained for the soil samples is consistent with the volume (89.5%) obtained for the experimental

Table 2
Percentage particle size distribution (μm) of the sampled PM_{10} suspension.

Sample ID	Matrix	<1.00	<2.50	<5.00	<7.50	<10.0
RM69	Soil	9.54	18.6	46.6	70.4	84.7
RM19	Soil	9.05	17.9	47.7	72.0	86.1
RM71	Soil	12.0	24.2	53.5	75.8	87.3
RM77W	Smelter waste	95.5	95.5	98.8	99.8	99.9

Table 3
Summary of the water-soluble losses as a result of the sedimentation method for PM$_{10}$ fractionation.

Element	As	Cd	Cr	Cu	Ni
Number of samples	33	3	NA	25	25
Mean (mg kg^{-1})	0.60	22.0	NA	6.25	0.88
Minimum (mg kg^{-1})	0.07	14.2	NA	1.25	0.04
Maximum (mg kg^{-1})	1.85	33.6	NA	25.5	4.51

NA: below the detection limit of ICP-MS i.e. <2.3 mg kg^{-1} Cr.

test soil sample employed for the optimization of the PM$_{10}$ extraction method. The lower yield of the PM$_{10}$ fraction obtained for soil samples compared to the metallurgic waste samples may be due to agglomeration of fine particles in-situ resulting in an apparent larger particle size distribution during centrifugation of dilute suspensions and decantation; these repetitive steps are needed to achieve a sufficient particulate concentration for subsequent analyses. This issue, associated with water-based fine particulate suspensions and subsequent agglomeration problems has been reported by others [51,52]. This variance in the % yield of the PM$_{10}$ fraction may therefore be due to sample matrix differences (e.g. smelter waste: RM77 versus soil: RM 19) [53].

A laser light scattering particle size analyser can also be used in the validation of the size distribution of particulate matter, as has been reported for a range of sample types including ash from the combustion of coal [54], rural ambient dust collected at about roof top height [55], fine dust emission from re-suspended soil [56], road dust [57,58], sediment [59] and as part of particulate matter abatement studies [60]. To verify the particle size distribution of the obtained PM$_{10}$ samples, representatives of the siphoned suspensions were submitted for particle size analyses using the Mastersizer and the results are shown in Table 2. It is observed that the average particle size fraction ($n = 4$) that is <10 μm is 89.5% (soil and smelter waste).

3.3. Undesired dissolution of PHEs in water-based PM$_{10}$ extraction methods

The water soluble fractions of PHEs can be a source of error for water-based PM$_{10}$ sampling methods. It has been suggested that a reduction in the volume of water applied in wet PM$_{10}$ sampling methods would minimize the dissolution of the PHEs of interest [32]; however, the use of a small volume of water may result in insufficient wetting and dispersion of the particulate matter making the results unreliable. In order to assess the suitability of our wet sedimentation method for sampling the PM$_{10}$ fraction from soil and mine wastes, portions of the visually clear liquid, obtained after centrifugation, were analysed by ICP-MS (Table 3). The maximum As, Cd, Cu and Ni concentrations lost (i.e. in the water-soluble component) during the sampling process were determined to be 1.85 mg kg^{-1}, 33.6 mg kg^{-1}, 25.5 mg kg^{-1} and 4.51 mg kg^{-1}, respectively (Table 3). Concentrations of Cr were all

below the detection limit of the ICP-MS. This equates to a maximum % loss (i.e. in the water-soluble component) for As, Cd, Cu and Ni during the wet separation process of 0.5%, 2.5%, 2.0% and 1.5%, respectively. As such, the wet sedimentation method for sampling the PM$_{10}$ fraction appears suitable for these samples, based on the minimal losses in the water-soluble component, in the sedimentation method. The maximum fraction lost in this study was 2.5% for Cd; this is similar to a maximum 2.0% lost as reported for Co, Cr, Cu, Mn, Ni, Pb and Zn [33] for a water-based sedimentation method for soil samples from Hong Kong. The higher loss observed for Cd in this work is consistent with values obtained in a similar investigation conducted by Ljung et al. [31].

3.4. Total PHE concentrations

In order to contextualise these results and consider the human risk assessment from inhalation it is necessary to determine the total PHE concentration of the PM$_{10}$ samples. This was done by microwave digestion, using aqua regia, of the samples followed by ICP-MS. The procedure for determination of the As, Cd, Cr, Cu and Ni concentration was initially validated by analysis of a CRM (BCR 143R). The results (Table 4) show excellent accuracy and precision. Typical accuracies ranged from 96.4% (for Cd) to 103.0% for (Ni); with precision of the measured samples varying from 0.3% RSD (for Cu) to 13.0% RSD (for Ni). The validated approach was then applied to the PM$_{10}$ samples. Summaries of the results for the PHE concentrations in the PM$_{10}$ fraction of the soil and mine waste samples are shown in Fig. 3(A and B). A consideration of the As, Cd, Cr, Cu and Ni content of the PM$_{10}$ soil and mine waste samples has then been done and compared to other known data from this area and a mining site in China.

The mean concentration of As in soil and mine wastes was 105 mg kg^{-1} (range: 25.0–254 mg kg^{-1}) and 8280 mg kg^{-1} (range: 788–14,300 mg kg^{-1}), respectively. The concentrations obtained with a PM$_{10}$ sampler from two sampling locations at a mining town in China [61] are consistent with our highest concentration reported data (13,100 and 17,400 mg kg^{-1}). Similarly the elevated As loadings in the re-suspendable fraction (PM$_{10}$) was reflected in the high atmospheric concentration (42 ± 40 ng m^{-3}) of As reported for suspended particulate matter at Mitrovica [62]. The As concentration range of PM$_{10}$ (25.0–254 mg kg^{-1}) derived from soil using the wet sampling method in this study was above the range (below detection to 40.6 mg kg^{-1}) for samples from a coal-based city (Fushun, China) reported for the PM$_{10}$ fraction derived from window sills and floor dust samples collected using a dry dust re-suspension approach [25]. The higher As concentration observed at Mitrovica (this study) compared to this coal-based city (Fushun, China) is most likely due to the atmospherically-derived contamination of surface soils by As-rich mine wastes that proliferate in the Mitrovica area.

The mean concentration of Cd in soil and mine wastes was 4.4 mg kg^{-1} (range: 1.2–17.0 mg kg^{-1}) and 523 mg kg^{-1} (range:

Table 4
Certified and measured values for aqua-regia microwave assisted digestion and analysis by ICP-MS for BCR-143 (sewage sludge amended soil).

Element	Certified value[a] (mean ± SD) (mg kg^{-1})	Measured value (mean ± SD) $n = 9$ (mg kg^{-1})	Recoveries (%)
As	NA	8.62 ± 1.12	NA
Cd	72.0 ± 1.8	69.4 ± 0.2	96.4
Cr	426 ± 12	436 ± 8	102.3
Cu	128 ± 7[b]	127.5 ± 1.5	99.6
Ni	296 ± 4	305 ± 20	103.0

NA = not available.
[a] Based on certified aqua-regia soluble content.
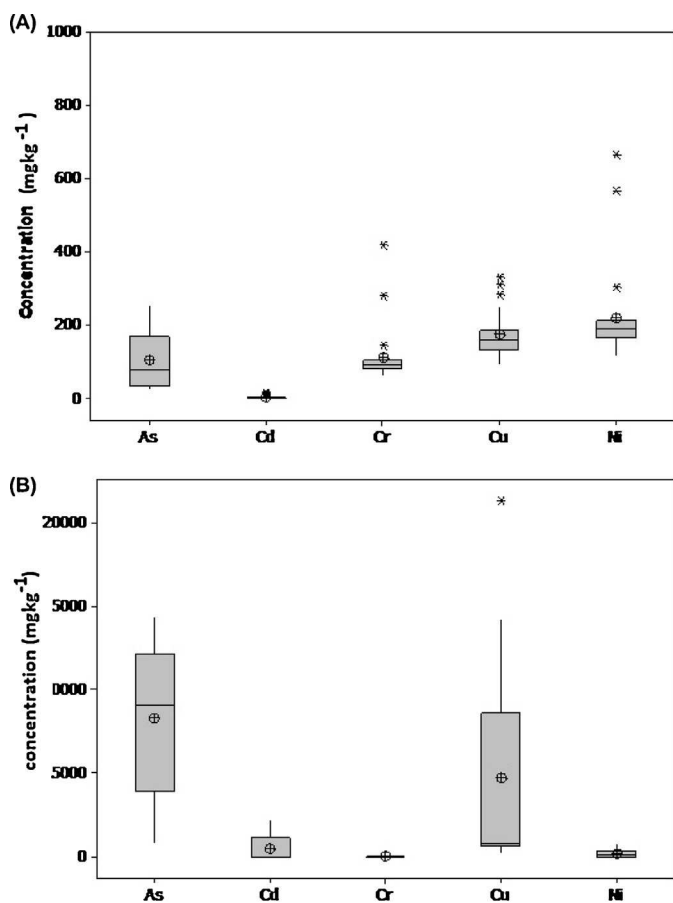[b] Indicative value only.

Fig. 3. Aqua regia concentration of As, Cd, Cr, Cu and Ni in (A) soil and (B) mine-wastes, of the derived PM_{10} fraction.

1.1–2,220 mg kg^{-1}), respectively. The concentrations obtained with a PM_{10} sampler for two sampling locations at a mining town in China [61] are within the range observed in this study for mine wastes (225 and 195 mg kg^{-1}). The lower Cd loadings in the re-suspendable fraction (PM_{10}) was reflected in the low atmospheric concentration (6.0 ± 4.2 ng m^{-3}) of Cd reported for suspended particulate matter at Mitrovica [62].

The mean concentration of Cr in soil and mine wastes was 113 mg kg^{-1} (range: 64.7–419 mg kg^{-1}) and 48.1 mg kg^{-1} (range: 6.7–83.9 mg kg^{-1}), respectively. The concentrations obtained with a PM_{10} sampler for two sampling locations at a mining town in China [61] are consistent with the range observed in this study for soil samples (210 and 234 mg kg^{-1}). The lower Cd loadings in the re-suspendable fraction (PM_{10}) was reflected in the low atmospheric concentration (26 ± 12 ng m^{-3}) of Cr reported for suspended particulate matter at Mitrovica [62]. Unlike the other PHEs, the Cr loading was greater in the soil than in the mine wastes and may suggest that Cr contamination of surface soil at Mitrovica did not result from mining activities. This deduction is in line with previous multivariate receptor modelling of the elemental composition of total suspendable particulates at the same site [62] who postulated that the Cr in the atmosphere maybe geogenic in origin.

The mean concentration of Cu in soil and mine wastes was 177 mg kg^{-1} (range: 96.7–330 mg kg^{-1}) and 4760 mg kg^{-1} (range: 195–21,300 mg kg^{-1}), respectively. The concentrations obtained with the PM_{10} sampler for two sampling locations at a mining town in China [61] are about two times the maximum value observed in this study for soil samples (675 and 671 mg kg^{-1}). The lower Cu loadings in the re-suspendable fraction (PM_{10}) was not reflected in

the high atmospheric concentration (114 ± 87 ng m^{-3}) of Cu reported for suspended particulate matter at Mitrovica [62]. It is therefore deduced that the principal source of Cu in the atmosphere may be the mine waste at Mitrovica.

The mean concentration of Ni in soil and mine wastes was 223 mg kg^{-1} (range: 116–667 mg kg^{-1}) and 219 mg kg^{-1} (range: 10.6–836 mg kg^{-1}), respectively. The concentrations obtained with the PM_{10} sampler for two sampling locations at a mining town in China [61] are below the range observed in this study for soil samples (46.0 and 46.8 mg kg^{-1}). The lower Ni loadings in the re-suspendable fraction (PM_{10}) was reflected in the low atmospheric concentration (18 ± 9.1 ng m^{-3}) of Ni reported for suspended particulate matter at Mitrovica [62].

Statistical analysis (Pearson correlation) of As, Cd, Cr, Cu and Ni in the aqua-regia extractable concentrations in the PM_{10} fraction indicated a high positive correlation between Cd and Cu (0.987); this suggests that the Cd and Cu at the site are probably from the same source. Results of previous multivariate receptor modelling of elemental composition of total suspendable particulates at Mitrovica have indicated that Cd and Cu in the atmosphere are primarily as a result of metal smelting and waste incineration [62]. Results from this study also indicate that the re-suspension of fine particulates from contaminated surface soils and exposed mine wastes are likely sources of As, Cd, Cr, Cu and Ni in the atmosphere at Mitrovica.

3.5. Inhalation of re-suspended particulates

Inhalation of soil and mine waste dust occurs both indoors and outdoors and the inhalable fine particles are usually associated with elevated concentrations of PHEs [25,63]. This is reflected in the concentrations of As, Cd, Cr, Cu and Ni obtained in this study for the sampled PM_{10} fraction from surface soil and mine wastes. The human average daily dose of a PHE from inhalation of re-suspended soil through atmospheric transport can be estimated as follows [64]:

$$D_{inh} = C_{soil} TSP IR F_d \left(\frac{1 - e^{\lambda ED}}{\lambda ATBW} \right) \qquad (5)$$

where D_{inh} is the average daily dose for PHE from inhalation suspended soil particles (mg kg$^{-1}_{BW}$ d^{-1}); C_{soil} is the average soil concentration (mg kg^{-1}); IR is the inhalation rate (m^3 d^{-1}); TSP is the concentration of total suspended particulates (kg m^{-3}); F_d is the fraction of days in a year that exposure occurred (unitless); λ is the environmental loss rate constant for PHE in soil (d^{-1}); ED is the exposure duration for PHE re-suspension pathway (yr); AT is the average time for exposure to suspended soil (yr); and, BW = body weight (kg).

The model [64] requires the environmental loss rate constant for each PHE investigated; a search of the published literature only yielded a value for Cd (0.08 d^{-1}). Therefore this model was applied to estimate the average inhalation dose of Cd alone. Details of all the input data used in the model are provided in Table 5. Previously Cassee et al. [67] have suggested that pulmonary toxicity of Cd salt for rats correlates with the amount of the salt inhaled. Inhaled particulate Cd may induce pulmonary cancer in humans since it has been implicated as a candidate for pulmonary cancer in rats [68]. The average daily dose for Cd at Mitrovica from the inhalation of suspended soil-derived PM_{10} particles for children and adults was 0.021 μg kg$^{-1}_{BW}$ d^{-1} and 0.010 μg kg$^{-1}_{bw}$ d^{-1}, respectively. Corresponding to an inhalation dose of 0.50 μg Cd d^{-1} and 0.70 μg Cd d^{-1} for a child (body weight 20 kg) and an adult (body weight 70 kg), respectively. An inhalable ambient Cd concentration range of 0.003–0.013 μg m^{-3} for the same study area has been reported [69] which corresponds to an inhalation dose range of

Table 5
Input data for estimating D_{inh}.

Parameter	Children (6–11 years)	Adult (21–60 years)
C_{soil} (mg kg^{-1})	223	223
TSP (kg m^{-3})	1.81×10^{-7a}	1.81×10^{-7a}
IR (m^3 d^{-1})	17[b]	21[b]
Fd (unitless)	1[c]	1[c]
ED (yr)	1	1
AT (yr)	1	1
λ (d^{-1})	0.08[d]	0.08[d]
BW (kg)	32[e]	80[e]

[a] Concentration of TSP (as reported by [62]).
[b] Exposure Factors Handbook [65].
[c] Fraction in a year = 365/365 = 1.
[d] Value from reference [66].
[e] Exposure Factors Handbook [65].

0.07–0.32 μg Cd d^{-1} (at the maximum inhalation rate of 24.6 m^3 d^{-1}) [65]. This range i.e. 0.07–0.32 μg d^{-1} for ambient Cd is similar (though lower) to the inhalable range (0.50–0.70 μg d^{-1}) derived from re-suspended soil in this study. The lower concentration reported [69] may be due to the fact that their atmospheric samples were more dissipated due to climatic conditions. However, the environmental risk from Cd at these sites may not be detrimental to human health as the estimated maximum dose of 0.70 μg d^{-1} is significantly lower than the global dietary Cd intake range of 10–40 μg d^{-1} [70].

4. Conclusion

The PM$_{10}$ separation method developed in this work requires equipment available in most science laboratories and does not require the addition of chemical sample-dispersants such as CaCl$_2$ or Na-hexametaphosphate. This simple sedimentation method was shown to be robust and repeatable with a mean particle size of the sampled PM$_{10}$ fraction determined to be 10.15 ± 0.11 μm. The very low PHE concentrations lost during the sampling process indicate the suitability of the method for sampling PM$_{10}$ from diverse matrices in areas influenced by the mining, flotation, smelting and processing of Pb ores.

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