The use of CF-IRMS as a tool in forensic soil analysis

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Main applications of forensic geology in serious crime investigations

- murder
- armed robbery
- rape
- drug smuggling / concealment
- terrorism
- arson
- hit and run road accidents

Main types of geological evidence

- Mud, sand, gravel, rock
- Dusts
- Biological material
  - MACRO - shells, plants and parts, insects, etc.
  - MICRO - spores, pollen grains, fungi, diatoms, etc.

- Mineral particles
- Organic particles
- Anthropogenic particles (contaminants)

History

- Sherlock Holmes publications 1887-1893
- Dr Watson observes of Holmes' knowledge of :

"... geology – practical but limited. Tells at glance different soils from each other. After walks he has shown me splashes upon his trousers, - and told me by their colour and consistence in what part of London he had received them."

Value of soil / geological materials

Samples from a restricted geographical area often possess highly singular properties and assemblages of constituents

These can be used to:

- Place people, vehicles or other items at a scene of crime
- Provide information about sequences and timing of events or movements
- Find bodies or other buried items
- Assist in elimination or inclusion of suspects

Potential sources of geological evidence

- footwear
- clothing
- skin / fingernails / hair / cavities
- bags, boxes, etc.
- vehicles
- implements (spades, spoons, rope etc.)
- household items (carpets, furniture, washing machine filters, u-bends, etc.)

Research Techniques

▪ Particle size	✓ laser diffraction
▪ Colour	✓ spectrophotometry / Munsell Values
▪ Texture/shape	✓ microscopy –binoc/SEM
▪ Mineralogy	✓ microscopy, XRD
▪ Chemistry	✓ ICP-AES / -MS, EDX
▪ Pollen & diatoms	✓ microscopy
▪ Organic compounds	✓ gas chromatography
▪ Stable Isotopes	✓ CF-IRMS (C & N)

Stable Isotopes

- **Carbon**

The two stable isotopes

	^{12}C	98.89%
	^{13}C	1.11%
Ratio	$\delta^{13}C$	parts per thousand ($^0/_{00}$)

- **Nitrogen**

The two stable isotopes

	^{14}N	99.64%
	^{15}N	0.36%
Ratio	δ^{15N}	parts per thousand ($^0/_{00}$)

Samples

- Soil, as appropriate

Standardised preparation:

- Wet sieved using deionised water to <150μm (used in other techniques)
- Settled, evaporated, dried and ground
- Weighed in pure tin capsules (max. 30mg) on a 4 figure balance
- Crimped and sealed

Standards for calibration / drift correction

Typical precision and accuracy for the instrument calculated as + / - 0.1% or better

- Carbon
- international standards (IEAA CO9 and NBS-21)
- laboratory standards (GF graphite and RHBNC carbonate)
- Nitrogen
- international standards (IEAA N1 and N2)
- Laboratory standard Sulfanilammide

Replicates

- e.g. for TH10J (n=3)

Mean C%	8.94	SD 0.76
Mean $\delta^{13}C$	-26.18	SD 0.20
Mean N%	1.77	SD 0.16
Mean $\delta^{15}N$	4.86	SD 0.08

- IAEA – N2 5 samples in run

$\delta^{15}N$	20.28 to 20.36	Mean	20.33
		SD	0.03

Examples of $\delta^{13}C$ ratios in nature

Source	$\delta^{13}C$
Total terrestrial range	-120 to +15
Atmospheric CO_2	- 7.7
Plants	- 8 to -30
Organic sediments (recent)	-10 to -30
Marine organisms	- 5 to –~~30~~ 40
Coal	-20 to -30

Examples of $\delta^{15}N$ ratios in nature

Source	$\delta^{15}N$
Total terrestrial range	-20 to +30
Atmospheric Nitrogen	0.00
Plants	- 8 to +10
Organic soils	- 4 to +20
- surface	- 4 to + 2
- 20 – 40 cm depth	+ 6 to +10
Soil with nitrates	+ 2 to +14
Fresh forest litter	- 5 to + 2

First thoughts …

- Is it possible?
- Ran triplicates of 10 soil samples drawn from cases all over the UK and came up with the range for $\delta^{13}C$ values of –20.3 to –28.3 $^{o}/_{oo}$

Primary transfer

- Shoes

  5 pairs – wellies, Doc Martyns, new shoes, worn trainers, work boots

  Lefts = 24hrs; Rights = 72hrs

  4 soil types (surface)
- Implements

  2 spades, 1 fork, 1 rake, 1 trowel

  4 soil types (to 50cm depth)

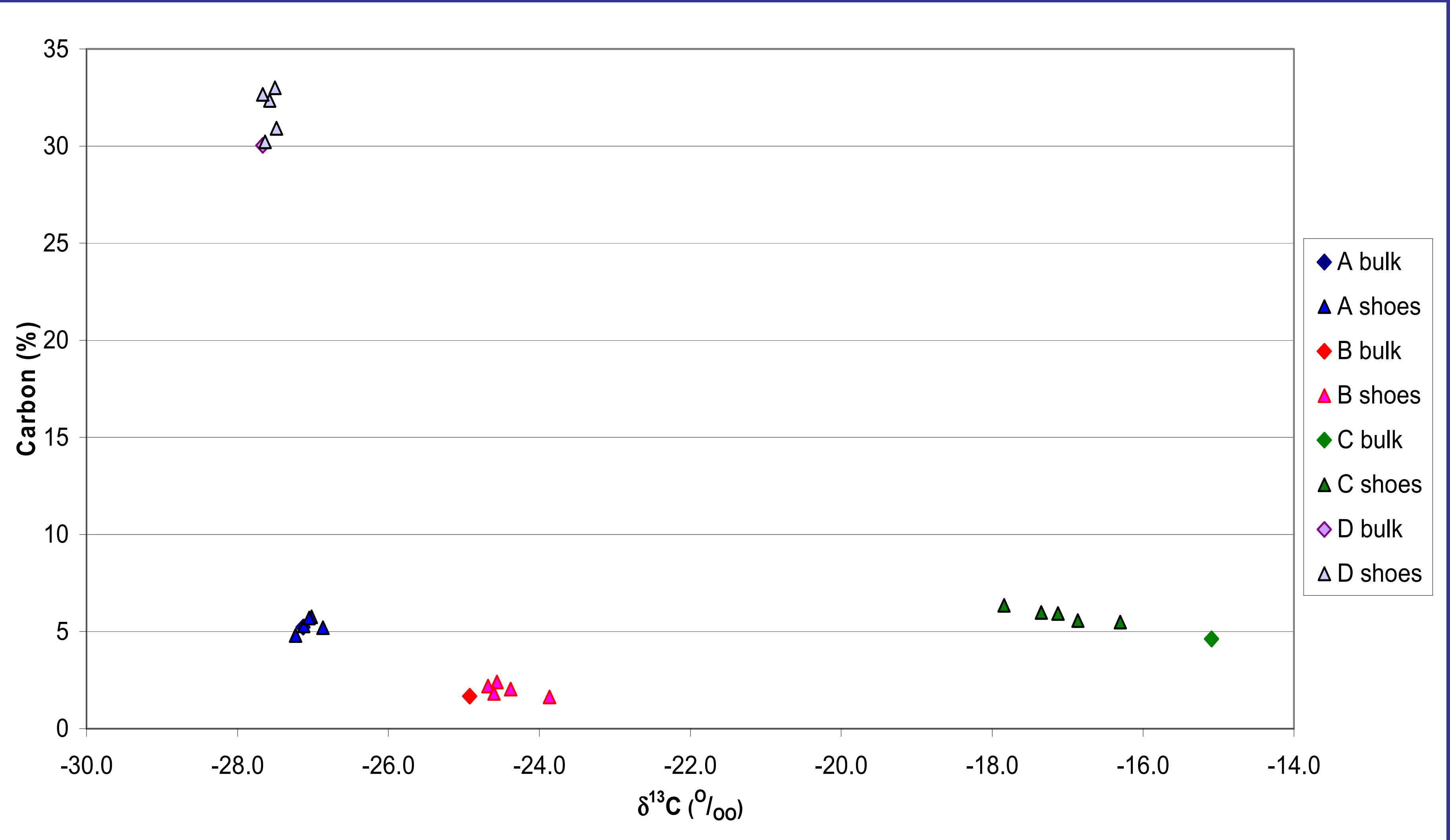
Primary transfer - soils

• Soil A	fallow area of a cultivated allotment
• Soil B	grassland / made land
• Soil C	river estuary (tidal dominated) overbank
• Soil D	stable woodland

Primary transfer - shoes

Sample source		$\delta^{13}C$	Carbon (wt %)
Soil A surface		-27.13	5.23
A Footwear samples	Mean	-27.06	5.35
	SD	-0.13	0.39
Soil B surface		-24.92	1.66
B Footwear samples	Mean	-24.42	2.01
	SD	-0.33	0.31
Soil C surface		-15.09	4.62
C Footwear samples	Mean	-17.10	5.86
	SD	-0.57	0.35
Soil D surface		-27.66	30.04
D Footwear samples	Mean	-27.57	31.83
	SD	-0.09	1.20

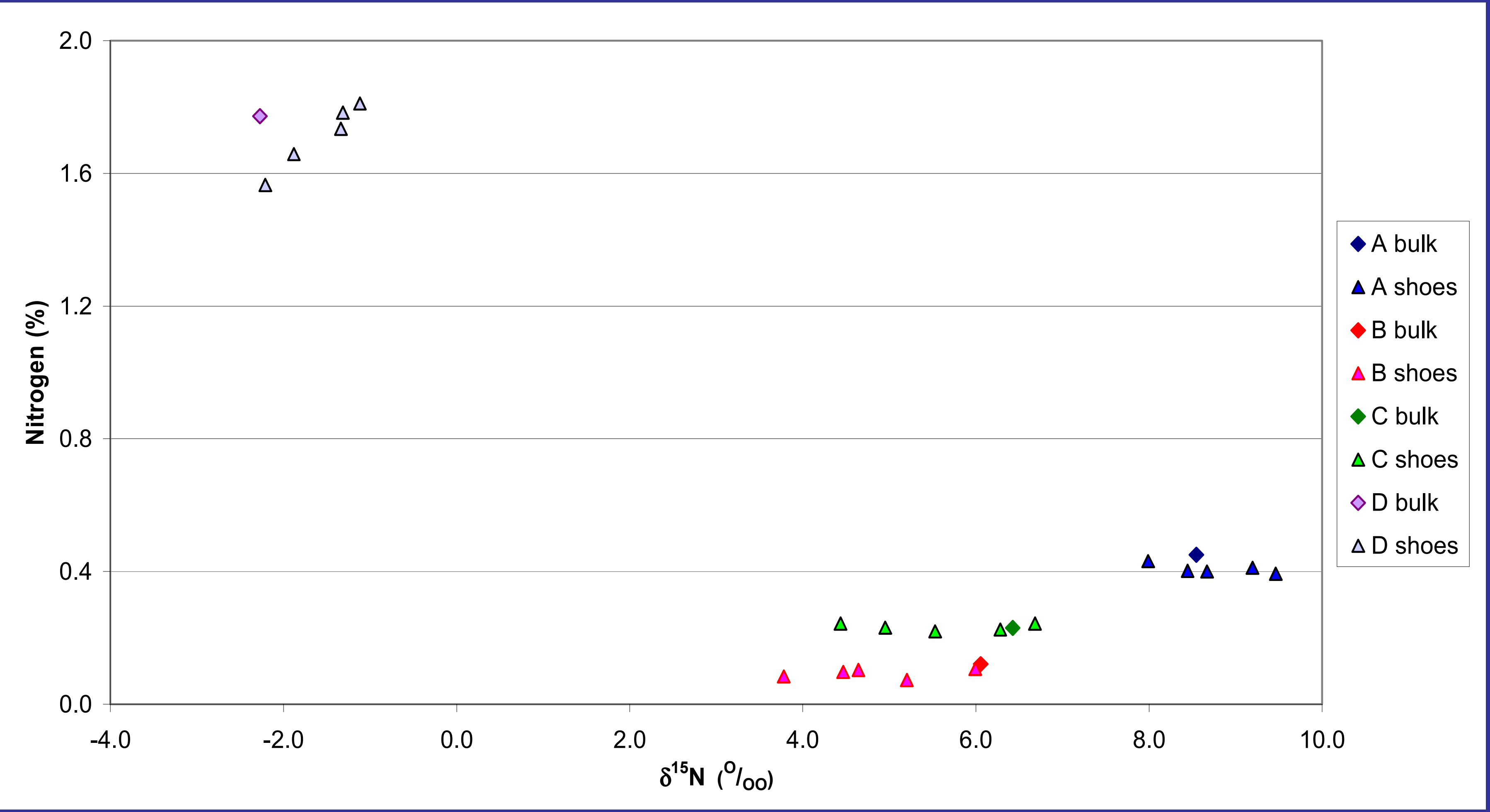
Bivariate crossplot $\delta^{13}C$ vs. C%
4 soils – surface and footwear



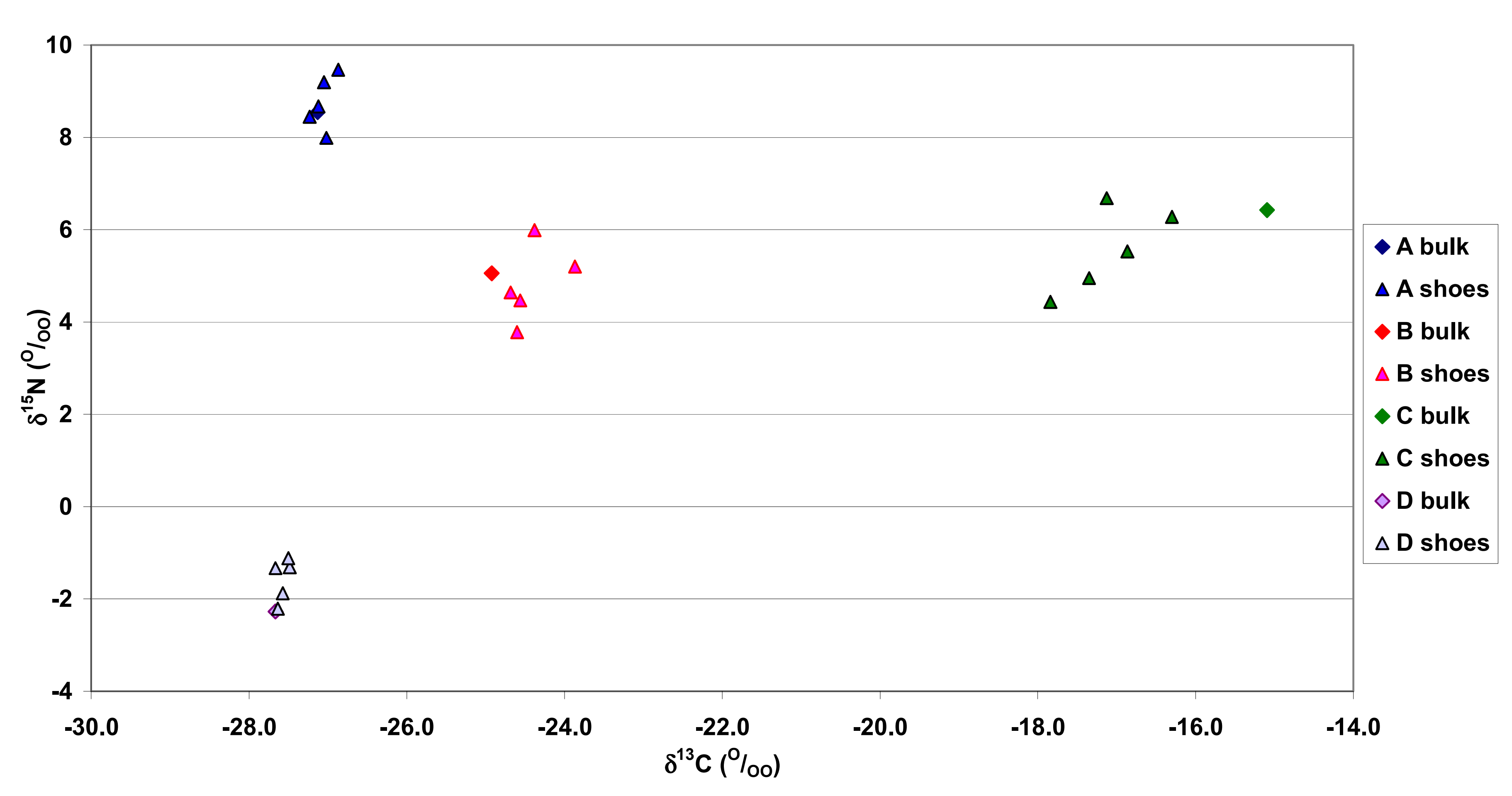
Primary transfer - shoes

Sample source		$\delta^{15}N$	Nitrogen (wt %)
Soil A surface		8.55	0.45
A Footwear samples	Mean	8.75	0.41
	SD	0.59	0.01
Soil B surface		5.05	0.12
B Footwear samples	Mean	4.82	0.10
	SD	0.83	0.01
Soil C surface		6.42	0.23
C Footwear samples	Mean	5.58	0.23
	SD	0.92	0.01
Soil D surface		-2.27	1.77
D Footwear samples	Mean	-1.57	1.71
	SD	-0.46	0.10

Bivariate crossplot $\delta^{15}N$ vs. N%
4 soils – surface and footwear



Bivariate crossplot $\delta^{13}C$ vs. $\delta^{15}N$
4 soils – surface and footwear



Primary transfer - shoes

CARBON

- Soils A, B, D – no statistically significant difference between surface and footwear samples (*p=0.95*) for isotopic ratio or carbon content
- Soil C – significantly different for both, possibly due to complex fractionation due to clay content

NITROGEN

- No statistically significant difference between surface and footwear samples (*p=0.95*) for isotopic ratio or nitrogen content for all four soil types.

Primary transfer - implements

Sample source	$\delta^{13}C$			Carbon (wt %)	
Soil A (00 – 50 cm)	Mean/SD	-25.7	-1.4	3.2	1.7
A Implement samples	Mean/SD	-26.2	-0.4	4.1	0.7
Soil B (00 – 50 cm)	Mean/SD	-22.5	-0.6	1.1	0.4
B Implement samples	Mean/SD	-22.4	-0.7	1.1	0.1
Soil C (00 – 50 cm)	Mean/SD	-16.5	-0.6	5.2	0.2
C Implement samples	Mean/SD	-15.8	-1.4	5.0	0.4
Soil D (00 – 50 cm)	Mean/SD	-25.9	-0.6	4.5	8.2
D Implement samples	Mean/SD	-26.5	-0.3	2.5	0.7

Primary transfer - implements

Sample source	**$\delta^{15}N$**			**Nitrogen (wt %)**	
Soil A (00 – 50 cm)	Mean/SD	9.1	0.9	0.21	0.13
A Implement samples	Mean/SD	8.4	0.8	0.28	0.05
Soil B (00 – 50 cm)	Mean/SD	6.6	2.4	0.04	0.02
B Implement samples	Mean/SD	5.6	1.0	0.03	0.00
Soil C (00 – 50 cm)	Mean/SD	6.5	0.5	0.17	0.03
C Implement samples	Mean/SD	6.2	0.4	0.13	0.01
Soil D (00 – 50 cm)	Mean/SD	3.9	3.8	0.11	0.16
D Implement samples	Mean/SD	2.1	1.6	0.10	0.03

Primary transfer - implements

- Soils A, B, C, D – no statistically significant difference between profile means and implement means (*p=0.95*) for isotopic ratios or carbon / nitrogen content. However, there is a large spread of data for some soil types reflecting sub-surface changes.
- Organic rich surface soils (such as in B and D) give very different values than their sub-surface samples (masked by the overall statistical measures)
- In casework, implements (and therefore control sampling) need to be treated in a different manner than simple primary transfer

Spatial & temporal variation

- 2 sites – Tower Hamlets Cemetery (east London) and Bushy Park (west of London)
- Geologically similar - post-Anglian (<350 ka) river deposits on London Clay
- Similar usage (public parks)
- Stable (no earth movement in recent past or planned)
- Contrasting vegetation

Sampling

- 15 at each location, less than 20m scale, sampled every 3 months over 2 years for TH and 1 year for BP
- Total of TH 120 samples / BP 60 samples
- Surface to 2cm, bagged and stored at low temperature
- Sieved, dried and ground $<150\ \mu m$ fraction, weighed to 4 dp
- ca. 1.5 – 2.0 mg for carbon / 16 – 18 mg for nitrogen

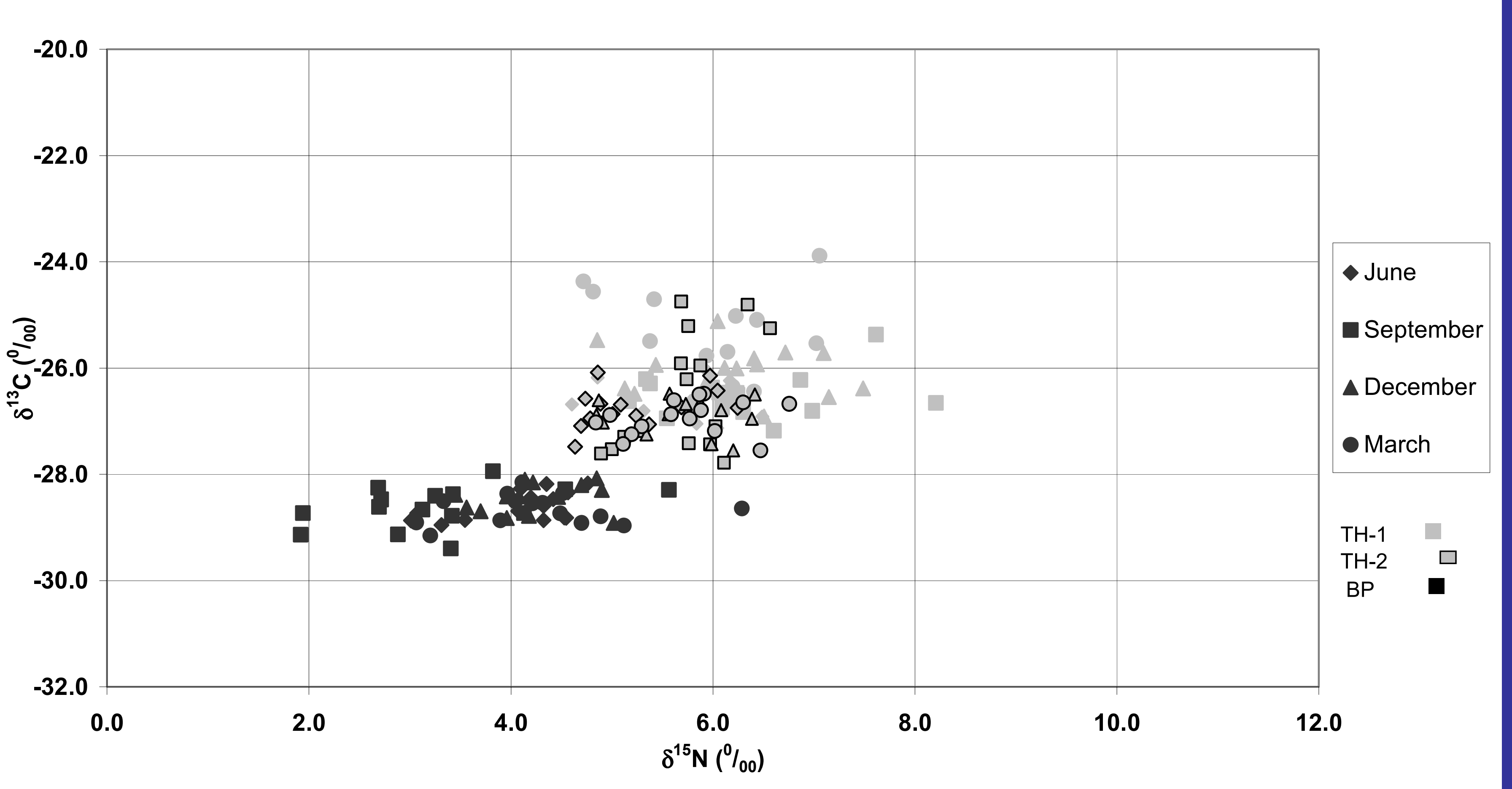
Summary data - annual

Samples		TH yr 1	TH yr 2	BP
$\delta^{13}C$	mean	-26.18	-26.77	-28.58
	SD	-0.51	-0.63	-0.09
Carbon wt%	mean	6.74	9.48	18.33
	SD	2.01	1.57	2.62
$\delta^{15}N$	mean	4.54	5.57	3.97
	SD	0.35	0.55	0.45
Nitrogen wt%	mean	0.38	0.61	1.34
	SD	0.09	0.11	0.27

Spatial variation

- Spatial data (up to 20m scale) shows no statistically significant differences at either site, for nitrogen or carbon
- The isotopic data appears more robust / less variable than the percentage content
- Contouring the data over the geographical area (using kriging for interpolation) shows no systematic directional component
- Extending this scale (to 50m and then 100m) did show significant differences in all parameters

Isotopic ratios – N vs. C



Temporal variation

- Annual data is variable, signified by relatively high SD, particularly for nitrogen (more dynamic cycling)
- Bushy Park : seasonal change is not statistically significant for nitrogen data, but is significant for C% and borderline for $\delta^{13}C$
- This difference in the carbon data is wholly explained by the differences between September and the other quarters
- At Bushy Park the nitrogen levels are very low, affecting the reliability of the data.

Temporal variation

- Tower Hamlets : seasonal change is not statistically significant for carbon data, but is significant for the nitrogen data
- The difference in the nitrogen data is wholly explained by the differences between March and the other quarters
- Variation in the nitrogen data is thought to be as a result of the mixed vegetation input filtering into the soil over the winter plus other factors including microbial action

Conclusions

- Carbon and nitrogen data, particularly used in combination, can be diagnostic of location
- Vegetation input over the annual cycle is important, with the incorporation of organic matter affecting values from season to season, and possibly over year on year cycles
- Variation in simple primary transfer (e.g. shoes and surface soil) is limited and comparisons can be reliably made
- Variation in multiple source primary transfer (e.g. implements used at depth) is more complex; needs careful collection and analysis of <u>appropriate</u> control samples

Future work

- Testing on ‘dead’ case data
- Testing on ‘live’ case data
- Continuation of the seasonal analysis over the next 2+ years to detect annual fluctuations (subject to the continued stability of the sites)

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