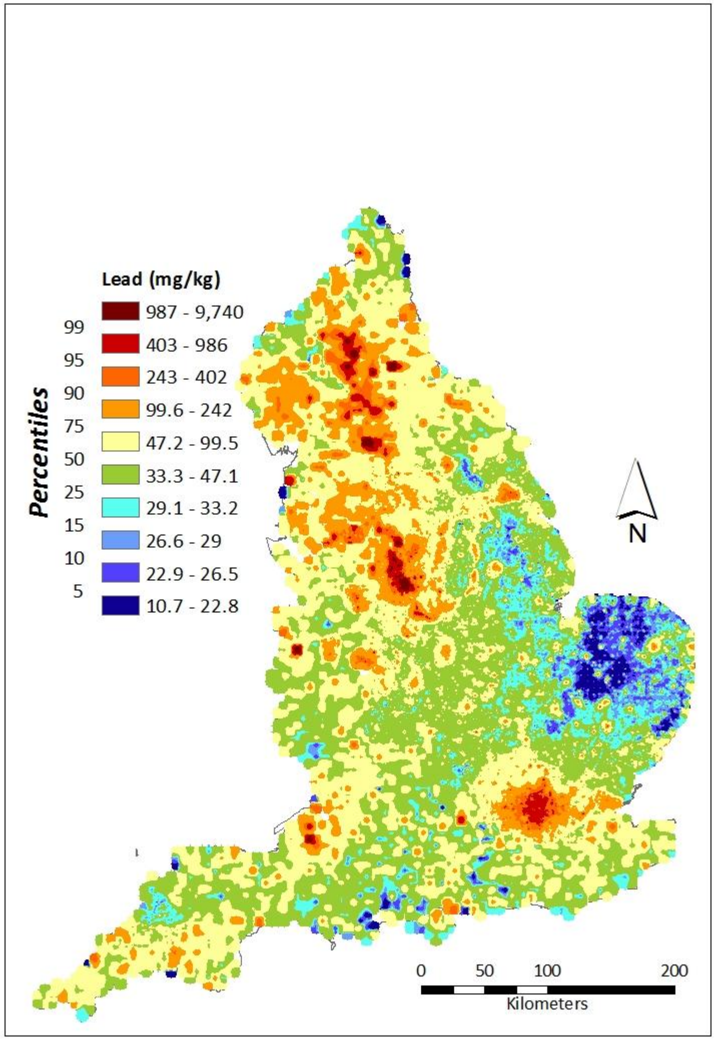
British Geological Survey
NATURAL ENVIRONMENT RESEARCH COUNCIL

Measurement of the Bioavailability of Potentially Harmful Substances in soil - The "How" and the "Why"

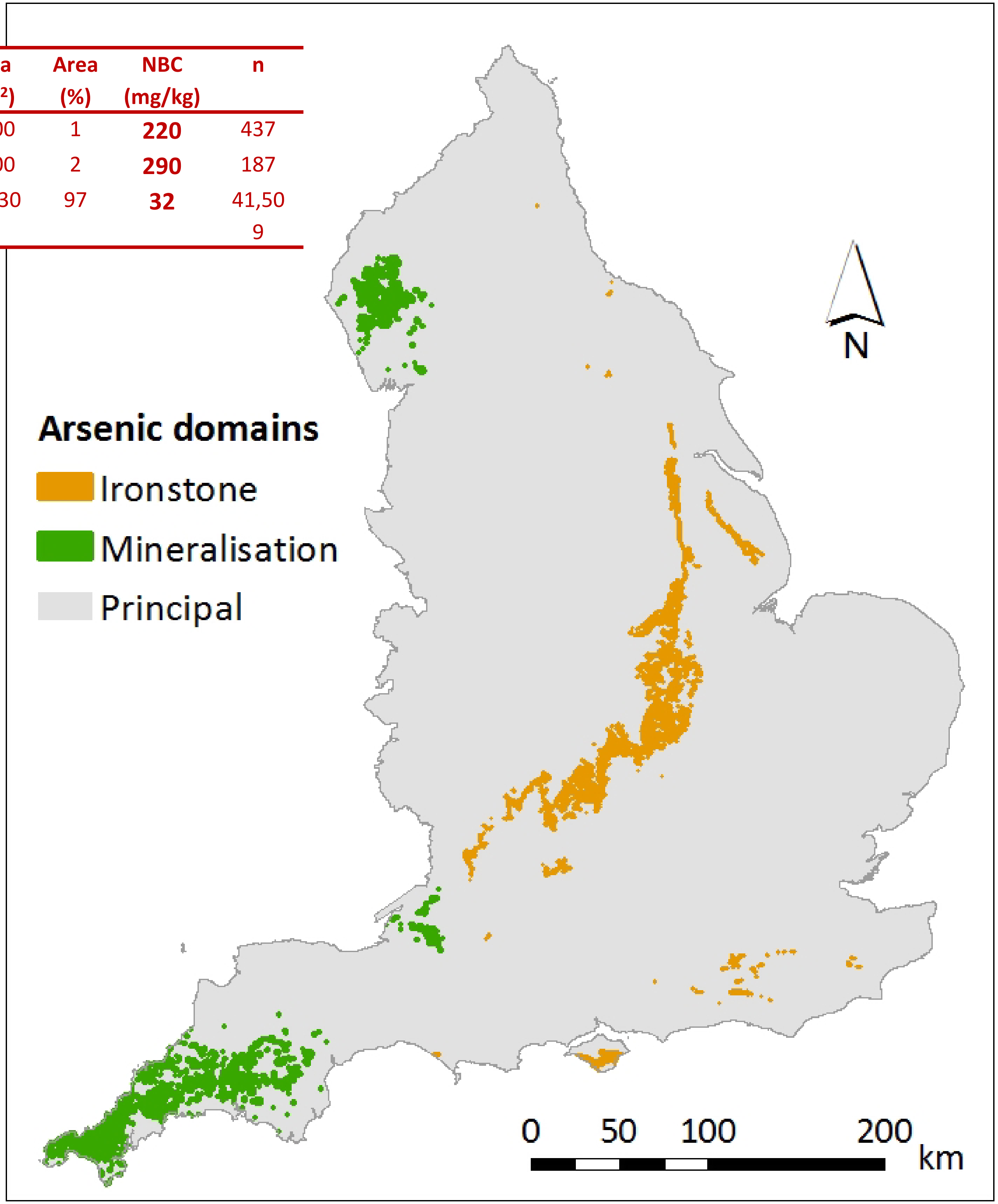
Mark Cave

Sources of Potentially Harmful Elements in soils

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



Domain	Area (km²)	Area (%)	NBC (mg/kg)	n
Ironstone	1,300	1	**220**	437
Mineralisation	2,300	2	**290**	187
Principal	129,300	97	**32**	41,509



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.

Short-term (recent exposure)

Long-term (past exposure)

Blood

Urine

Toenails

Fingernails

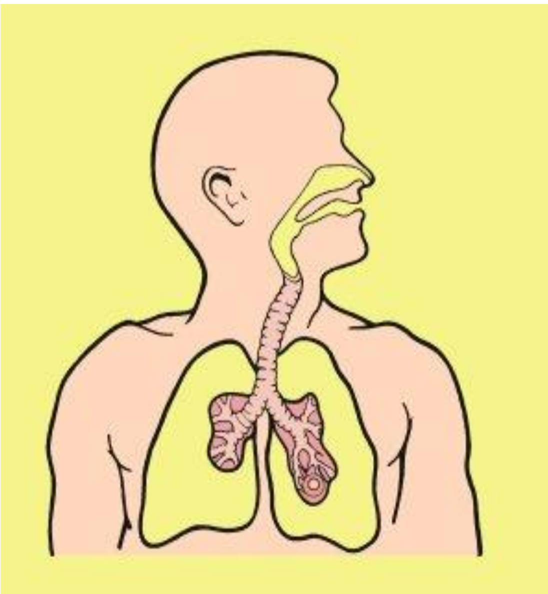
Hair



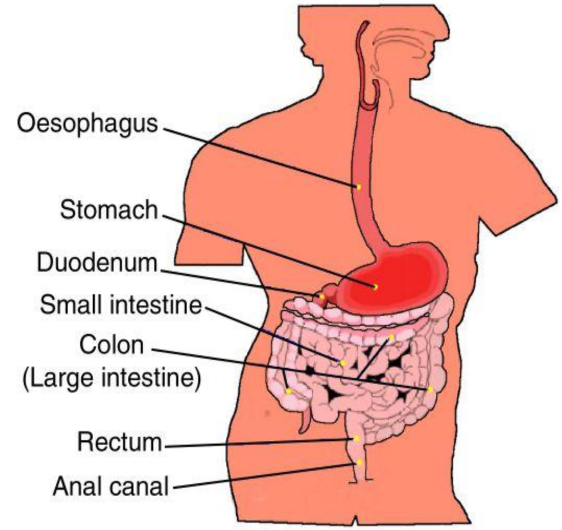


Exposure Pathways

Inhalation

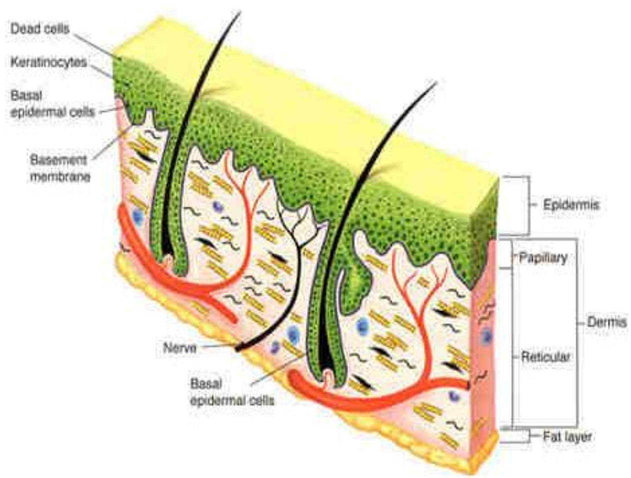


Ingestion

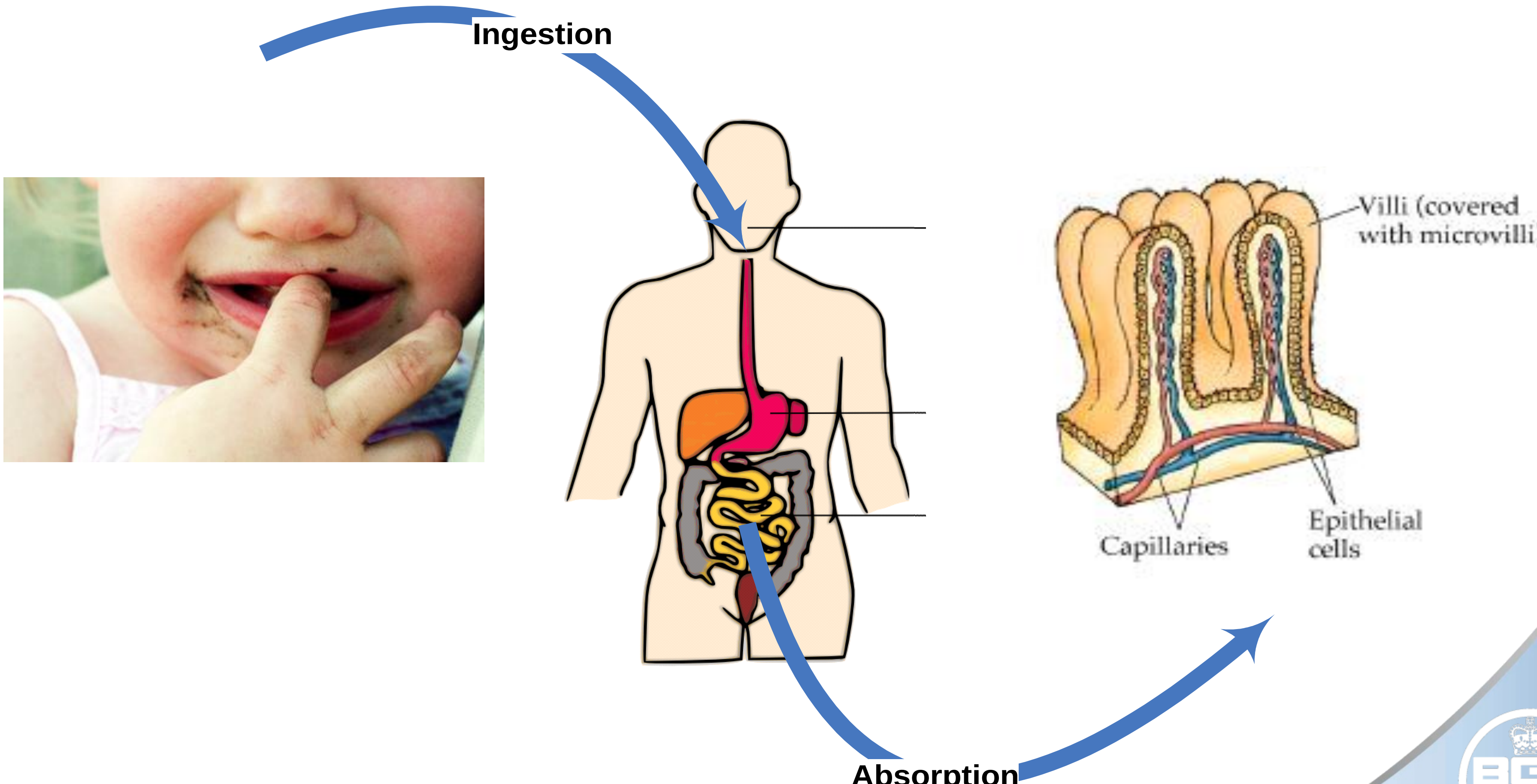


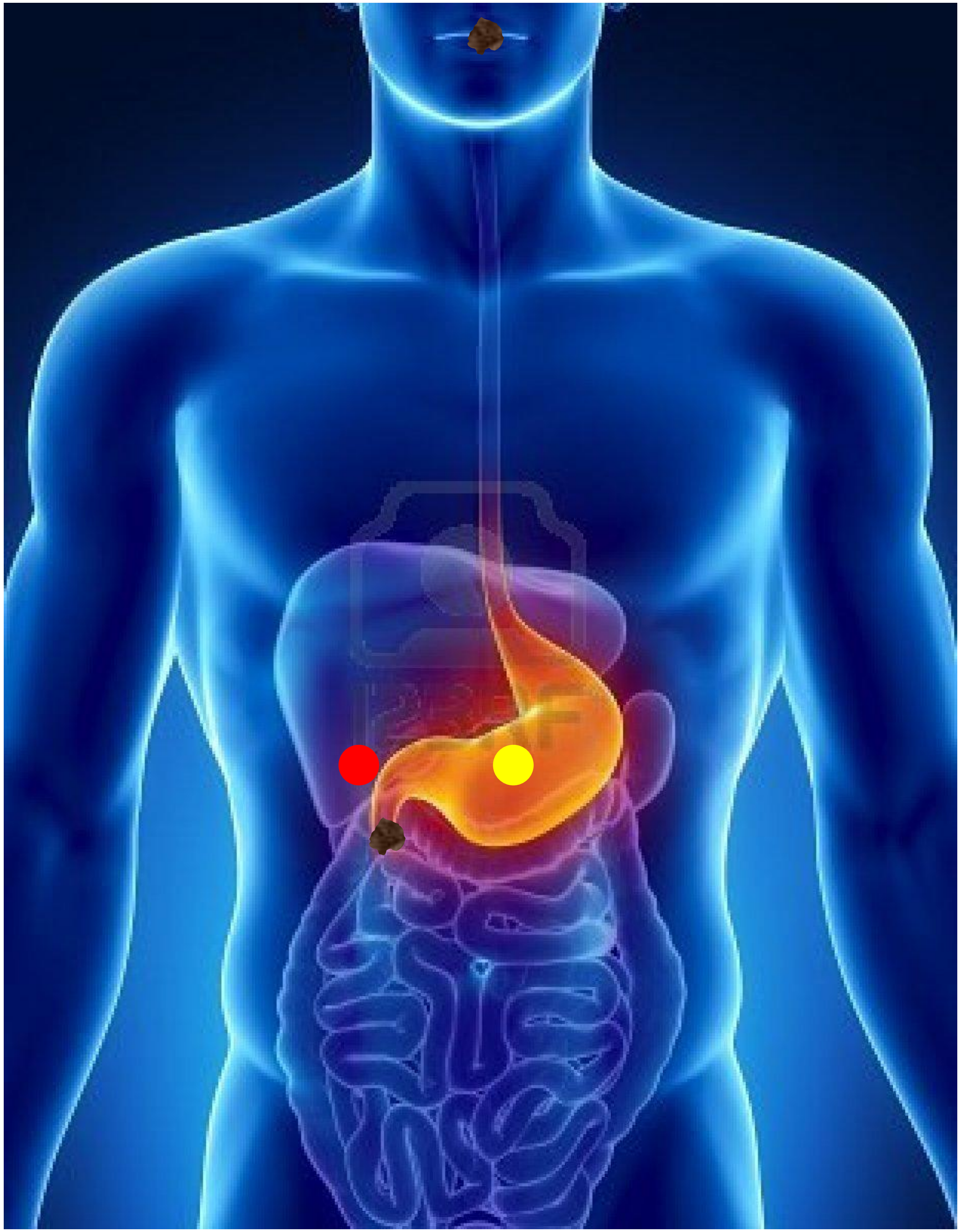
The Gastro-intestinal (Digestive) Tract

Dermal contact



What are we trying to achieve?





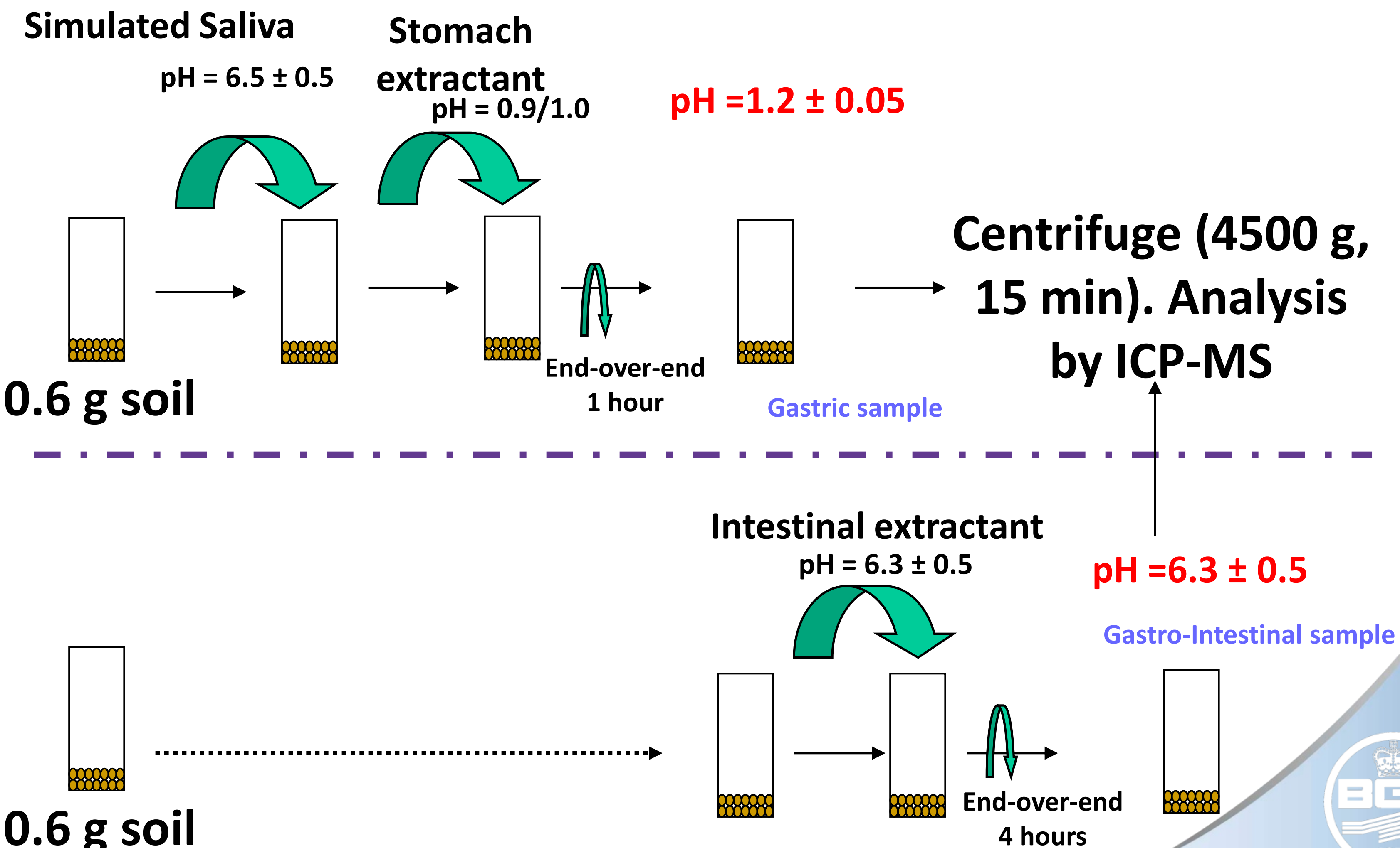
Metals associated with soil can be accidentally ingested

Bioaccessibility: The fraction of contaminant that is dissolved in the gastro-intestinal tract and available for uptake

Bioavailability: The fraction of the bioaccessible fraction that crosses the cell wall

Non bioaccessible metals are excreted with undigested soil

Practicalities of the UBM (Version 2)



The UBM method

Stomach and Intestine reagents are prepared according to the protocol

Soil samples are weighed into centrifuge tubes

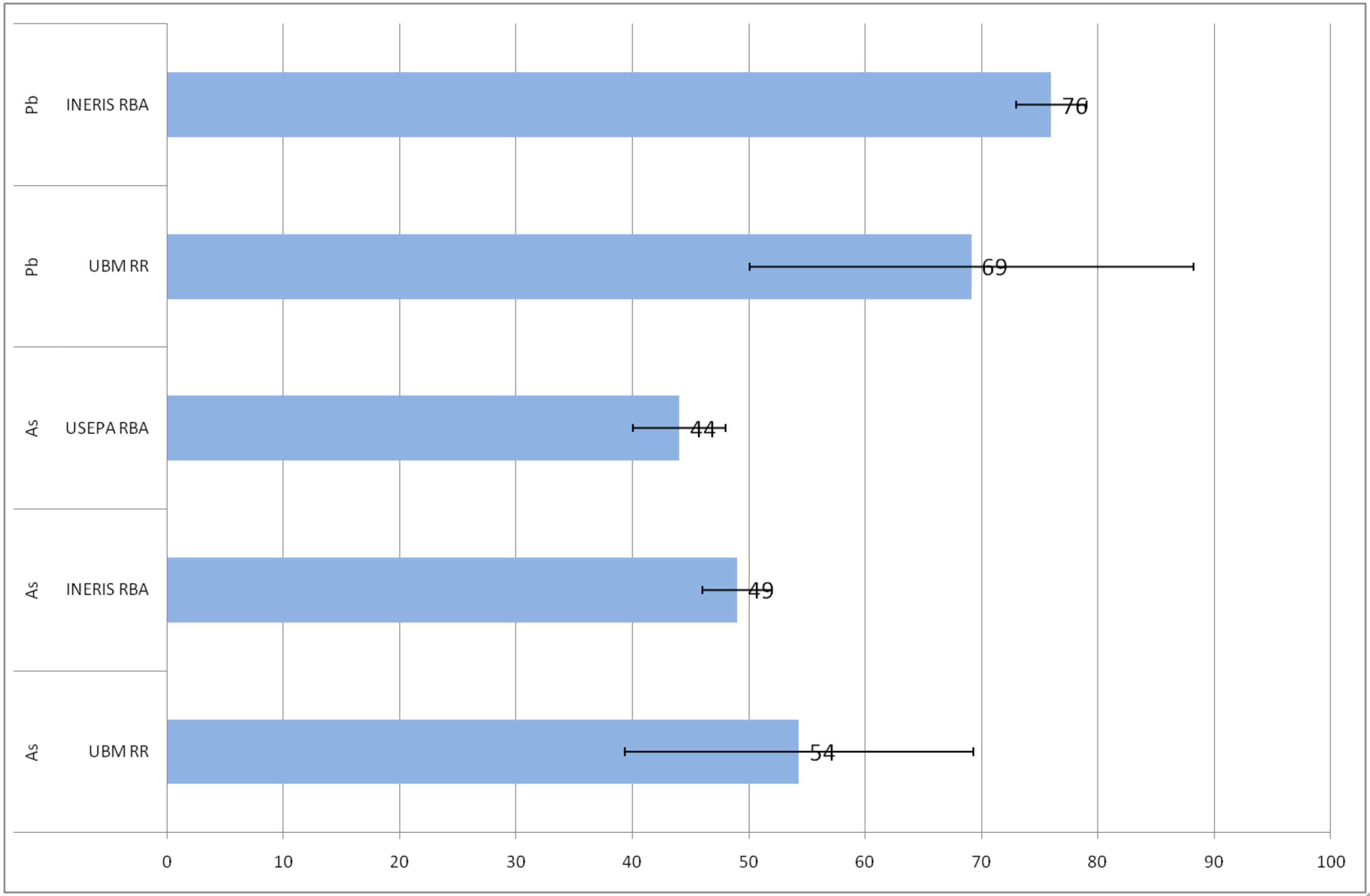
Soils are extracted with gastric and intestine solutions in a water bath at 37^0 C

Samples are Centrifuged

Decanted samples are diluted and preserved in 0.1 M HNO_3

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)



Environmental Science & Technology
Article
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In Vivo Validation of the Unified BARGE Method to Assess the Bioaccessibility of Arsenic, Antimony, Cadmium, and Lead in Soils

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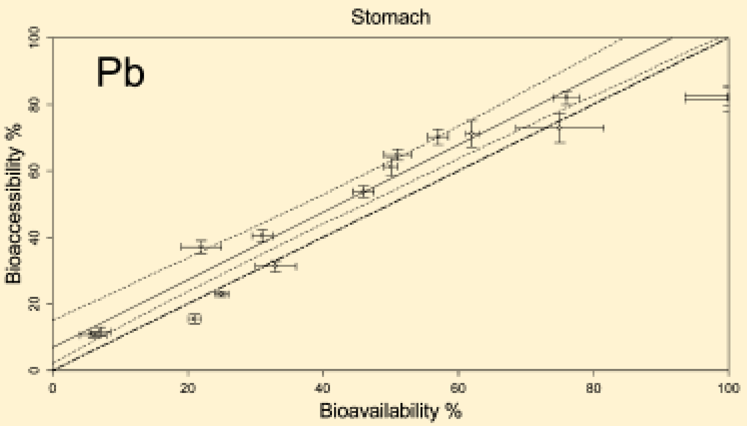
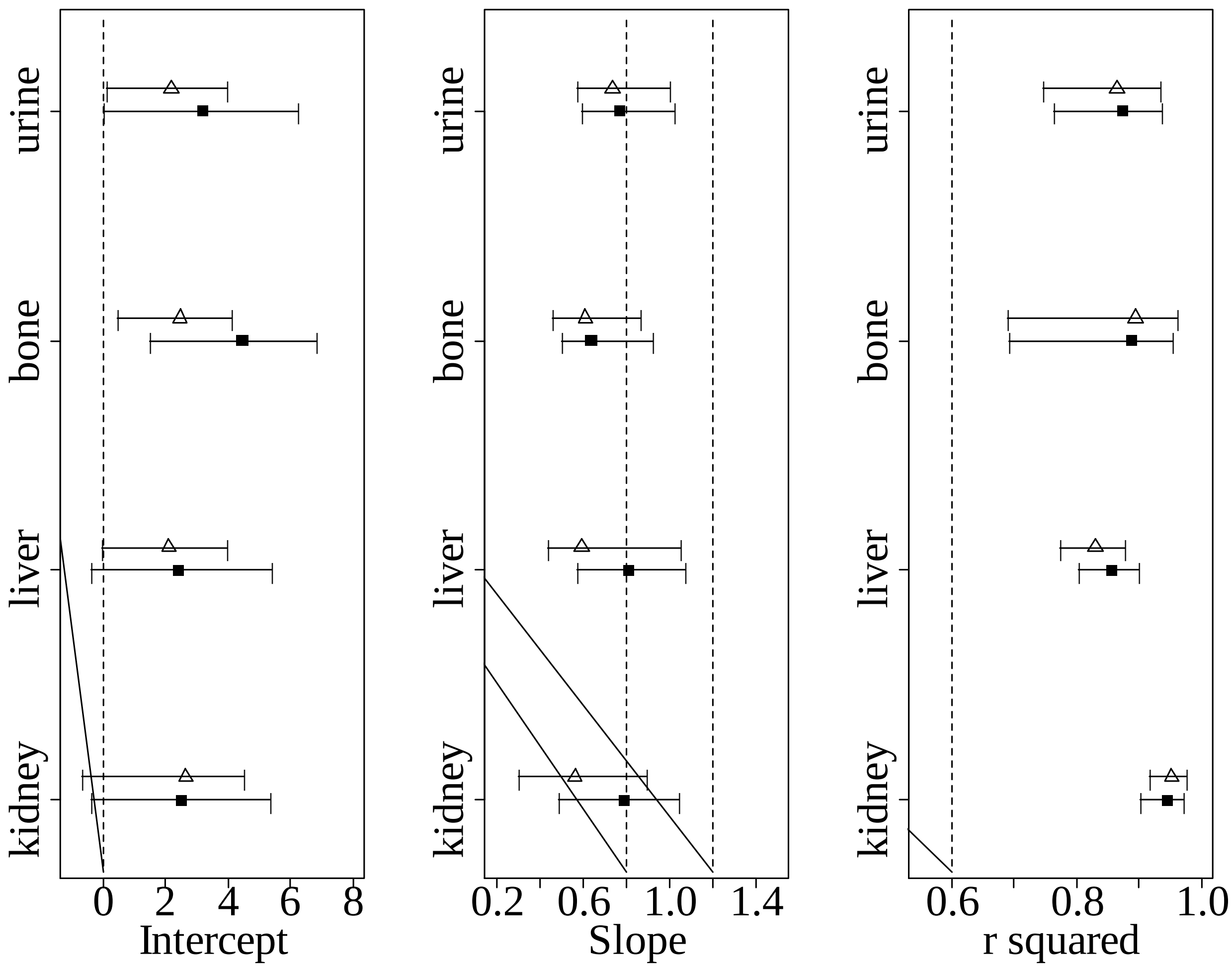
Supporting Information

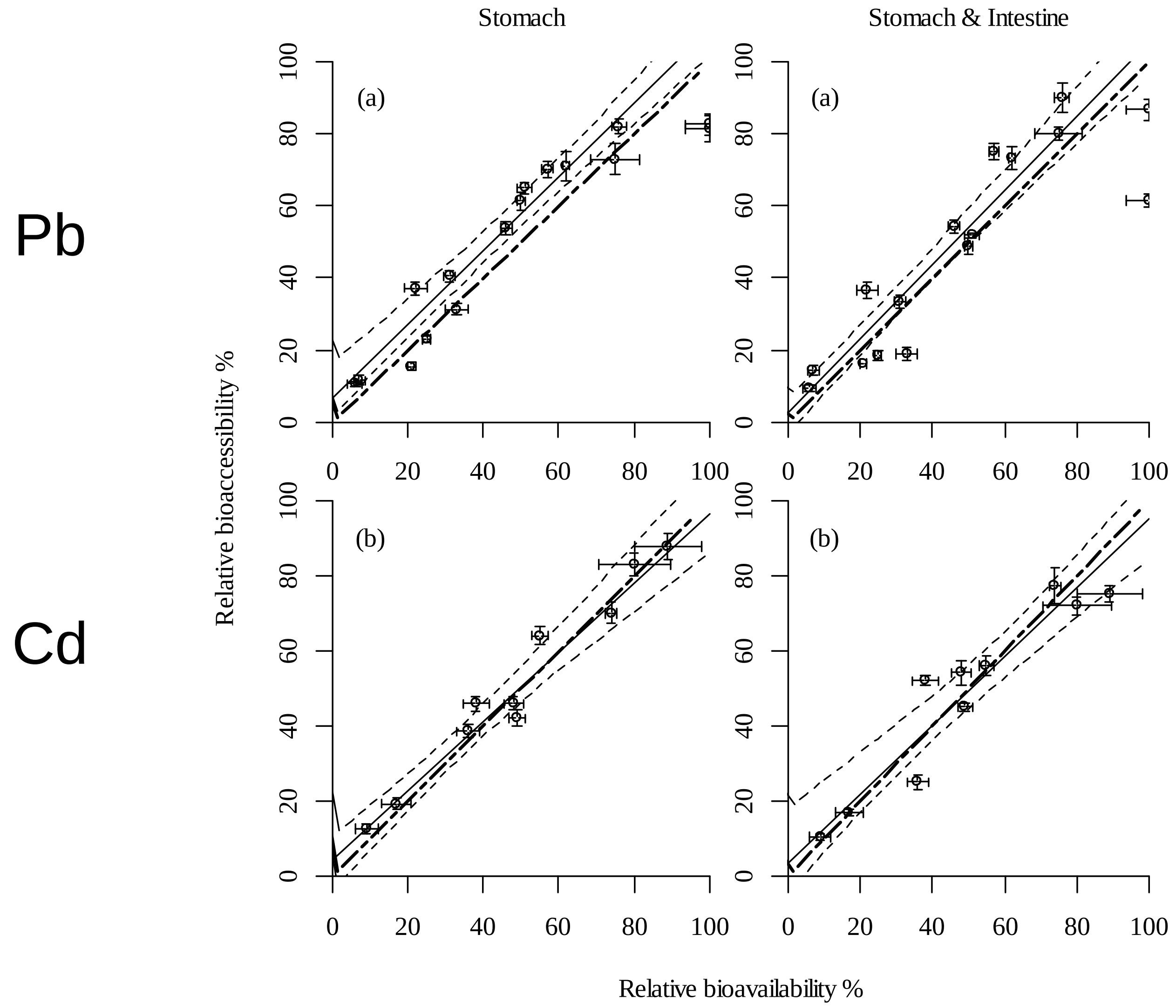


ABSTRACT: The relative bioavailability of arsenic, antimony, cadmium, and lead for the ingestion pathway was measured in 16 soils contaminated by either smelting or mining activities using a juvenile swine model. The soils contained 18 to 25 000 mg kg^{-1} As, 18 to 60000 mg kg^{-1} Sb, 20 to 184 mg 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 of As and Pb compared to the relative bioavailability measurements of 3% and 5% respectively. Sb did not meet the criteria due to the small range of bioaccessibility values found in the samples.

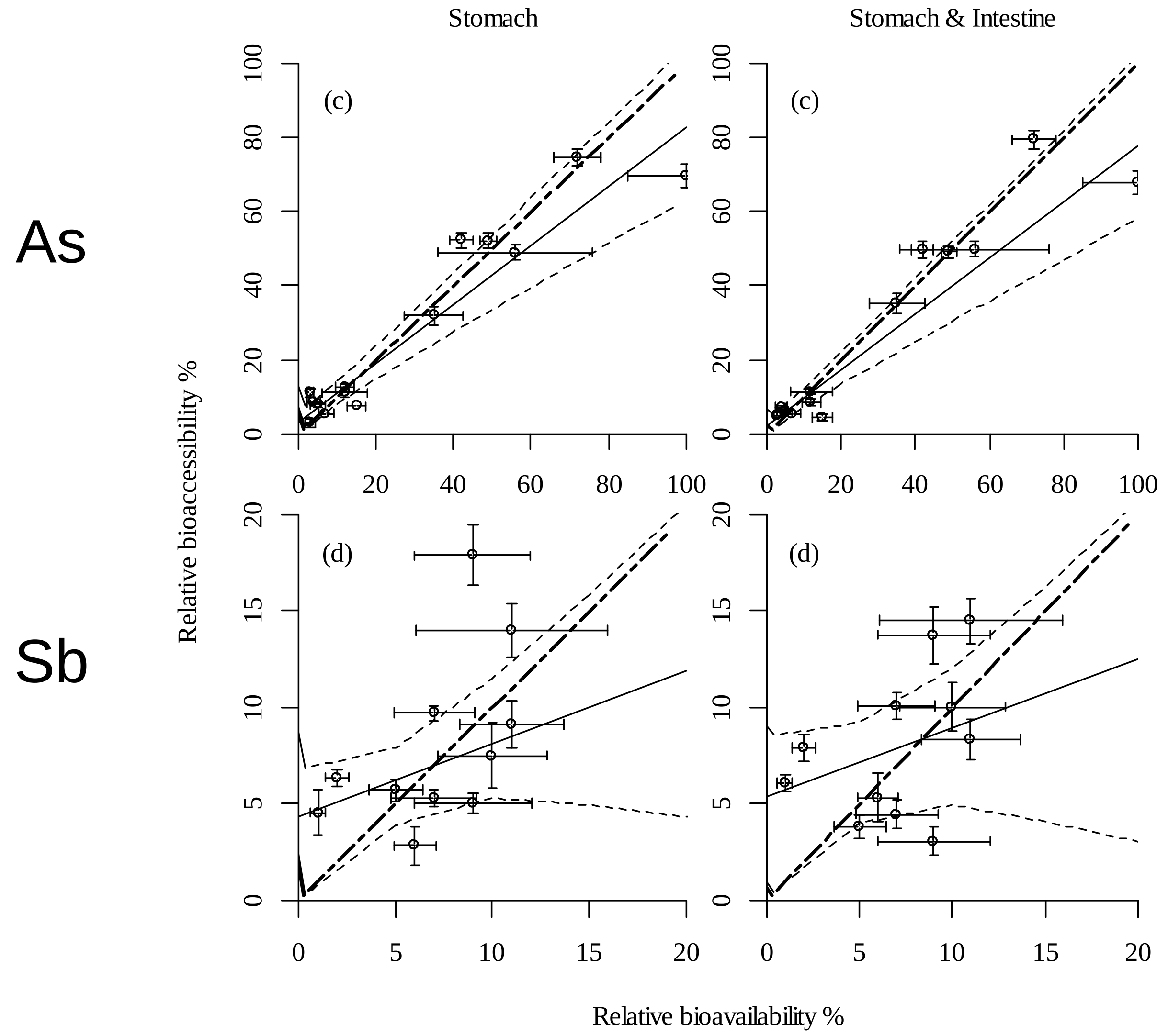
As



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.



correlation plots for 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



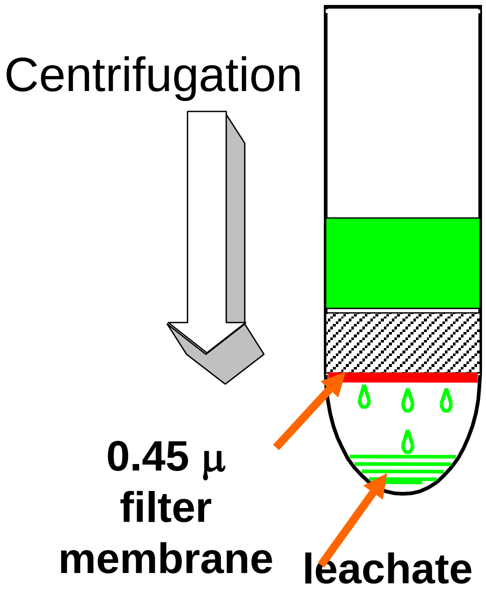
correlation plots for RBAc against RBA for (c) As and (d) Sb for the 'stomach' and 'stomach & intestine' phases for the urine end point. Bold dashed dotted line is the line of equivalence, dashed lines are the 95% confidence intervals and the solid line is the best line of fit.

How are PHE distributed in the soil components?

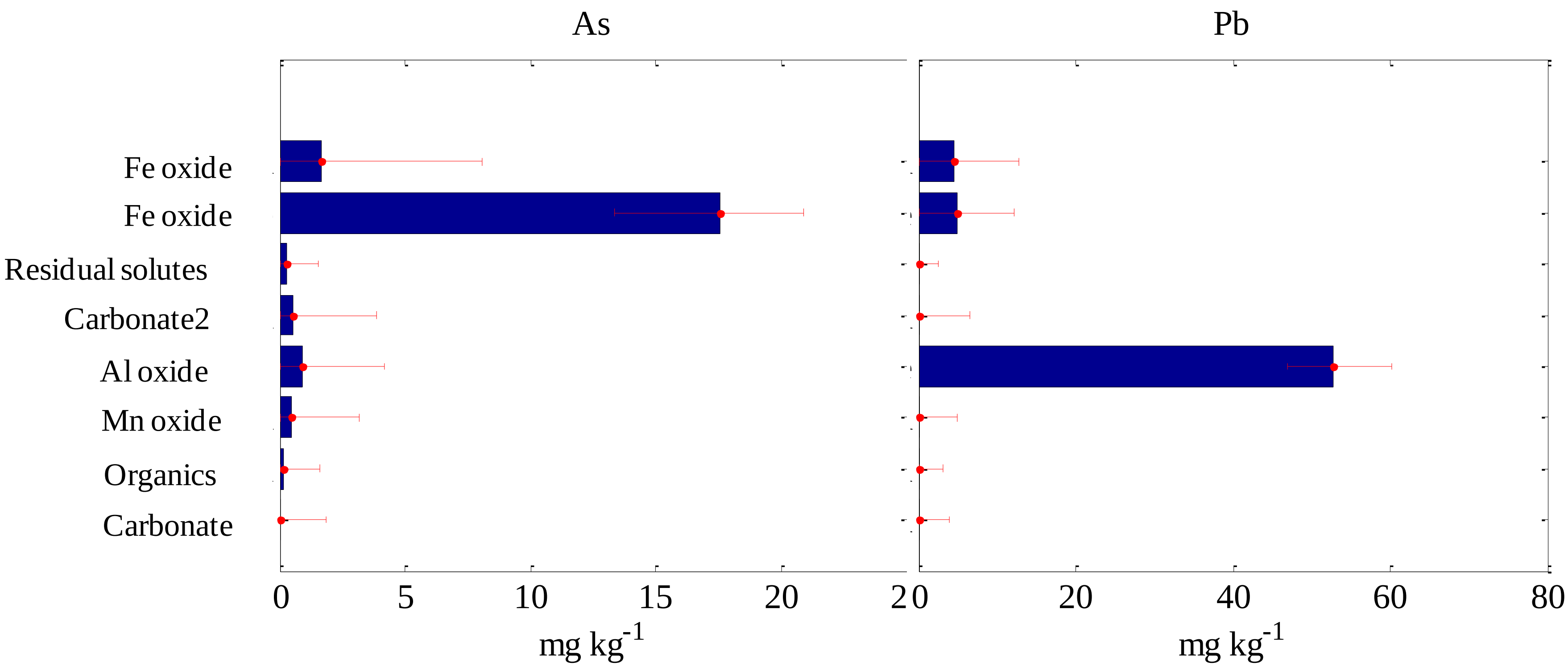
CISED Test

Chemometric Identification of Substrates and Element Distributions

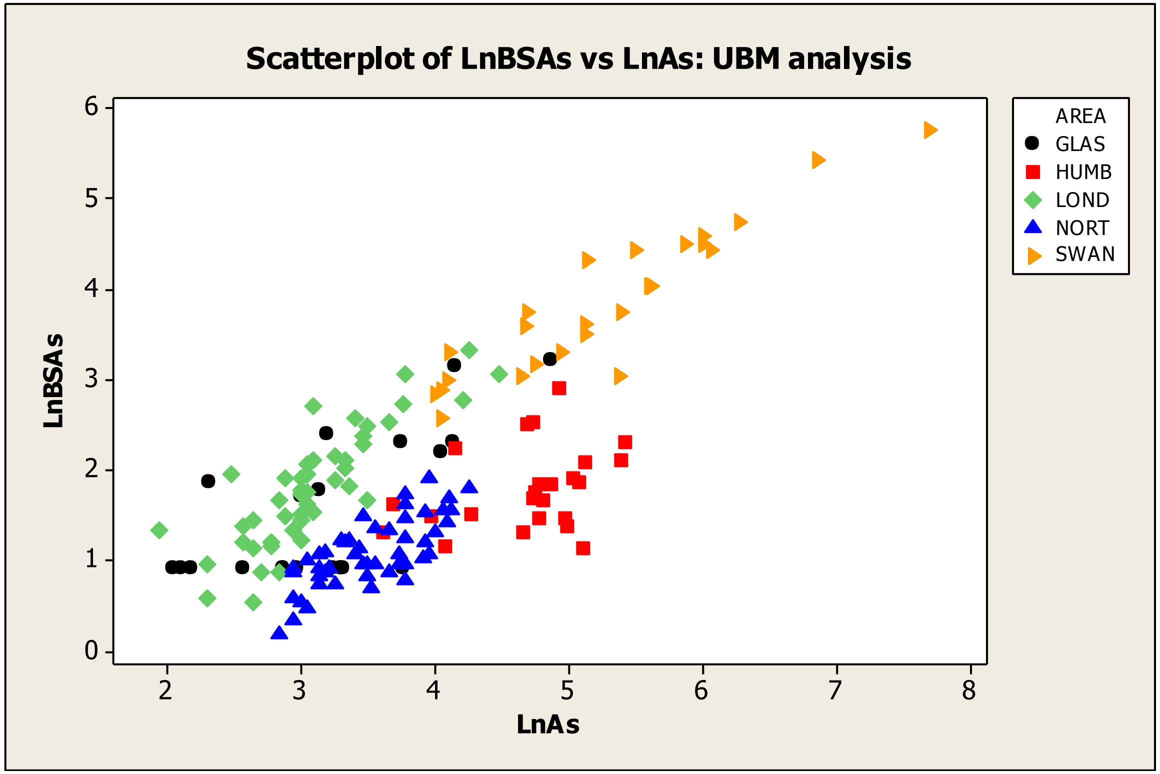
- Separate aliquots of aqua regia of increasing concentration.
- Passed through the sample under centrifugal force.
- Determination by ICP-AES.
- Chemometric data processing .
- Identification of physico-chemical hosts and the metal distributions within the sample under test.

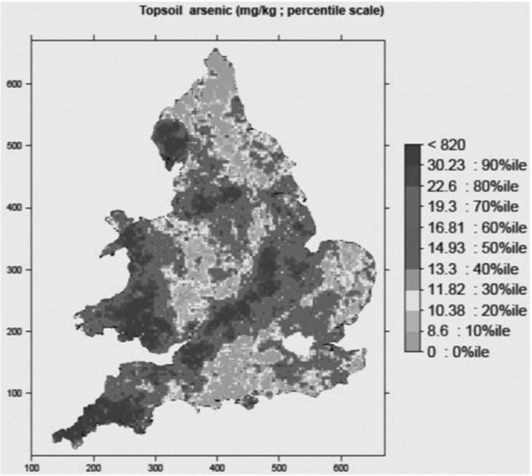


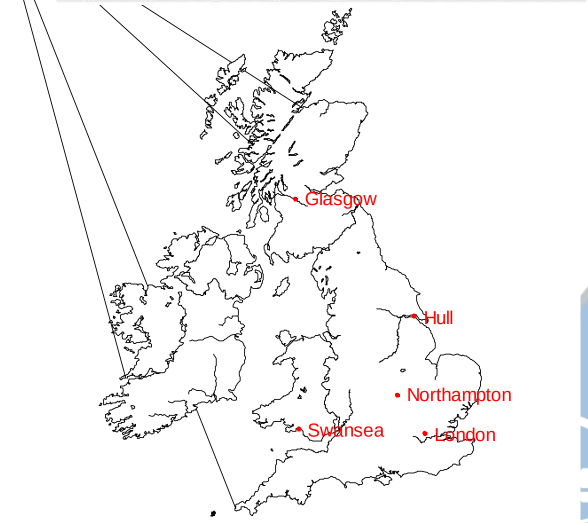
Example output of CISED



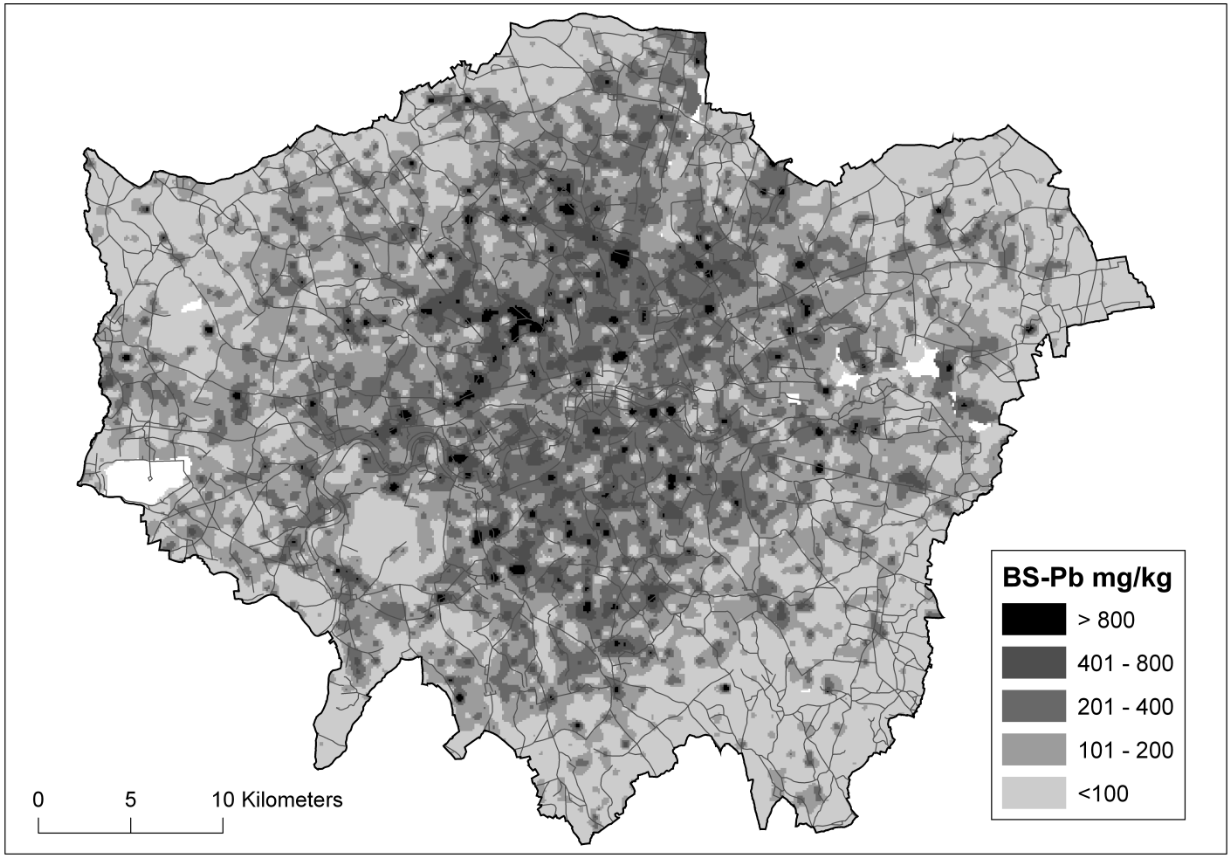
Comparison of the Relative Bioaccessibility of As in the UK







Bioaccessible Pb in London Soil

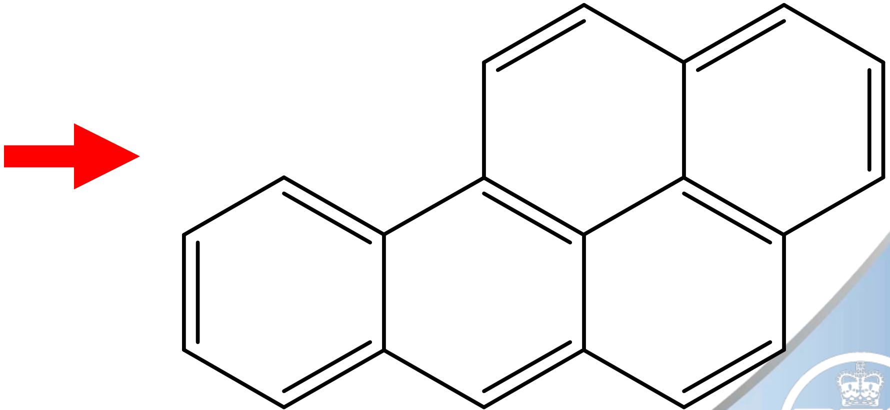


Appleton J, Cave M, Wragg J. Modelling lead bioaccessibility in urban topsoils based on data from Glasgow, London, Northampton and Swansea, UK. Environmental Pollution 2012.

Organics

Added Difficulties for Organics

- Addition of food
- Glassware
- Analysis (aqueous/organic phases)
- Metabolites



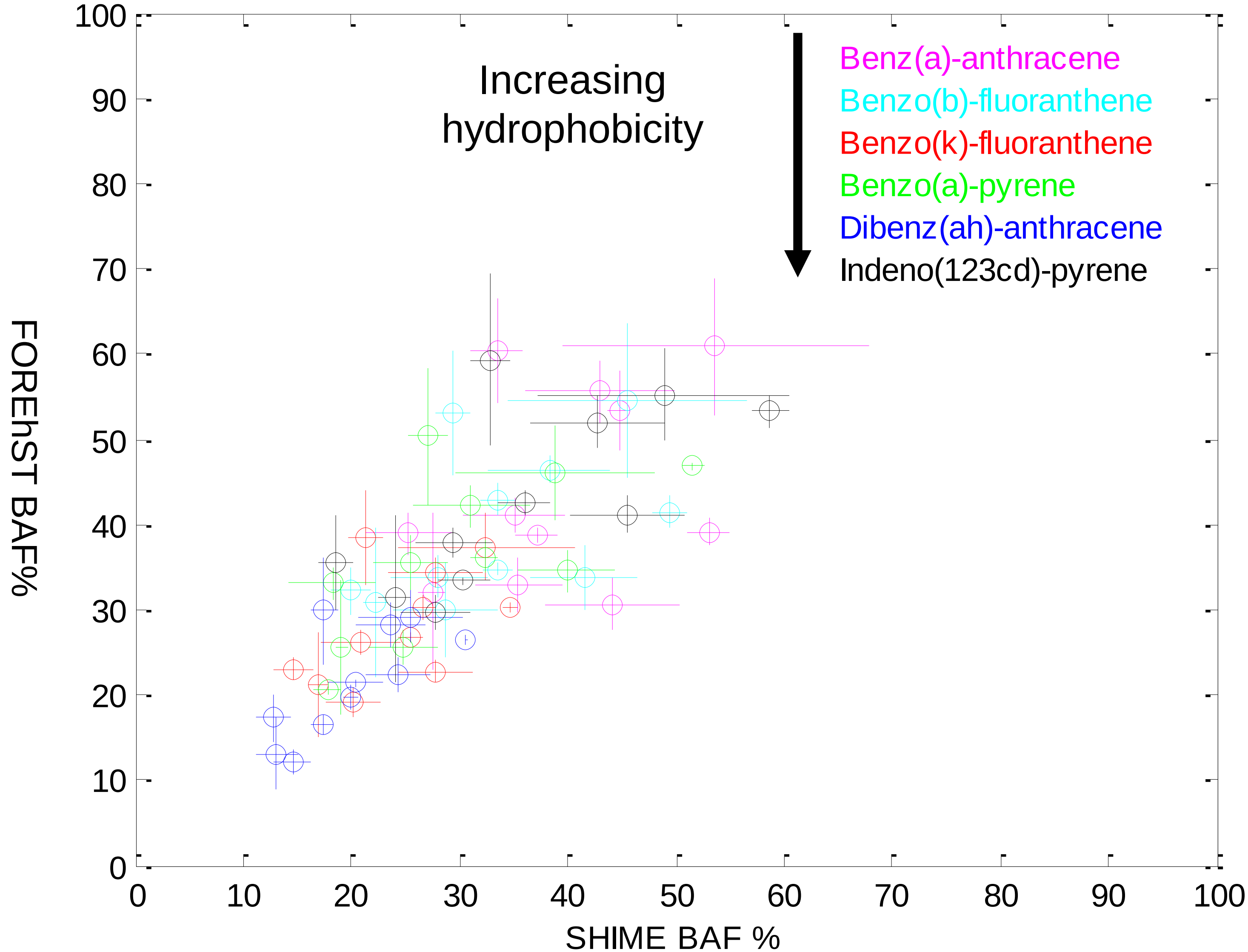
FOREhST

Fed ORganic Extraction human Simulation Test

- BGS has modified the RIVM fed state model and combined this with an optimised method for PAH analysis.
- We have developed a robust procedure for PAH in the extraction matrix that could be used by a testing laboratory.

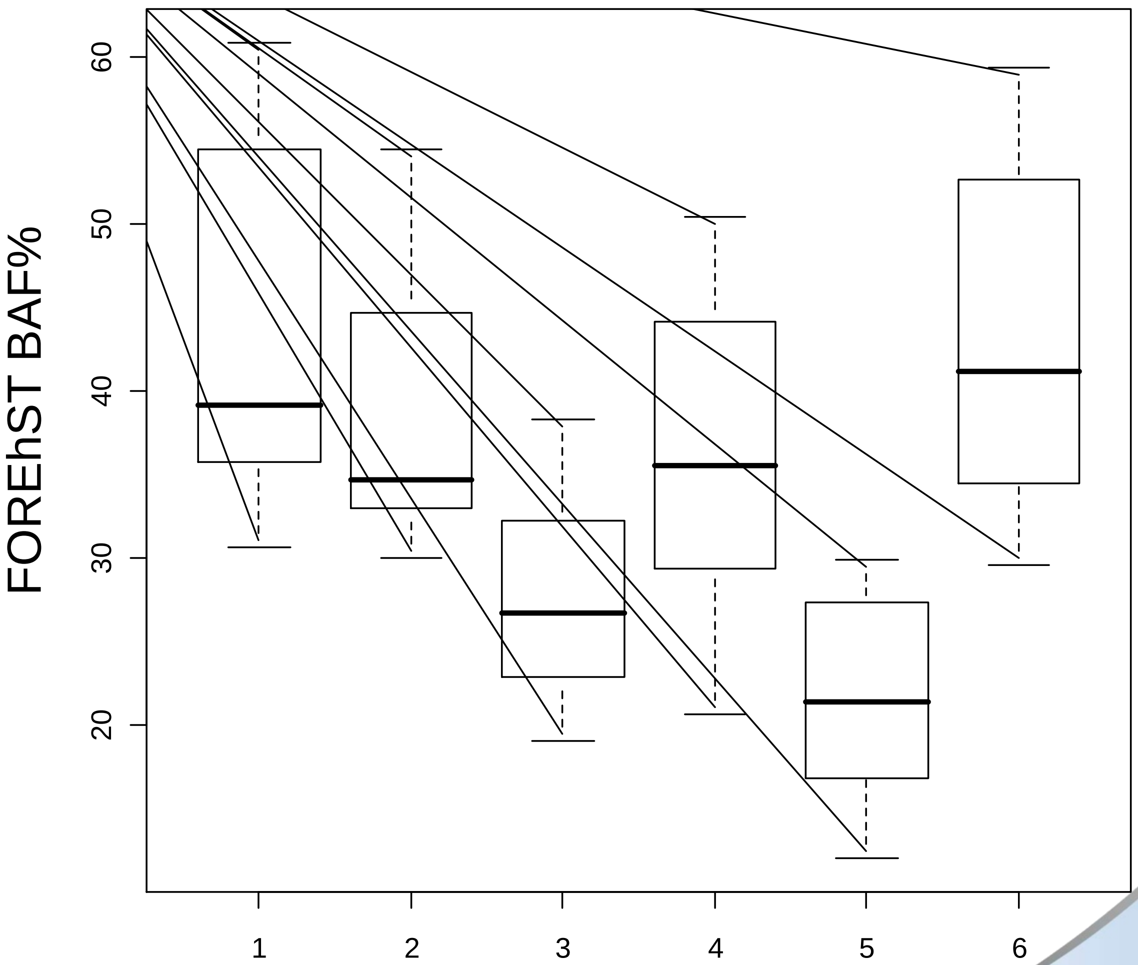
FOREhST

- Simulated the nutritional status of a 2-3 yr old
- Only intestine phase sampled
- PAH separation and analysis by HPLC-Fluorescence detection
- PAHs investigated
  - Benzo(a)anthracene;
    Benzo(b and k)fluoranthene;
    Benzo(a)pyrene;
    Dibenzo(ah)anthracene;
    Indeno(123cd)pyrene.



Increasing hydrophobicity
Benz(a)-anthracene
Benzo(b)-fluoranthene
Benzo(k)-fluoranthene
Benzo(a)-pyrene
Dibenz(ah)-anthracene
Indeno(123cd)-pyrene
FOREhST BAF%
SHIME BAF %
0
10
20
30
40
50
60
70
80
90
100

PAH name	MW	log Kow	PAH No
Benz(a)-anthracene	228	5.61	1
Benzo(b)-fluoranthene	252	6.04	2
Benzo(k)-fluoranthene	252	6.06	3
Benzo(a)-pyrene	252	6.06	4
Dibenz(ah)-anthracene	278	6.5	5
Indeno(123cd)-pyrene	276	6.58	6

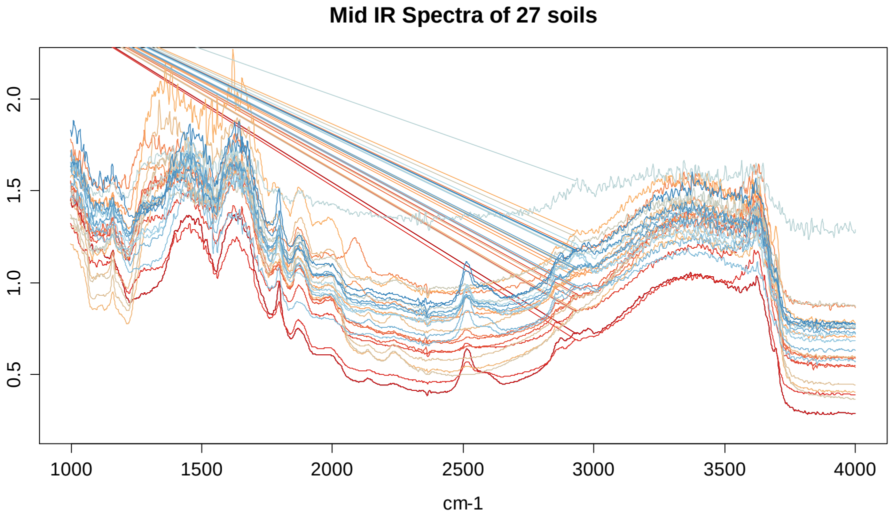


Follow up Study

- 26 soil samples from 3 gas works sites of varying ages
- 8 samples from a small horizontal gasworks that was closed in 1950
- 5 samples from an uncontaminated urban garden,
- 4 samples from a small gasworks which was closed 1900 and
- 9 samples from an early small gasworks closed in 1860
- The samples were freeze dried and sieved to <250 µm. Total PAH and FOREhST extractions
- NIR and Mid-IR spectra of the soils

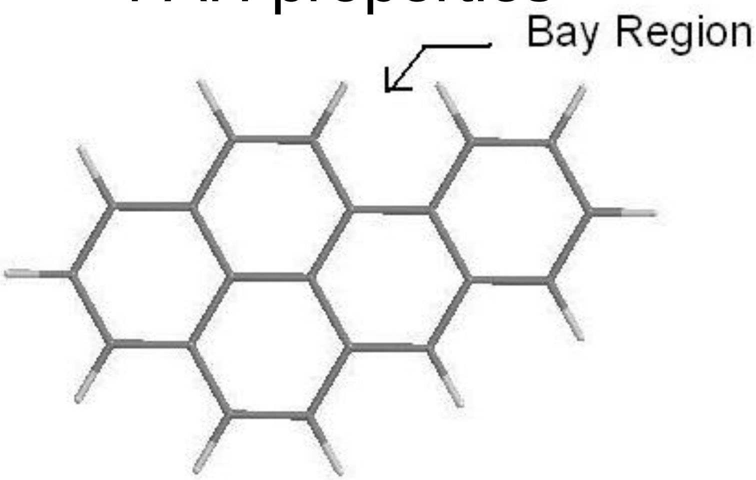
PAHs studied

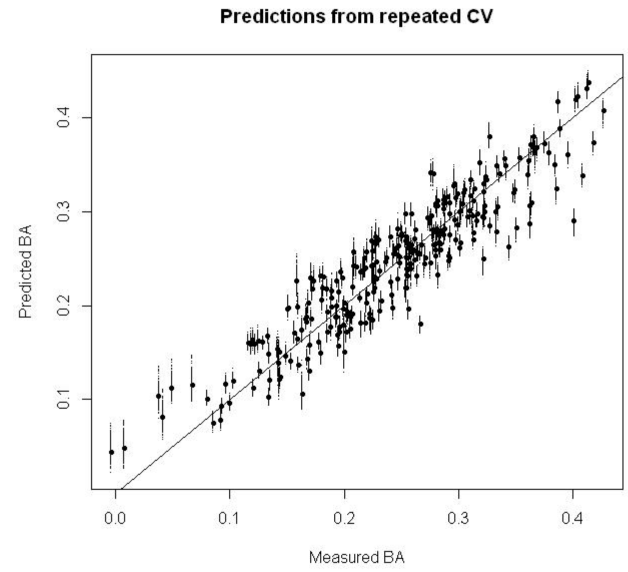
N	naphthalene
Ay	acenaphthylene
Ae	acenaphthene
F	fluorene
Ph	phenanthrene
An	anthracene
Fl	fluoranthene
Py	pyrene
BaA	benz[a]anthracene
Ch	chrysene
BbF	benzo[b]fluoranthene
BkF	benzo[k]fluoranthene
BjF	benzo[j]fluoranthene
BeP	benzo[e]pyrene
BaP	benzo[a]pyrene
Per	perylene
IdPy	indeno[1,2,3-cd]pyrene
DBA	dibenz[a,h]anthracene
BPer	benzo[ghi]perylene



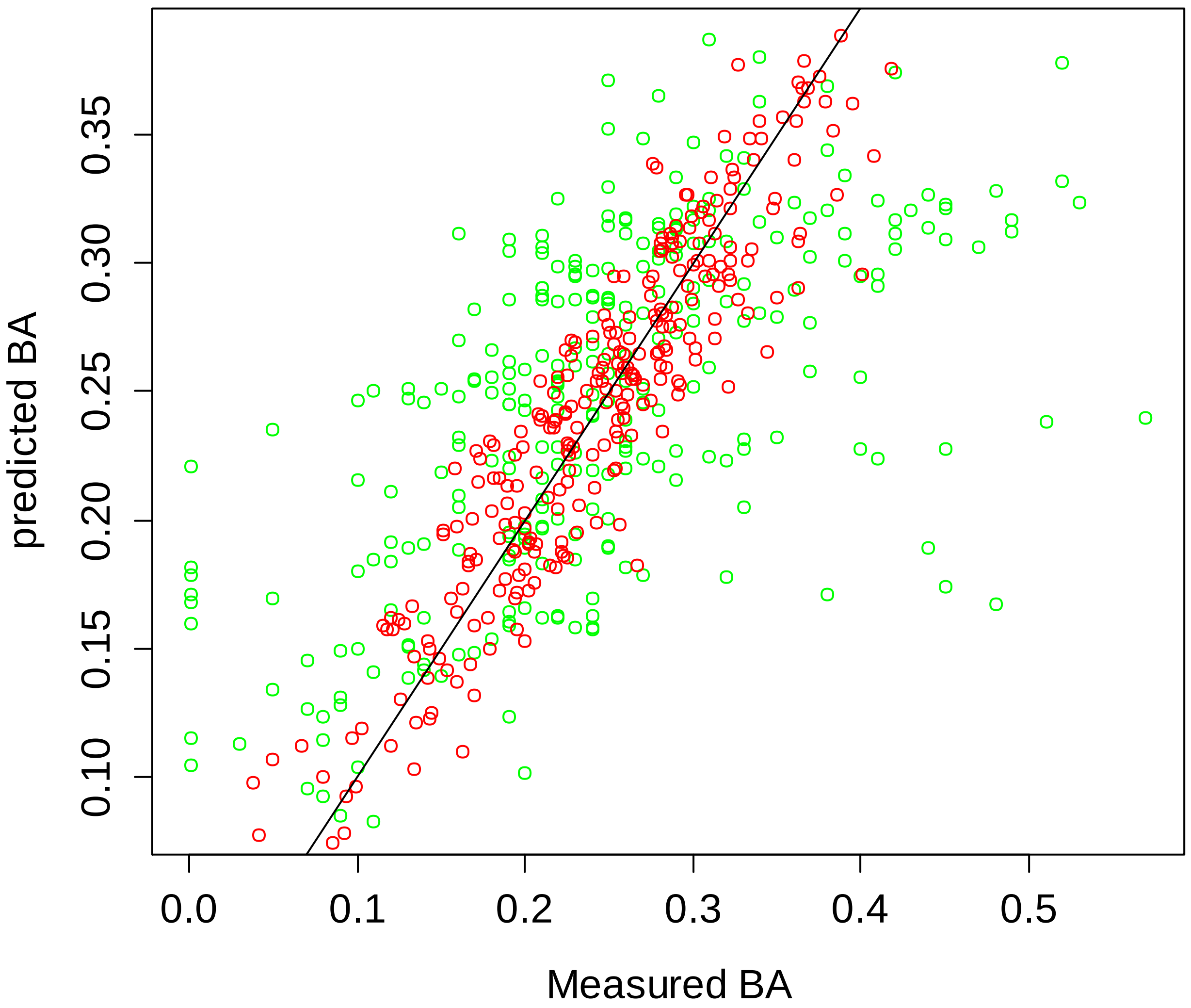
Model of PAH Bioaccessibility

PAH properties

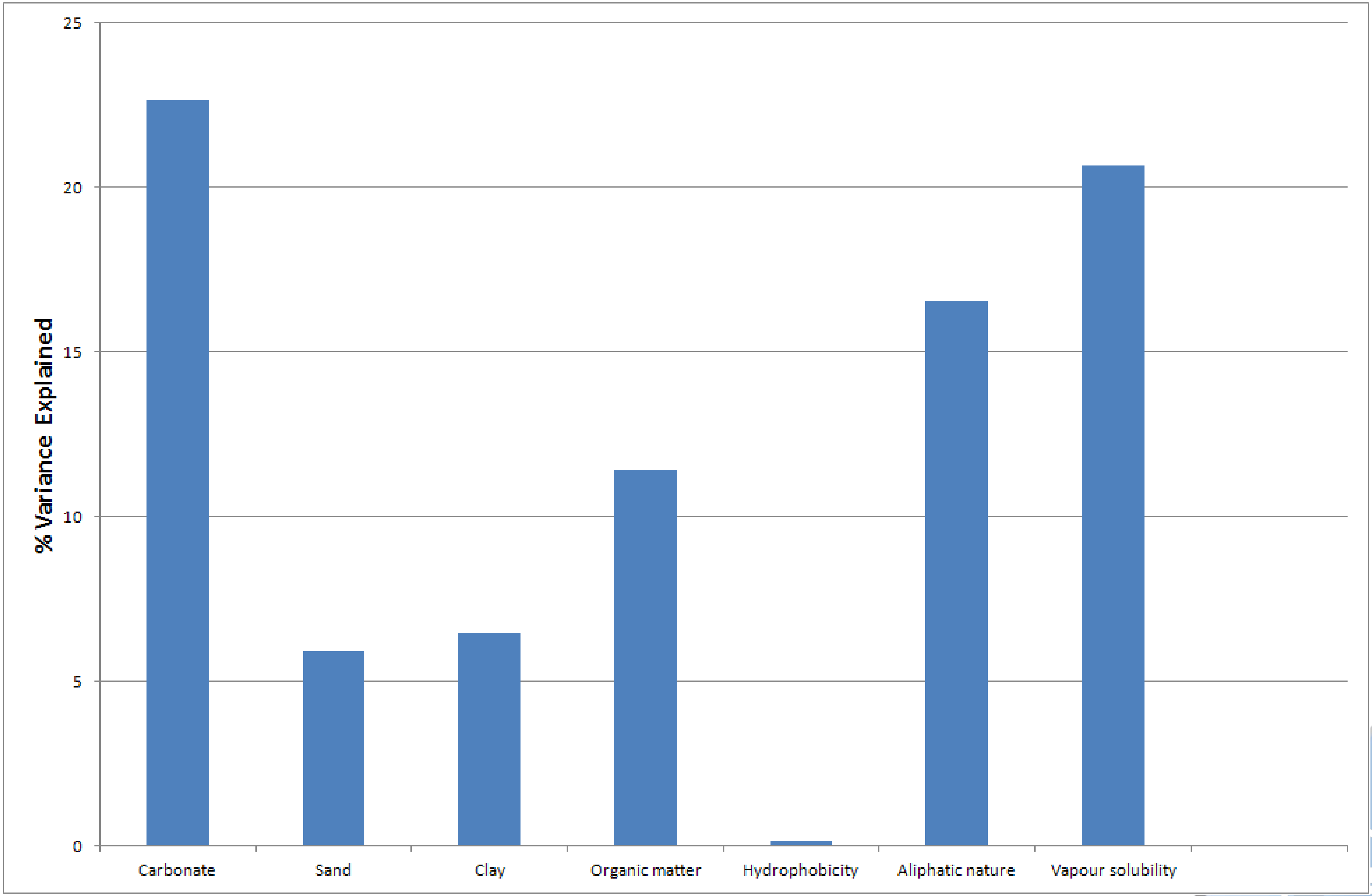




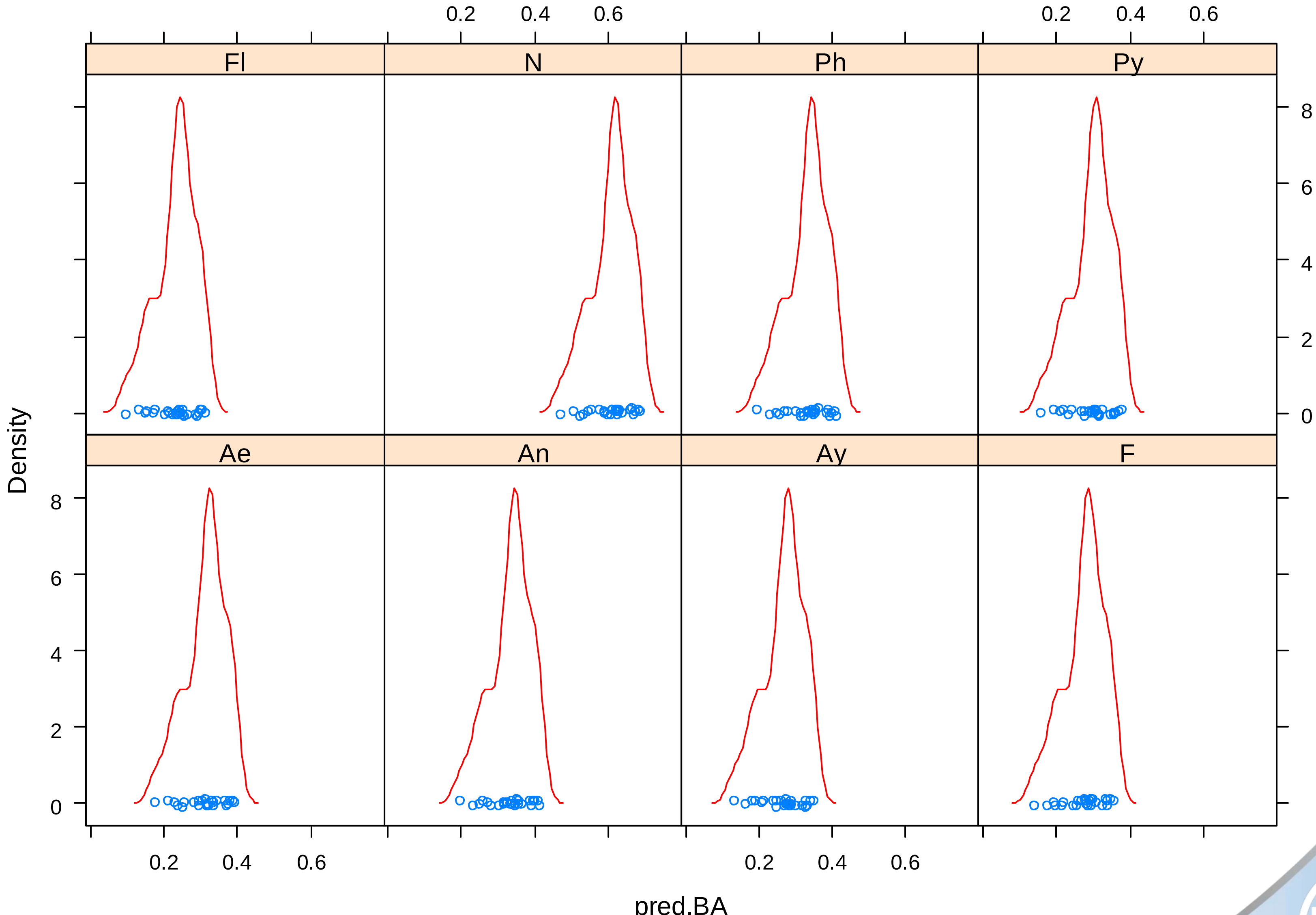
Noise reduction by PCA filtering



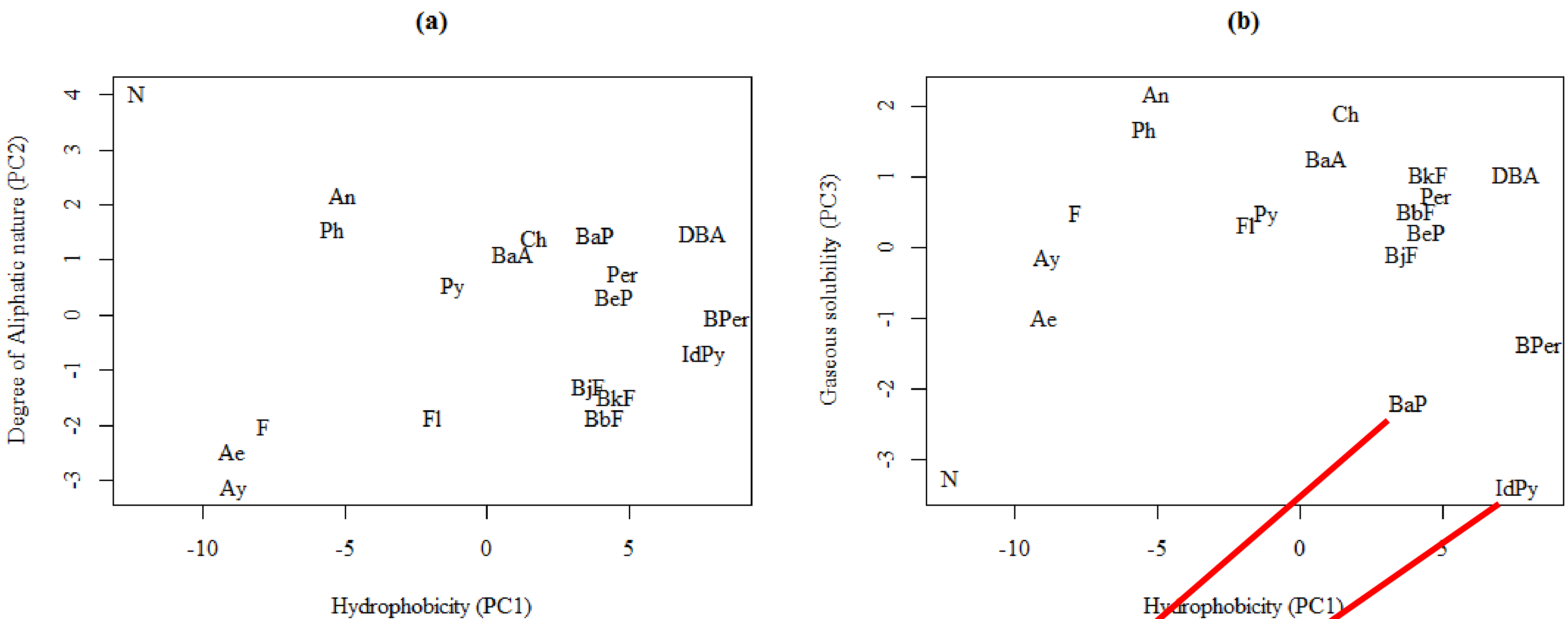
Model Interpretation

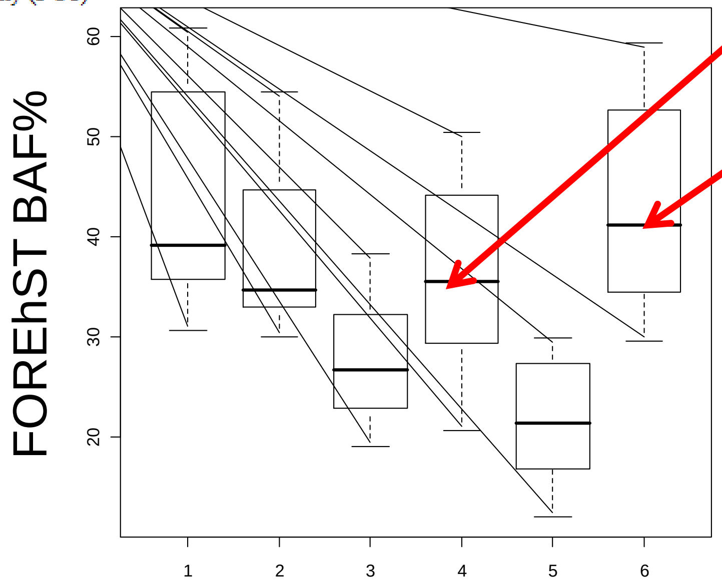


Model Predictions



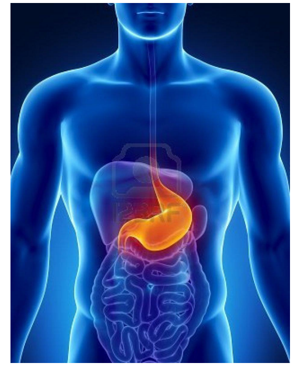
Able to predict BA values for PAHs not analysed

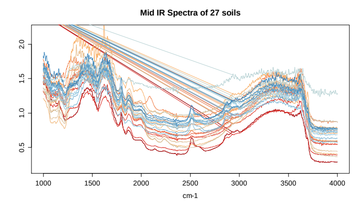




Second study explains first study anomalies

Conclusions





- Quantification is essential – validated methods are desirable before bioavailability/bioaccessibility research can be attempted (How?).
- It is not enough to measure "how much" but we also need to understand what makes the contaminant bioavailable (Why?)