COMPARISON OF THE BIOACCESSIBILITY OF POTENTIALLY HARMFUL ELEMENTS IN SOILS FROM URBAN SITES IN PORTUGAL AND THE UK USING A NEWLY VALIDATED IN-VITRO TESTING METHODOLOGY

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1. Objectives

One of the main pathways for potentially harmful elements (PHE) in soils to enter the human body is via ingestion. Once in the human gastrointestinal (GI) tract the PHE will only cause risk to human health if it is mobilised from the soil and enters systemic circulation. The BioAccessibility Research Group of Europe (BARGE) has developed and validated (through its partner members) an *in vitro* test for estimating the fraction of the PHE mobilised in the human GI tract.

The objective of this study is to compare the bioaccessibility of Pb and As in soils from selected urban areas in Portugal and the UK using the BARGE methodology.

2. Study areas

Lisbon is the capital of Portugal (Figure 1), covering an area of 284 km^2, with 521 774 inhabitants and divided into 53 districts. The smaller districts are those near the Tagus River, which have a higher population and housing density, a predominance of old buildings, narrow and steep roads, and a high traffic density. The majority of public gardens and playgrounds in the city are located in this area. Soil samples were collected from 51 locations distributed across the town, depending on the location of public parks, public gardens, playgrounds and schools, which are urban open spaces frequently used by children. Children spend more time playing outdoors and through their hand-to-mouth actions (which is very common in the early stages of their lives), are particularly vulnerable to the risks posed by PHE in soils. The geology of the city is composed by: the Miocenic formations (ML) that are mostly sedimentary rocks; the Benfica unit (Ob) that is composed by shales and conglomerates, also with some intercalations of carbonate rocks; the Lisbon Volcanic Complex (Vc); and a band of limestone (C). The climate is Continental Maritime, with rainy winters and dry, mild summers.

The county town of Northampton, in the UK (Figure 1), in central England has a population of c. 200, 000 and a strong industrial heritage past, which includes shoe making and leather tanning. Although traditional industries in this area has decreased over time, strong rail and road links are present because of the thriving financial and distribution industries. The area was surveyed as part of the BGS Geochemical BAseline Survey of the Environment (G-BASE) project, which identified that 45% of the soils had an arsenic concentration above the UK soil guideline value (SGV) of 32 mg kg^{-1} for residential land use. The Northampton geology is based on sedimentary layers of the Jurassic period comprising of: Lias clays (lower, middle and upper divisions) and the Oolitic series (limestone, ironstone and Northampton Sands).

Figure 1: Locations of Lisbon and Northampton in Portugal and the UK respectively

3. Materials and Methods

Fourteen topsoil samples from Lisbon and fifty samples from Northampton were selected for bioaccessibility testing. Bioaccessibility measurements were made using the Unified BARGE Method (UBM), which is validated against a swine model.

Sample Preparation

All samples were air dried or dried in a fan assisted oven at <40ºC and sieved to provide the <250 µm soil fraction.

UBM

START

Saliva gastric, bile and duodenal solutions were prepared following the BARGE protocol

2 x 0.6 g sub-samples of soil weighed into a polycarbonate centrifuge tubes

Saliva and gastric fluids were added to each tube, the pH was fixed at 1.2

End over end extraction at 37ºC for 1h (represents the stomach)

1 sample centrifuged at 4000g for 15 min, 1 ml supernatant removed and diluted with 9 ml of 0.1 M HNO_3

END GASTRIC PHASE

Bile and duodenal fluids were added to 2nd sample, the pH was adjusted to 6.3±0.5

End over end extraction at 37ºC for 4h (represents the small intestine)

Sample centrifuged at 4000g for 15 min, 1 ml supernatant removed and diluted with 9 ml of 0.1 M HNO_3

END INTESTINE PHASE

Quality control

Duplicate samples, blanks and the bioaccessibility guidance material BGS 102 (an ironstone soil with geogenic As total As concentrations of circa. 100 mg kg^{-1}) were extracted with every batch of UBM bioaccessibility extractions. Duplicate extraction of samples indicated good repeatability of the UBM methodology by both laboratories (summarised in Table 1). The data obtained for BGS 102 for both studies (summarised in Table 2) was in good agreement with the consensus values (5.4±2.4 mg kg-[1] As and 13±6 mg kg^{-1} Pb), within the 95% confidence interval.

Table 1: Repeatability data for duplicate UBM extracts from Lisbon and Northampton sampling areas

	As		Pb	
	Lisbon (n=4)	Northampton (n=7)	Lisbon (n=4)	Northampton (n=7)
Mean stomach repeatability, %	9.98	7.81	3.29	11.1
Mean intestine repeatability, %	9.06	5.95	-0.47	5.98

Table 2: Bioaccessibility values achieved for the guidance soil BGS 102 returned in the extraction of the Lisbon and Northampton studies

	As		Pb	
	Lisbon (n=2)	Northampton (n=7)	Lisbon (n=2)	Northampton (n=7)
Bioaccessibility, mg kg^{-1}	3.46	3.24	21.0	14.3
standard deviation	0.14	0.28	0.57	2.43

4. Results

The total As concentrations in Lisbon were measured at up to circa. 14 mg kg^{-1} (Figures 2 and 10) and the total Pb concentrations across the city were measured at up to 441 mg kg^{-1}, which were more comparable with the total Pb concentrations in Northampton (Figure 3, 7 and 11).

Arsenic

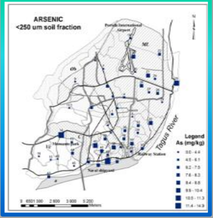

Figure 2: Total As concentrations in the Lisbon urban area

Total As concentrations in Northampton ranged from circa. 17 to 70 mg kg^{-1} (Figs. 6 and 10, with the lowest concentration greater than the highest As concentration observed in Lisbon (Fig. 2). Pb concentrations ranged from circa. 27 to 335 mg kg^{-1} (Figs 7 and 11).

Lead

Figure 3: Total Pb concentrations in the Lisbon urban area

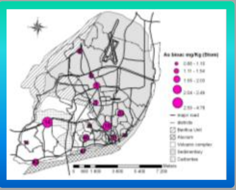

Figure 4: Bioaccessible As in selected samples in the Lisbon urban area

Figure 5: Bioaccessible Pb in selected samples in the Lisbon urban area

Low bioaccessible As concentrations (<5 mg kg^{-1}, Figure 4) were measured in 1 public park and 1 playground and bioaccessible Pb was measured in 2 small public gardens and 3 playgrounds (Figure 5) in Lisbon; previous studies indicate that these are man-made soils. In Northampton, bioaccessible As concentrations are all below the UK residential As SGV and are influenced by the background geology i.e. Inferior oolite (Figure 8). Bioaccessible Pb concentrations ranged between circa. 4 and 185 mg kg^{-1} and are thought to be derived from environmental inputs such as road dusts (Figure 9).

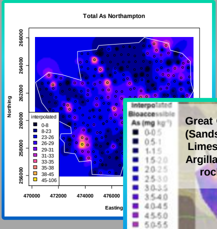

Figure 6: Total As in the Northampton urban area

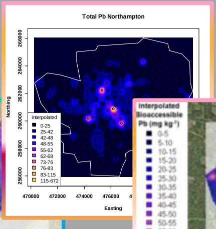

Figure 7: Total Pb in the Northampton urban area

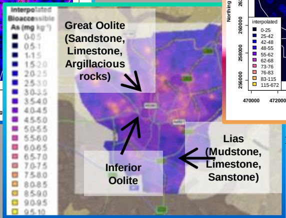

Figure 8: Bioaccessible As in the Northampton urban area

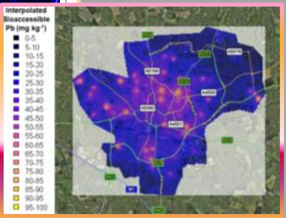

Figure 9: Bioaccessible Pb in the Northampton urban area

5. Conclusions

• This study is the 1st use of the UBM as a standardised bioaccessibility method for making valid comparisons between urban soils.

• For Pb, similar concentrations (within a factor of 2) were found in both urban centres, with bioaccessibility values of around 50% of the total Pb. It is thought that Pb from both study areas is derived from anthropogenic sources.

• Concentrations of As are significantly higher in Northampton and both total and bioaccessible As are geogenically controlled.

• Arsenic in Lisbon is lower in its total concentration, but there is a higher bioaccessible proportion compared to Northampton. It is thought that the source of the As in Lisbon may be derived from anthropogenic sources.

Figure 10 shows the total As content of Northampton soils to be higher by a factor of c. 5 than those in Lisbon (median values 34.3 and 6.7 mg kg^{-1} respectively), for the bioaccessible fraction there is a factor of c. 2 difference (median values of 2.88 and 1.48 mg kg^{-1} respectively). Figure 12 shows a regression line for Northampton with a slope of 0.06. The Lisbon data suggests that there could be a linear relationship with a much higher slope than in Northampton.

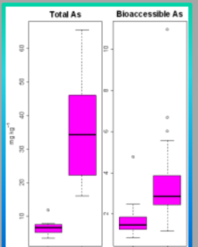

Figure 10: Box & whisker plot of the total and bioaccessible As content of the soils

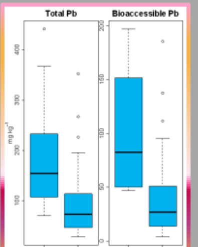

Figure 11: Box & whisker plot of the total and bioaccessible Pb content of the soils

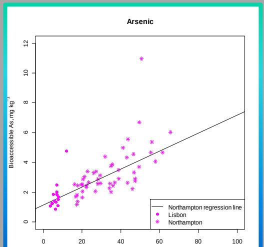

Figure 12: Relationship between total and bioaccessible As (regression line for Northampton only – not enough samples for Lisbon)

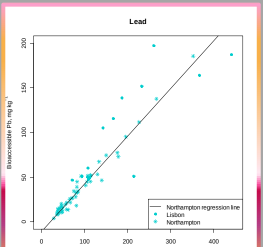

Figure 13: Relationship between total and bioaccessible Pb (regression line for Northampton only – not enough samples for Lisbon)

Figure 11 shows the total Pb content of the Northampton soils to be lower by a factor of c. 2 than those in Lisbon (median values 73.4 and 154.7 mg kg^{-1} respectively), for the bioaccessible fraction there is a factor of c. 3 difference (median values of 26.5 and 82.7 mg kg^{-1} respectively). Figure 13 shows a regression line for Northampton with a slope of 0.53. The Lisbon data suggests that there is a similar relationship to that in Northampton.