



Sources, Mobility and Bioaccessibility of Potentially Harmful Elements in UK Soils

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Sources of Potentially Harmful Elements in soils

- Natural geogenic sources
- Anthropogenic pollution
 - Point source (single identifiable source)
 - Diffuse pollution (dispersed over a wide area)













How do we measure PHE mobility?

- Geo availability PHE fractionation, mineralogy, sequential extraction, SEM, XAFS,XANES
- Bioaccessibility/bioavailability

 measure in-vivo or mimic inhalation, ingestion, dermal contact.





Exposure biomarkers

Biological markers (biomarkers) can be utilised to estimate levels of exposure to harmful substances.

Following exposure, soluble arsenic is adsorbed from the gastro-intestinal tract and distributed to all bodily systems in the blood, accumulating in many body parts.



Bioaccessibility : Unified BARGE Method (UBM)



The PBET method



Soils are extracted with gastric and intestine solutions in a water bath at 37[°] C



Soil samples are weighed into centrifuge tubes



Stomach and Intestine reagents are prepared according to the protocol



Samples are Centrifuged



Decanted samples are diluted and preserved in 0.1 M HNO₃



Samples are analysed by ICP-AES

Comparison of *in vivo* and *in vitro* data for NIST 2710 for the UBM inter-laboratory trial (2006/2007)





Article pubs.acs.org/est

In Vivo Validation of the Unified BARGE Method to Assess the Bioaccessibility of Arsenic, Antimony, Cadmium, and Lead in Soils

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Supporting Information



2012,<u>46</u>, pages 6252-6260

ABSTRACT: The relative bioavailability of arsenic, antimony, cadmium, and lead for the ingestion pathway was measured in 16 soils contaminated by either smelting or mining activities using a juvenile swine model. The soils contained 18 to 25 000 mg kg⁻¹ As, 18 to 60 000 mg kg⁻¹ Sb, 20 to 184 mg kg⁻¹ Cd, and 1460 to 40 214 mg kg⁻¹ Pb. The bioavailability in the soils was measured in kidney, liver, bone, and urine relative to soluble salts of the four elements. The variety of soil types, the total concentrations of the elements, and the range of bioavailabilities found were considered to be suitable for calibrating the in vitro Unified BARGE bioaccessibility method. The bioaccessibility test has been developed by the BioAccessibility Research Group of Europe (BARGE) and is known as the Unified BARGE Method (UBM). The study looked at four end points from the in vivo measurements and two compartments in the in vitro study ("stomach" and "stomach and intestine"). Using benchmark criteria for assessing the "fitness for purpose" of the UBM bioaccessibility data to act as an analogue for bioavailability in risk assessment, the study shows that the UBM met criteria on repeatability (median relative standard deviation value <10%) and the regression statistics (slope 0.8 to 1.2 and *r*-square > 0.6) for As, Cd, and Pb. The data suggest a small bias in the UBM relative bioaccessibility measurements of 3% and 5% respectively. Sb did not meet the criteria due to the small range of bioaccessibility values found in the samples.



Summary of the RBA vs RBAc regression statistics for the four end points for As. Black squares show data for the 'stomach' phase and white triangles for the 'stomach & intestine' phase. Error bars represent 95% confidence limits dotted lines show benchmark values.



Summary of the RBA vs RBAc regression statistics for the four end points for Cd. Black squares show data for the 'stomach' phase and white triangles for the 'stomach & intestine' phase. Error bars represent 95% confidence limits, dotted lines show benchmark values



Summary of the RBA vs RBAc regression statistics for the four end points for **Pb**. Black squares show data for the 'stomach' phase and white triangles for the 'stomach & intestine' phase. Error bars represent 95% confidence limits, dotted lines show benchmark values.



RBAc against RBA for (a) Pb and (b) Cd for the 'stomach' and 'stomach & intestine' phases for the kidney endpoint. Bold dashed dotted line is the line of equivalence, dashed lines are the 95% confidence intervals and the solid lines is the best line of fit



RBAc against RBA for (c) As and (d) Sb for the 'stomach' and 'stomach & intestine' phases for the urine end point. Bold dashed dotted line is the line of equivalence, dashed lines are the 95% confidence intervals and the solid line is the best line of fit.



Comparison of the Relative Bioaccessibility of As in the UK



Don't just rely on the bioaccessibility test

- Always use geochemical tests to back up your bioaccessibility results.
- Helps the risk assessor put the bioaccessibility value in context.
 - Bioaccessibility is no longer just a 'black box' or a black art in the eyes of the regulators and policy makers
- Allows decisions to be made regarding current and future land use.
- Gives the regulator added confidence in the risk assessment.



How are PHE distributed in the soil components?

CISED Test Chemometric Identification of Substrates and Element Distributions

•Separate aliquots of aqua regia of increasing concentration.

•Passed through the sample under centrifugal force.

•Determination by ICP-AES.

•Chemometric data processing .

•Identification of physico-chemical hosts and the metal distributions within the sample under test.



Example of CISED



Northampton

- Large Market town in central England
 - Population of c. 200,000
 - Busy Road and Rail links
- Primary industrial activities were shoe making and other leather industries
 - Now a hub for finance and distribution industries
- BGS surveyed the area as part of the G-BASE programme
- Ironstone soils, naturally elevated in arsenic
- 45% of the soils have As concentrations above the residential SGV of 32 mg mg⁻¹





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Measurement of the diffuse reflectance spectra of soils using a mug light.





MLR model of bioaccessible As using NIR spectral components and Major element compositions

Coefficient	Value	Standard Error	P value	% Variance
				explained
Intercept	-0.56	1.22	<0.64	-
рН	0.41	0.12	< 0.05	22.6
As	0.05	0.01	< 0.05	37.6
Mg	0.00	0.00	< 0.05	4.9
SC1	-21.1	3.6	<0.05	2.5
SC2	16.2	2.5	< 0.05	16.5

R square = 0.84





CV predictions the Total Element and NIR Model



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A Structured Approach

