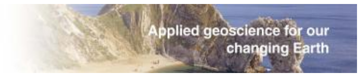
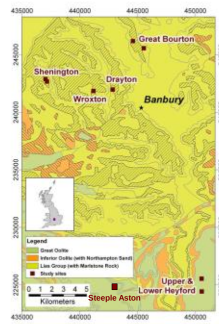


The solid phase distribution and bioaccessibility of potentially harmful elements in natural ironstone soils in the UK

Joanna Wragg

Study location



- 7 sampling sites
  - Residential and allotments at each
- Underlying parent geology – Northampton Sand Formation (NSF)
  - Jurassic Ironstone
  - Stratified by
    - Great Oolite
    - Inferior Oolite
    - Lias Group

Study Aim

- Assess the potential availability of As, Cr and Ni in ironstone derived soils from the Cherwell district via the oral ingestion route.
- Why?
- The Advanced soil geochemical atlas of England and Wales'

	Min	Max	Mean
As mg kg^{-1}	0	820	20
Cr mg kg^{-1}	5.1	1141	68
Ni mg kg^{-1}	0.26	459	23

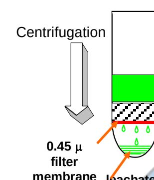
- Other studies of Jurassic ironstones have shown soil PHE concentrations above UK soil guideline and generic assessment criteria (at the time of the study)

Land use	Soil Guideline Value (mg kg^{-1} DW)		
	Inorganic As	Cr^{+}	Ni
Residential	20 (32)	200 (627)*	75 (130)*
Allotment	20 (43)	130 (15300)	50 (230)

- Most work in the UK has been carried out on As and Pb

Study Aim II

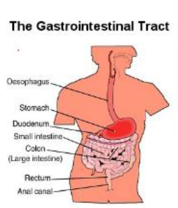
- Identification of the source of the bioaccessible PHEs
  - The source components
- Identification of any relationships with the underlying parent geology



Experimental

- Total of 30 soil samples for analysis
  - Lias and Inferior Oolite
  - 12 residential, 18 allotment
  - Sampled as per BGS standard geochemical field survey
  - Dried at 35 ± 2°C
  - Sieved to <250 µm
- Total As, Cr and Ni
  - Pressed powder pellet, XRF analysis
- Bioaccessible As, Cr and Ni
  - BGS modified PBET (pre-UBM)

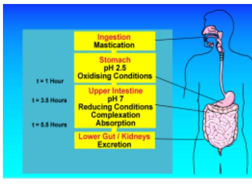
•Auger soil sampling



• Sieving Ø< 250um

BGS Modified PBET

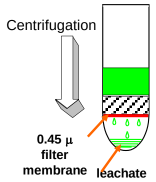
- Study used the BGS Modified PBET
  - Carried out before the UBM was developed enough for use
- Mimics kinetic and chemicals changes in the human GI environment
- Considers Stomach and Small Intestine Conditions
- 2-3 year old child
- 37°C
- Stomach pH @ 2.5
- Small Intestine pH @ 7.0



How PHEs are distributed between the soil components?

CISED Test
Chemometric Identification of Substrates and Element Distributions

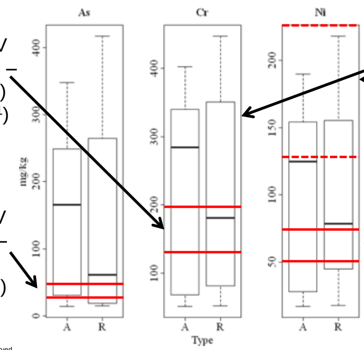
- Separate aliquots of aqua regia of increasing concentration.
- Passed through the sample under centrifugal force.
- Determination by ICP-AES.
- Chemometric data processing .
- Identification of physico-chemical hosts and the metal distributions within the sample under test.



Results – Total PHEs

Cr SGV (130 (A) – 200 (R) mg kg^{-1})

As SGV (32 (R)– 43 (A) mg kg^{-1})

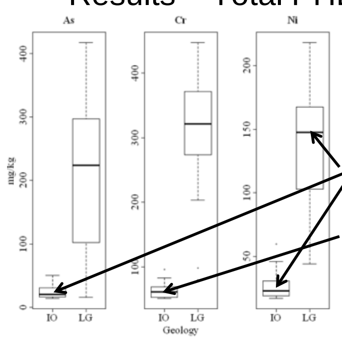


New Ni SGV (130 (R) – 230 (A) mg kg^{-1})

Below new Cr GAC

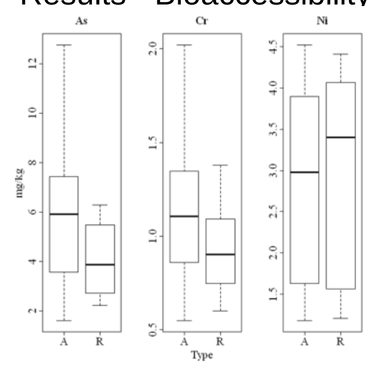
Ni SGV (50 (A) – 75 (R) mg kg^{-1})

Results – Total PHEs



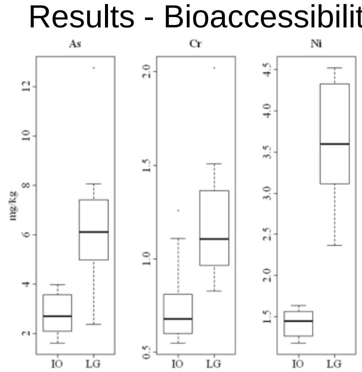
- Total PHE concentrations significantly higher in the LG
- Median IO As below new SGV for residential and allotment sites
- Median IO Ni below old SGV for residential sites
- Median IO Cr below new SGV for residential and allotment sites

Results - Bioaccessibility



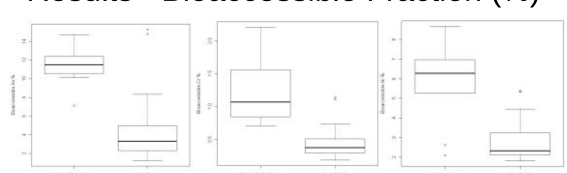
- All results based on highest of the two phases
- All results below the SGV/GAC – current or previous
- Not statistically different (A-R)
  - In general a wider range of values for allotment soils
  - Why?

Results - Bioaccessibility



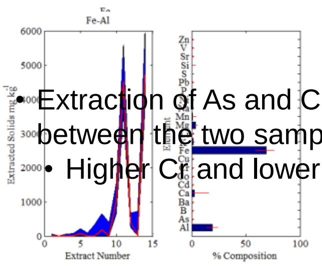
- Bioaccessibility significantly higher in soils from the Lias group
- LG bioaccessibility *ca.* double IO

Results - Bioaccessible Fraction (%)



- BAF is the value used in a risk assessment
- % BAF for the IO group is higher for all PHE than LG
  - Opposite to the observations using the actual mg kg^{-1} bioaccessibility values
- WHY???
  - Because of the lower total PHE concentrations for this group

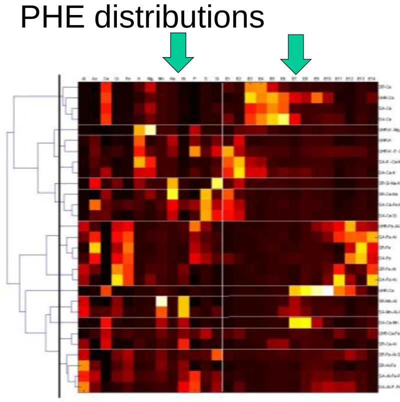
Results - CISED



- Extraction of As and Cr differed between the two samples
  - Higher Cr and lower As at Drayton

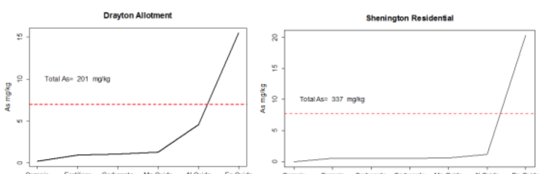
- Drayton Allotments sample
- Shenington Residential sample
- Identified as Fe oxide
- Identified as Fe oxide
- Extracted by 1.0 – 5.0 M Aqua Regia
- Extracted by 0.5 – 5.0 M Aqua Regia
- Extracted earlier than for Shenington sample
- Median As Distribution – 10.9 mg kg-1
- Median Cr Distribution – 19.2 mg kg-1
- and of extraction window
- Median As Distribution – 11.1 mg kg-1
- Median Ni Distribution – 4.56 mg kg-1
- Median Cr Distribution – 21.3 mg kg-1
- Median Ni Distribution – 5.73 mg kg-1

PHE distributions



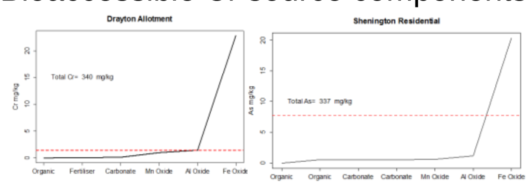
5. Carbonate
4. Fertiliser
3. Fertiliser
2. Organic
1. Organic
11. Fe Oxide
9. High Carbonate
7. Mn Oxide
8. Mn Oxide
6. Carbonate
10. Al Oxide

Bioaccessible As source components



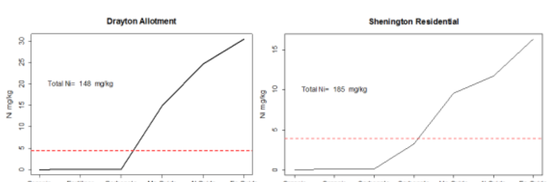
- Similar for both LG samples
  - Sequential dissolution of organic, fertiliser, carbonate, Mn and Al oxides
  - More As association with Al oxides at Drayton
- Some bioaccessible As with Fe oxide – but this is the host of the non-bioaccessible form
  - At other sites – carbonate/high carbonate play a larger host role

Bioaccessible Cr source components



- As with As, sequential dissolution of organic, fertiliser, carbonate, Mn and Al oxides
- Some bioaccessible Cr with Fe oxide – but this is the host of the non-bioaccessible form

Bioaccessible Ni source components



- Geochemical hosts of bioaccessible Ni
  - Organic, fertiliser, carbonate, Mn oxide (small amounts)
- Non bioaccessible hosts
  - High carbonate, Mn, Al and Fe oxides

Conclusions

- The combination of methodologies has been useful for understanding process control
  - Identifying host soil components *etc,*
- Bioaccessible As and Cr appear to result from the same geochemical host components
- Bioaccessible Ni results from more environmentally mobile host components – e.g. carbonates
- Parent geology is key
  - IO PHEs have higher bioaccessibility as a %
- Land use may play an important role in understanding contaminant bioaccessibility
  - – Allotments indicate a broader range of bioaccessibility
    - different / changed distributions
    - Additives – fertilisers, manure *etc,*

British Geological Survey
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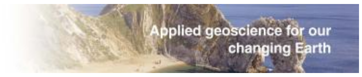

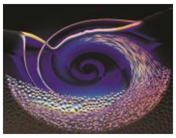

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