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Uranium anomalies identified using G-BASE data - Natural or anthropogenic? A uranium isotope pilot study

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BRITISH GEOLOGICAL SURVEY

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Uranium anomalies identified using G-BASE data - Natural or anthropogenic? A uranium isotope pilot study

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Foreword

This report is the product of collaboration between several BGS projects and programmes (Geochemical Baseline Survey of the Environment (G-BASE), Development of Capability for Geochemical Laboratories & Pollution & Waste Management and Extraction Industry Impacts) to establish an analytical technique which has been tested on existing (archived) G-BASE samples to resolve ambiguity in the origin of uranium anomalies observed during routine baseline data interpretation.

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Summary

The rapid quantitative analysis by inductively coupled plasma quadrupole mass spectrometry (ICP-QMS) for uranium isotope ratios has been successfully established and tested. The method is fully documented in this report.

The rapid and cost effective nature of the methodology has allowed the analysis of a selection of G-BASE soil and stream sediment archive material to be undertaken, which was not possible previously. These samples were chosen by careful consideration of the findings of previously published G-BASE atlases. During the course of mapping Britain, the G-BASE project has encountered anomalously high concentrations of uranium in several areas, in comparison to the regional background values. Samples from regions believed to be enhanced in uranium due to natural processes alone were chosen to allow the variability of uranium isotope ratios to be quantified, and hence provide an isotopic baseline. Samples which had been recognised during geochemical baseline mapping as having anomalously high uranium concentrations in the locale of nuclear fuel installations were also selected for comparison with this isotopic baseline.

As would be expected from literature values, the $^{238/235}\text{U}$ ratio was constant in all the natural enhanced samples, whilst some variation in $^{238/234}\text{U}$ was observed. This was also the case for samples from the urban industrial fringes of Greater Merseyside, which had high concentrations of heavy metal contaminants. In contrast, all samples associated, by proximity, with nuclear fuel facilities were found to have isotope ratios reflecting a contribution from enriched uranium. These results are consistent with the limited suite of RIFE (Radioactivity in Food and the Environment) data available, but are of better precision.

Difficulties exist in quantifying the contribution of processing facility uranium to stream sediments and soils, due to the limited information available on the likely composition of the original materials entering the stream course, or soil profile. These factors are highlighted, along with possible further investigations to elucidate dissemination of anthropogenic uranium in the environment.

1 Introduction

The natural concentrations of uranium in stream sediments, soils and waters are controlled both by the occurrence of uranium in the underlying lithologies and the subsequent mobility of uranium in that environment. These concentrations can vary widely, depending on the source rock and weathering environment (e.g. Eh, pH, $[\text{HCO}_3^-]$). The stream sediments associated with the uranium rich granites of Cumbria and Dumfries and Galloway have uranium concentrations in excess of 10 mg kg^{-1} (up to 800 mg kg^{-1}), whilst the regional median value is $\sim 3 \text{ mg kg}^{-1}$ (British Geological Survey, 1992; 1993). Elevated concentrations of uranium in the environment are of concern due to the potential chemical and radiological risks to human and ecosystem health (e.g. WHO, 2001). Historically, concerns have been primarily associated with the activities of the civilian and military nuclear industries. More recently, interest has focussed on the dissemination into the environment of depleted uranium (DU) due to its use in armour piercing weapons or high density ballast in aircraft and ships. This has also coincided with greater recognition of the importance of the chemical toxicity of uranium, as opposed to previously held perceptions of a purely radiological toxicity (WHO, 2001).

The principle diagnostic tool for evaluating the occurrence of nuclear fuel cycle uranium in natural environments is the measurement of the isotopic composition of uranium. The isotopic composition of natural uranium in the Earth's surface environment is reasonably well constrained i.e. $^{238/235}\text{U}$ is constant, with the single exception of the very ancient natural reactor at Oklo in Gabon. The range of $^{238/234}\text{U}$ is affected by leaching processes, preferentially removing ^{234}U from solid phases, which may increase the ratio from that expected by equilibrium calculations in the solid and decrease the ratio in the aqueous phase or solid phases later precipitated. These data are summarised in Table 1:1. The deliberate perturbation of the proportions of the respective isotopes, is the basis for all nuclear fuel processing. When uranium is added to natural systems via the waste products of fuel cycle processes, it is most diagnostically reflected in variations to the $^{238/235}\text{U}$ ratio, which is constant in nature. A summary of the some of these perturbations in terms of the processing undergone, is shown in Table 1:2. The incorporation of fuel cycle uranium wastes into the environment results in the superimposition of anthropogenic $^{238/234}\text{U}$ on the natural $^{238/234}\text{U}$ variation, making source apportionment more difficult than using $^{238/235}\text{U}$.

BGS has been contributing to the understanding of uranium sources, pathways and sinks for many years. This has involved all aspects from uranium exploration (from which the development of inductively coupled plasma – quadrupole mass spectrometry (ICP-QMS) technology was funded in the early 1980s), to characterisation of candidate nuclear waste disposal sites in the 1990s for NIREX.

Mapping of the concentration of uranium, and a wide suite of other elements, has been undertaken at BGS for the last 30 years by the ongoing national survey “Geochemical Baseline Survey of the Environment” (G-BASE) and its precursors. The mapping of stream sediments has been undertaken from the Orkneys southwards to the present field area of East Anglia (Figure 1:1). The addition of stream waters and soils to the sampling suite occurred more recently as the survey programme moved southwards, commencing in north-west England in 1989. However, importantly for this study, pH and dissolved uranium, fluoride and bicarbonate have been measured since the commencement of G-BASE sampling. Inspection of the G-BASE uranium concentration maps enabled the identification of naturally elevated regions. Localised anomalously high levels of uranium can also be seen, which are not thought to be geological in origin. Of the latter group, some appear to be geographically associated with known uranium processing facilities.

The current pilot study was instigated with two aims. *Firstly*, to determine whether these anomalies were natural or anthropogenic using uranium isotope ratio measurements. *Secondly*, to show whether measurements could be made, in a fit-for-purpose and cost effective fashion, using the Analytical Geochemistry Laboratories ICP-QMS facility.

Initially, a limited suite of 18 G-BASE stream sediment samples were selected, some that might contain uranium of anthropogenic origin due to their location and a control set of samples thought likely to contain only uranium of natural origin. These samples were subjected to a rapid acid leach in a microwave digestion system to liberate potentially available uranium, but not uranium held strongly in detrital minerals such as zircon. The samples were analysed first in multi-element mode to determine the leached uranium concentration thus allowing optimal dilution for isotope ratio measurements. The ICP-MS instrument was subsequently optimised for uranium isotope ratio measurements and the $^{238/235}\text{U}$ and $^{238/234}\text{U}$ ratios determined without further chemical processing. Data were corrected for mass fractionation effects using a rock reference material with a natural $^{238/235}\text{U}$ ratio. The resultant uranium isotope ratios were compared with values expected for natural, depleted and fuel cycle uranium and grouped accordingly. Potential mechanisms controlling the isotope ratios are briefly considered.

As part of the regulatory process a government radiological monitoring program of environmental samples, collected from the vicinity of facilities handling nuclear materials, is conducted annually. The results of this survey are published in the Radioactivity in Food and the Environment (RIFE) reports. Data from this study has been compared to those published in 1989, 1996 & 1999 (MAFF, 1989; 1996; 1999). While this report was being prepared, another site associated with the nuclear fuel / weapons cycle came into the public eye. This was a disposal site operated by Rolls Royce, at Crich in Derbyshire, licensed for the disposal of low level radioactive waste. Inspection of the G-BASE data for the area around the site did not show anomalous uranium concentrations, typically being below 5 mg kg^{-1} . However, in view of the current interest, and as we had recently developed a separation and pre-concentration methodology for uranium in lower concentration samples (Chenery et al., 2002, in prep), it was decided to measure the uranium isotopic ratios from 8 samples in the area around the site. The results of this supplementary study are included for comparison and discussion.

Table 1:1: Ranges of $^{238/234}\text{U}$ (atom ratio) found in natural environments

	$^{238/234}\text{U}$	
Underground waters	1563	31250
Terrestrial surface waters	7500	23438
Open-ocean water	15890	17045
Waters of uranium mineralisation	2131	15625
Various surficial carbonates	6250	20833
Fossil shells and bones	75	18750
Igneous rocks	8929	31250
Volcanic tuffs	11719	37500
Minerals and extracts of minerals	2344	23438
Sandstones	9375	23438
Peat deposits	9375	20833

data recalculated from the activity ratio data of Scott (1982)

Table 1:2 Isotopic composition of uranium in selected uranium containing materials.

	Isotope (atom %)		
	^{238}U	^{235}U	^{234}U
Natural equilibrium	99.27	0.72	0.0054
Natural waters	99.217-99.277	0.72	0.00318-0.0635
Enriched uranium*	96.47	3.5	0.02884
Depleted uranium*	99.80	0.20	0.0006
Weapons grade*	2.00	98.00	0.0006

* - these values are approximations that will vary according to the exact conditions of manufacture and source material; table adapted from information in WHO (2001) and Scott (1982).

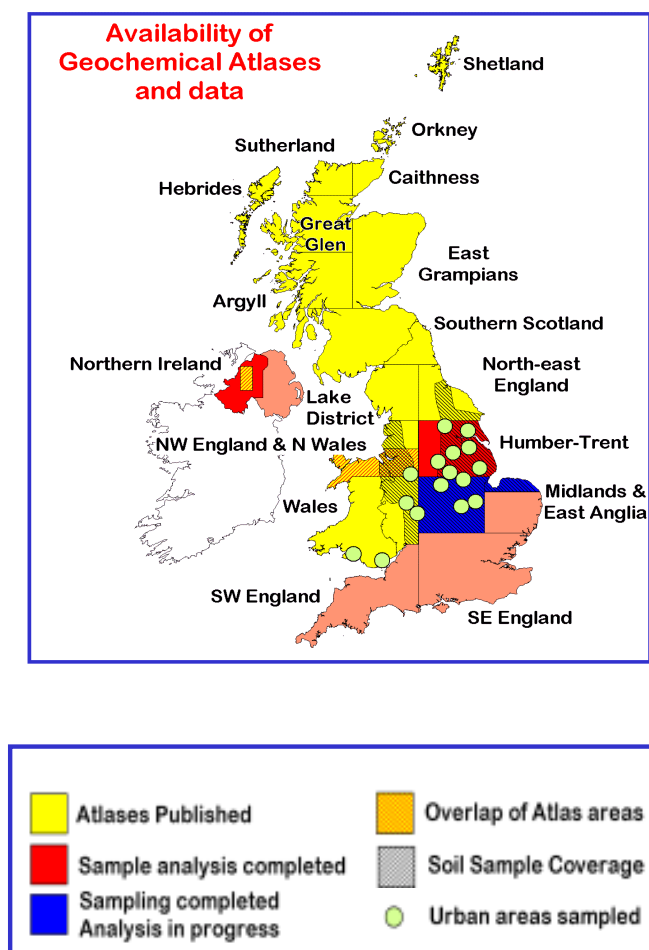


Figure 1:1 Progress of the Geochemical Baseline Survey of the Environment (G-BASE) project to date.

2 Methodology

2.1 SAMPLE SELECTION

The samples were selected on three geochemical criteria and their locations are shown in Figure 2:1. These criteria were: previously recognised anomalously high uranium concentrations in the vicinity of nuclear fuel cycle installations; anomalously high uranium in industrialised regions of the Wirral and Preston and high uranium concentrations observed in the Forest of Bowland and Cowgill in the Teesdale valley, derived from natural sources. The context of these samples can be seen in the regional uranium stream sediment maps for the Lake District and North-west England (British Geological Survey, 1992; 1997). Selected summary analytical data and the date of sampling are provided in Table 2:1. Analyses of stream sediments and soils were carried out by X-ray fluorescence spectrometry (XRFS) on pressed powder pellets (e.g. British Geological Survey, 1997), with the exception of the stream sediment samples from Drigg and Cow Green, which were analysed by delayed neutron activation analysis (DNAA) (e.g. British Geological Survey, 1992).

The naturally elevated samples were chosen well away from any potential industrial sources and at the upper end of the range for that lithology to ensure that any non-geological source was dwarfed by the natural component. The Forest of Bowland natural anomaly is associated with the presence of the Bowland Shale Group, Upper Dinantian (British Geological Survey, 1997), which is enriched in many trace elements. Stream sediments in this area fall into the upper 10% of the uranium concentration data, generally over 4.4 mg kg^{-1} , compared with a regional median of 2.9 mg kg^{-1} . Four sites were selected from this region to give a representative sample of the isotope ratios associated with this natural source, having concentrations ranging from $9.5 - 16.7 \text{ mg kg}^{-1}$. One other sample was selected from an extreme natural accumulation at Birkdale Hush, near Cow Green reservoir in Upper Teesdale. The uranium concentration at this site was 590 mg kg^{-1} , believed to be associated with localised uranium mineralisation (British Geological Survey, 1992), also suggested by the presence of a “green-yellow” mineral in the pan concentrate, which may be a carnotite $[\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot n\text{H}_2\text{O}]$ or torbernite / autinite $[(\text{Cu}, \text{Ca})(\text{UO}_2)_2(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}]$ phase, which would be consistent with the description and the presence of such a high uranium concentration.

The “industrial” samples were located in streams on the Wirral and in the Runcorn area. This area has a long legacy of heavy industry, which may have contributed uranium to the local system. Possible industrial sources include phosphatic fertiliser manufacture, ceramic glazes and chemical catalysts (WHO, 2001). These samples contain $4 - 7 \text{ mg kg}^{-1}$ uranium, and it can be seen from the geochemical images of the region (British Geological Survey, 1997) that the area is generally enriched in a wide range of metals usually associated with industrial contamination.

The samples selected for uranium isotope analysis adjacent to fuel cycle facilities are shown in Figure 2:1. A brief summary of the composition of each sample is given in Table 2:1. Of particular note for these samples, and those associated with other industrial contamination is the date of sampling. All the samples selected in this suite were collected between the years of 1979 – 1989, and therefore current levels (2001) may be different, if industrial processes and discharges have changed.

The sample at Drigg (part of the Sellafield complex, Figure 2:2a) was recorded by the field team as being “downstream of a BNFL chemical dump” and drains an area containing low-level radioactive waste (British Geological Survey, 1992). This sample locations is potentially subject to ingress of marine derived uranium wastes from the Sellafield complex, due to its low altitude

and proximity to a tidal creek (Figure 2:2a). This sample contains 48 mg kg^{-1} uranium, and was notable at the time of collection for its unusual association with an aqueous uranium anomaly ($62 \mu\text{g l}^{-1}$) at the same site (British Geological Survey, 1992). This concentration of uranium represents a significant anomaly when compared with other sites over the Permo-Triassic rocks of the region, where uranium has a median concentration of 3.4 mg kg^{-1} .

The sample downstream of the BNFL Springfields facility, near Preston, is the location of a significant anomaly overlying the Triassic Helsby Sandstone Formation. This sample has 60 mg kg^{-1} uranium, compared with a background concentration ($3\text{-}4 \text{ mg kg}^{-1}$) close to that observed for Triassic sediments in the Lake District mapping (British Geological Survey, 1997). Field observations at this site, on Deepdale Brook, record that the stream bed comprised a thin veneer of sediment overlying black organic rich material. No aqueous sample was collected from this site. Like the sample from Drigg, this sample does not have anomalously high concentrations of classical contaminants from general industrial processes, such as copper, lead, zinc and arsenic (Table 2:1). Of additional interest, due to the low solubility of uranium in poorly oxic, organic rich, low carbonate sediments, is the presence of Lea Marsh (Figure 2:2b) and series of tidal marshes along the estuary banks further to the west. A plausible hypothesis would be that these environments are favourable for uranium accumulation, via sorption or secondary mineral precipitation, from the aqueous phase.

Two stream sediment samples were taken from Rivacre Brook, approximately 3 km and 4.5 km downstream of the URENCO Capenhurst uranium processing complex (Figure 2:2c). Both these samples were taken within the urban area of Ellesmere Port, and show general enrichment of elements such as lead and copper; observations of physical contamination were also made by the field team. However, the uranium concentration is also anomalously high for the Permo-Triassic sediments underlying the streams, with 27 and 30 mg kg^{-1} uranium, respectively (Table 2:1). Unlike the Drigg sample, aqueous uranium concentrations were low for the Ellesmere Port samples (British Geological Survey, 1997). In addition, the Wirral peninsula lies close to the area where soil sampling was initiated by G-BASE, and a soil sample was collected adjacent to the most proximal sediment sample (Figure 2:2c). This sample is a composite of three augers, collected from a 10m sample line at a depth of $\sim 30\text{-}45 \text{ cm}$. This sample contains only 2.1 mg kg^{-1} uranium, and was selected largely due to its proximity to the stream sediment samples.

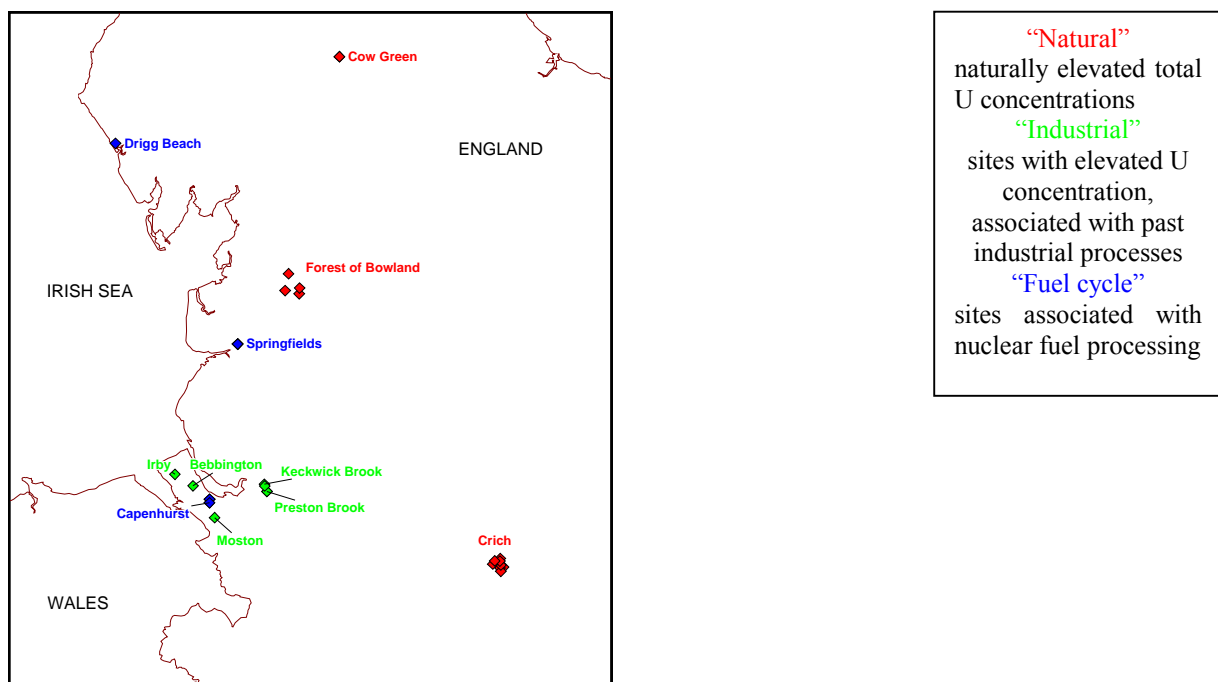


Figure 2:1 Location of G-BASE samples selected for uranium isotope analysis

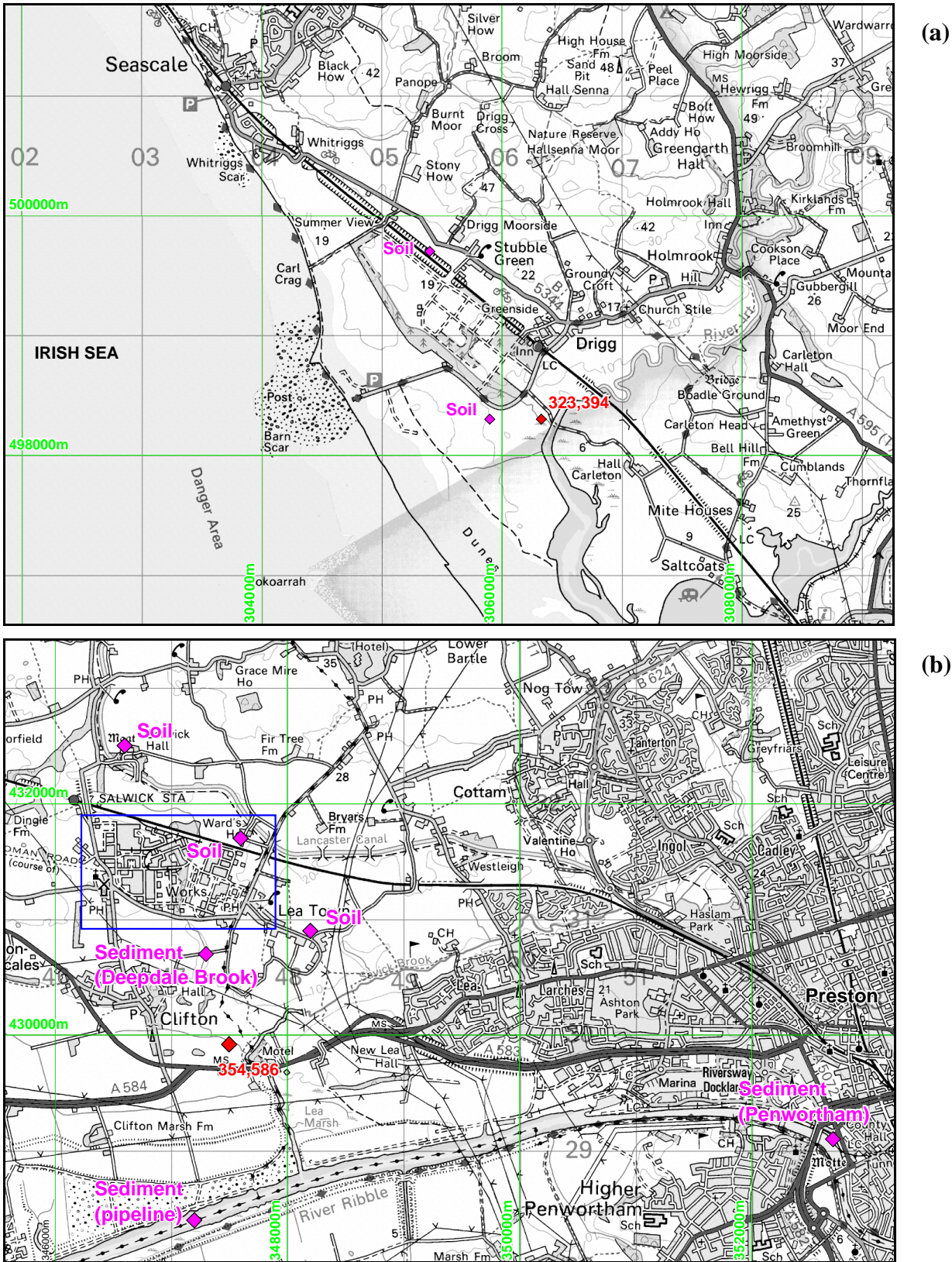
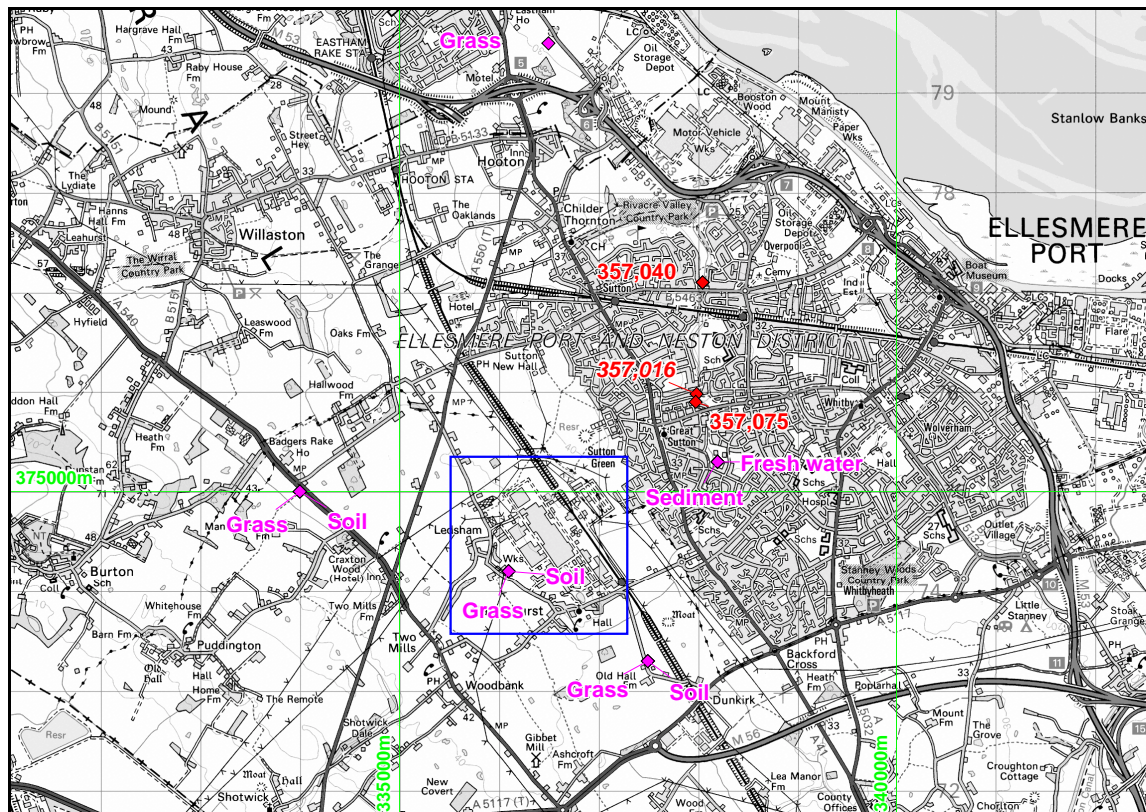


Figure 2:2 Location of the selected G-BASE samples in the vicinity of nuclear fuel establishments, and RIFE sample locations

(a) Un-named stream, Drigg, Cumbria (one GBASE stream sediment sample).(b) Deepdale Brook, Springfields, Preston (one duplicate GBASE stream sediment site). G-BASE samples are identified according to their unique sample number. RIFE samples are shown in pink according to sample type, however, no individual site labels are supplied by RIFE (MAFF, 1996; 1999). Nuclear fuel establishment is outlined in blue.



(c)

Figure 2:2 (cont...) Location of the selected G-BASE samples in the vicinity of nuclear fuel establishments, and RIFE sample locations

(c) Rivacre Brook, Ellesmere Port, downstream from Capenhurst (two G-BASE stream sediment samples). Additionally one soil sample (# 357016). G-BASE samples are identified according to their unique sample number. RIFE samples are shown in pink according to sample type, however, no individual site labels are supplied by RIFE (MAFF, 1996; 1999). Nuclear fuel establishment is outlined in blue.

Table 2:1 Selected geochemical data for G-BASE stream sediment and soil samples

Sample	Location	Date of collection	U	Zr	Zr/U	Cu	Pb	U _(aq)	pH _(aq)
			mg kg ⁻¹	mg kg ⁻¹		mg kg ⁻¹	mg kg ⁻¹	mg l ⁻¹	
356608	Preston Brook	25/0789	4	298	23	42	85	0.0003	7.4
356629	Keckwick Brook	25/0789	5	2980	16	83	145	0.001	7.6
356686	Keckwick Brook	25/0789	5	775	16	99	205	0.0009	7.4
356871	Moston	31/07/89	6.7	5192	10	15	51	0.0016	7.2
357248	Irby	21/08/89	3.4	250	18	13	15	0.0018	7.4
357300	Bebbington	21/08/89	6	3779	13	76	155	0.0014	6.8
323898	Cow Green	03/09/80	591	494	0.8	68	6542	dry	dry
352959	Forest of Bowland	01/08/88	16.7	135	9	67	189	dry	dry
352979	Forest of Bowland	01/08/88	10.8	140	22	60	101	0.0013	7.4
353130	Forest of Bowland	03/08/88	11.2	524	13	71	282	0.0004	4
353169	Forest of Bowland	01/08/88	9.5	790	11	26	54	dry	dry
323394	Drigg	03/08/79	47.7	2285	2	18	58	0.0616	5.6
354576	Springfields	21/06/89	62.8	525	2	46	106	0.0012	8.2
354578	Springfields*	21/06/89							
354581	Springfields	21/06/89	67.8	620	1.8	47	108	0.0012	8.2
354586	Springfields*	21/06/89							
357016	Capenhurst **	31/07/89	2.1	530	45	26	70	soil	soil
357040	Capenhurst	31/07/89	11.6	517	7	202	208	0.0007	7.1
357075	Capenhurst	31/07/89	7.1	674	13	223	412	0.0012	7.1

* subsample numbers. ** soil sample.

2.2 PHYSICAL AND CHEMICAL SAMPLE PREPARATION

All samples were collected using the G-BASE sample collecting procedure (British Geological Survey, 1998) between 1979 and 1989. They were air dried and ground to a less than 50 μm powder using P5 agate planetary ball mills in the field laboratory (Wragg et al., 2000). Subsequent storage of archive material has been in the National Geoscience Data Centre (NGDC) at BGS Keyworth.

A twelve place CEMTM microwave digestion unit was used to dissolve the powdered samples. An approximate 0.2g sub-sample was accurately weighed into a clean PTFE microwave digestion vessel and 5.0 ± 0.1 ml of concentrated nitric acid (HNO_3) was added using a micro-pipette. The sample was allowed to stand for approximately one hour to allow oxidation of organic compounds present that might produce excessive heat and over-pressure in the microwave digestion unit. The vessels were then sealed and heated using the time/temperature/pressure program in Table 2:2. After cooling the resultant liquids and solids were washed into 60 ml LDPE pre-cleaned bottles using 45 ml of Milli-QTM quality water ($18\text{M}\Omega$), resulting in a final volume of 50 ml and a nitric acid concentration of 10% v/v. The aqueous sub-samples were stored in this way until required for analysis.

For quality control purposes when using the microwave digestion unit each batch of 12 consisted of, in addition to the G-BASE samples, at least one random duplicate G-BASE sample, one SDO-1 reference material (this is a shale type rock), one blank and one S15B G-BASE stream sediment in-house reference material. This last sample was always placed in position 1, the temperature and pressure monitored position, known to be susceptible to contamination. Thus 8 individual samples were produced per batch and 3 batches in all.

Table 2:2 Microwave digester program for acid extraction

STAGE	POWER (W)	RAMP TIME (min)	TEMPERATURE ($^{\circ}\text{C}$)	TEMPERATURE HOLD (min)	PRESSURE OF SYSTEM (psi)
1	1200	5	150	1	25
2	1200	5	175	2	60
3	1200	5	200	15	200

2.3 DETERMINATION OF ELEMENTAL URANIUM CONCENTRATIONS

All samples were further diluted by a factor of 500, except sample 323898 which was diluted 5000 times due to its high uranium concentration. Indium and Bi were added as internal standards at a concentration of $10 \mu\text{g l}^{-1}$. The elemental concentrations were determined using a VG PQ2+ ICP-MS instrument in scanning mode. The uranium response was measured as the $^{238}\text{U}^+$ ion and calibrated using a $50 \mu\text{g l}^{-1}$ SPEXTM multi-element standard containing uranium. A multi-element monitor solution of $10 \mu\text{g l}^{-1}$ and run blanks spiked with In and Bi were interspersed regularly throughout the analytical procedure. Data was post-processed to correct for sensitivity and zero point changes using the monitors and blanks. Matrix suppression effects were corrected for using the Bi internal standard.

2.4 OPTIMISATION OF THE ICP-QMS INSTRUMENT FOR THE DETERMINATION OF URANIUM ISOTOPE RATIOS $^{238/235}\text{U}$ AND $^{234/238}\text{U}$

The precision of uranium isotope ratios as determined by ICP-QMS is primarily limited by the counting statistics for the minor isotopes and instrument stability. Therefore, these isotope ratio measurements were made on the newer of the two ICP-QMS instruments at BGS, a VG PQ

ExCell. For optimal precision, the signal of the $^{238}\text{U}^+$ response must be maximised within the linear limitations of the detector system. Firstly, the instrument gas flows and ion lenses were tuned for maximum sensitivity of the $^{238}\text{U}^+$ ion (approximately 65 Mcps/ppm) and conditions are given in Table 2:3.

Table 2:3 ICP-QMS conditions optimised for $^{238}\text{U}^+$ sensitivity

(a) Lens settings

Extraction	LI	L2	L3	D1	Focus	Pole bias
-717	2.7	-72.7	-115	-24.1	24.1	-4.7

(b) Torch settings

Forward power (W)	Reflected power (W)	Horizontal	Vertical	Depth
1350	7	-90	41	386

(c) Vacuum and nebuliser pressures

Analyser (mBar)	Expansion (mBar)	Nebuliser (Bar)
5.1	1.7	2.5

The PQ ExCell instrument is fitted with a dual mode detector allowing simultaneous collection of analogue and pulse counting signals. For the isotope ratio measurements, only the pulse counting mode was used to avoid problems of cross-calibration. The pulse counting mode is linear to 2 Mcps providing the dead-time correction of the detector is accurately applied. Thus, the second part of the optimisation procedure was to establish the correct dead time for uranium. A series of uranium solutions with concentrations close to the linear limit of the detector were analysed with different dead-time correction values. The measured $^{238/235}\text{U}$ ratios were compared, and the optimal dead time value derived using the assumption that at the correct value the isotope ratio will be constant, despite changes in concentration. These results are given in Table 2:4 and a dead-time of 40 ns was chosen; this compares with a previous value of 35 ns. It is known that dead-time for a detector will change over its lifetime and Held & Taylor (1999) recommended that it be checked prior to isotope ratio measurements.

Table 2:4 Changes in $^{238/235}\text{U}$ isotope ratio with concentration and dead time.

Dead time (ns)	2ppb U	10ppb U	20ppb U	40ppb U
0	294	288	285	276
35	296	293	294	291
50	301	295	299	299
70	297	303	301	309

Note: This uranium does not have a natural isotopic composition.

The third parameter optimised was dwell time. This is the time the mass spectrometer sits at a particular mass, acquiring data. There are a number of competing factors limiting the choice of

dwelt time for each isotope: (i) relative abundance of the isotope i.e. counting statistics; (ii) time for the quadrupole to jump to a new mass position and settle; and (iii) noise sources in the plasma. The choice of conditions has been reviewed in detail by Begley & Sharp (1997). They concluded that to minimise (iii) the settle time should be as short as possible until data were limited by (i) and (ii). Three possible combinations of dwell time were tested (see Table 2:5) and dwell times of 5ms for $^{234}\text{U}^+$ and $^{235}\text{U}^+$ and 2.5 ms for $^{238}\text{U}^+$ were chosen.

Table 2:5 Variation in precision with different dwell times for different isotopes

	EXPERIMENT 1 *	EXPERIMENT 2 **	EXPERIMENT 3 ***
	$^{238} / ^{235}\text{U}$	$^{238} / ^{235}\text{U}$	$^{238} / ^{235}\text{U}$
MEAN	293.7	293.4	294.5
SD	6.1	2.8	3.4
% RSD	2.1	1.0	1.1

*EXPERIMENT 1 = U234/235/238 DWELL TIMES 5ms/5ms/5ms RESPECTIVELY

**EXPERIMENT 2 = U234/235/238 DWELL TIMES 5ms/5ms/2.5ms RESPECTIVELY

***EXPERIMENT 3 = U234/235/238 DWELL TIMES 10ms/10ms/5ms RESPECTIVELY

2.5 DETERMINATION OF URANIUM ISOTOPE RATIOS $^{238}/^{235}\text{U}$ AND $^{234}/^{238}\text{U}$ IN G-BASE SAMPLES

Using the total element concentration data and the measured sensitivity of the instrument test solutions were diluted to give either a $^{238}\text{U}^+$ response of approximately 1 Mcps or a minimum dilution of 500 times relative to the solid mass. Lower dilutions were felt to be inappropriate because of the likelihood of excessive total dissolved solids blocking the instrument interface, resulting in a severe loss of response with time. A chemical uranium standard was run every 5 samples to monitor instrument mass bias. This bias is the inherent systematic change in instrument sensitivity with mass and is known to vary with time and cone blockage. Solution uptake into the ICP was via an auto-sampler in the following manner: 2 minutes uptake and stabilisation; 50 integrations each of 10 seconds duration; and a 2 minute wash with 2% v/v nitric acid between solutions.

Data were post-processed in the following manner: (i) digestion blanks were checked and not found to be significant; (ii) $^{238}/^{235}\text{U}$ isotope ratios were normalised to the first uranium standard by interpolation between subsequent standards; (iii) $^{238}/^{234}\text{U}$ isotope ratios were normalised to 4/3 the $^{238}/^{235}\text{U}$ factor to take account of the relative mass difference; and (iv) the $^{238}/^{235}\text{U}$ and $^{238}/^{234}\text{U}$ isotope ratios were further normalised to the mean $^{238}/^{235}\text{U}$ values for the SDO-1 reference material that can be assumed to have a natural isotopic ratio. Quality control (QC) data derived from these procedures are given in Table 2:6.

The data are reported with precisions associated with the individual sample measurements presented as standard deviation (SD) and 2 standard errors of the mean (2sem). These 'internal' precisions allow confidence intervals on the reported mean to be calculated. For these isotope ratios, which are the mean of 50 integrations, the sem value is equivalent to a 95% confidence interval (Miller and Miller, 1993) of that mean ratio. They are particularly helpful in studies such as this where the precision of some sample measurements are limited by counting statistics, which are in turn limited by the uranium concentration being measured.

Table 2:6 Uranium isotope ratios and associated errors from QC samples

Sample	Mean	Std Dev	2sem	Mean	Std Dev	2sem
	U238/U235	U238/U235	U238/U235	U238/U234	U238/U234	U238/U234
Mean of 20ppb DU	300.2	3.4	0.13	60933	7491	300
Mean of 20ppb DU	300.4	3.6	0.14	58459	6589	264
Mean of 20ppb DU	300.6	3.9	0.16	59996	6038	242
Mean of 20ppb DU	299.9	3.7	0.15	64473	8101	324
Mean of 20ppb DU	300.2	3.3	0.13	60122	6112	244
Mean of 20ppb DU	300.0	3.9	0.15	62401	6968	279
Mean of 20ppb DU	300.1	3.6	0.15	59936	6374	255
Mean of 20ppb DU	300.5	4.6	0.18	58629	6422	257
Mean of means	300.2			60618		
2std. dev.	0.5			3990		
Mean of S15b/1	138.3	2.7	0.11	21278	3917	157
Mean of S15b/2	137.4	1.1	0.04	21332	3744	150
Mean of S15b/3	138.2	2.8	0.11	20082	5662	226
Expected from isotopic equilibrium	137.9			18383		
Mean of means	138.0			20897		
2std. dev.	1.0			1413		
Mean of SDO-1/1	137.3	1.5	0.06	29138	2356	94
Mean of SDO-1/2	138.1	3.8	0.15	29210	2396	96
Mean of SDO-1/3	138.1	0.3	0.01	30193	2201	88
Mean of SDO-1/4	138.0	3.1	0.12	29481	2659	106
Expected from isotopic equilibrium	137.9			18383		
Mean of means	137.9			29505		
2std. dev.	0.7			963		

3 Results and Discussion

3.1 COMPARISON OF LEACHED AND WHOLE ROCK URANIUM CONCENTRATIONS

The results for total uranium concentration (taken from the G-BASE database), leached uranium concentration, % recovery of the leachable uranium, $^{238/235}\text{U}$ and $^{238/234}\text{U}$ isotope ratios with their associated internal errors are given in Table 3:1, along with sample number and location details.

Figure 3:1 is a plot of $^{238/235}\text{U}$ isotope ratio versus extraction recovery (expressed as a percentage of the XRF/DNAA measured total concentration). The variation in the stream sediments can be seen to wholly depend on the classification of the sources of uranium. The extraction method chosen was expected to liberate uranium contained in hosts such as phosphate and organic compounds, the sheet lattice structure of clays and mica, or sorbed on to the surface of most mineral grains. It is unlikely to liberate uranium from the core lattice structure of major mineral forming grains such as feldspar, pyroxene or amphiboles. Resistate detrital minerals such as zircon will almost certainly remain untouched. If the zirconium concentration in the samples is taken as a proxy for the amount of these resistate minerals present (Table 2:1) it may be compared to the extraction efficiency (Table 3:1). No clear correlation is observed, but the very highest zirconium concentrations do have low percentage recovery. However, even if zircons containing 1000 mg kg^{-1} were present this would not account for the low proportion of leached uranium.

The “fuel cycle” stream sediment samples all have uranium extraction recoveries between 80-110%, which is comparable to the “natural” stream sediments, having a range of extraction efficiencies between 71-120%. This suggests that both sample groups have a high proportion of uranium in secondary minerals, or on sorption sites of other phases, that is readily leached. This may be attributed to in-stream precipitation processes rather than the physical transport of detrital lithological fragments from the catchment. Interestingly, the soil sample from Ellesmere Port has an extraction efficiency closer to that of the “industrial” stream sediment samples, rather than the fuel cycle stream sediment samples. Figure 3:1 shows that uranium was poorly extracted from all the industrial stream sediment samples compared to the reported XRFS results. However, there may be several contributory factors associated with this. Firstly, these samples had the lowest uranium concentrations of all those selected for analysis (Table 2:1), consequently differences between the two analytical methods are proportionally higher. Additionally, the presence of contaminants (Pb, Cd, Zn, Cu *etc.*) above background concentrations in these samples may cause increased analytical bias in the XRFS results through imperfect correction of interferences, which is compounded by the low concentrations of uranium in these samples.

However, in this study we should also consider the possibility that we are not observing the “true” degree of isotopic disequilibrium. These samples were only subjected to partial acid extractions and, where the extraction efficiency was significantly less than 100%, two scenarios must be considered. Preferential isotopic leaching of ^{234}U relative to ^{238}U , could have occurred, as ^{234}U could be removed more easily from the defect sites; this would imply that true bulk solid sample values of $^{238/234}\text{U}$ should be even higher. Alternatively, certain minerals may already have undergone preferential leaching of ^{234}U , e.g. clays, this would imply our values of $^{238/234}\text{U}$ should be lower for bulk samples as these secondary minerals are more completely digested. Inspection of Figure 3:2 shows no significant correlation between $^{238/234}\text{U}$ and extraction efficiency, suggesting neither of these effects is dominant.

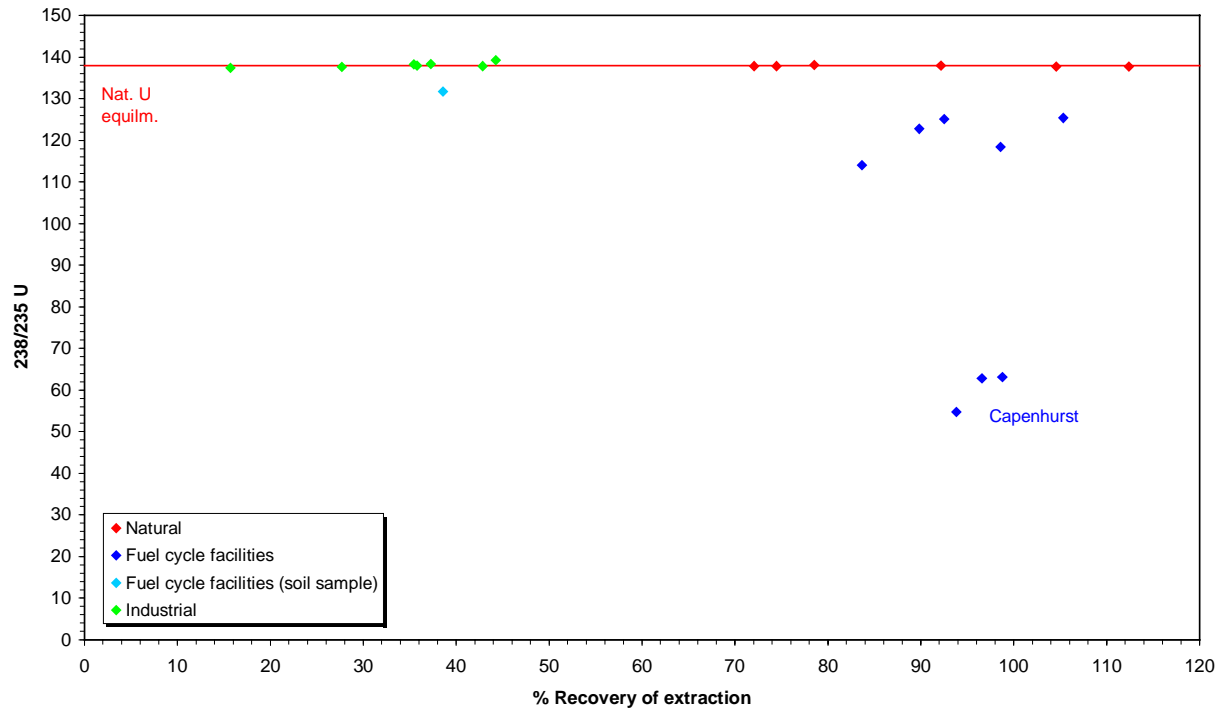


Figure 3:1 Plot of percentage uranium extracted by microwave digestion versus ²³⁸/₂₃₅U showing deviations from expected natural uranium isotope ratios

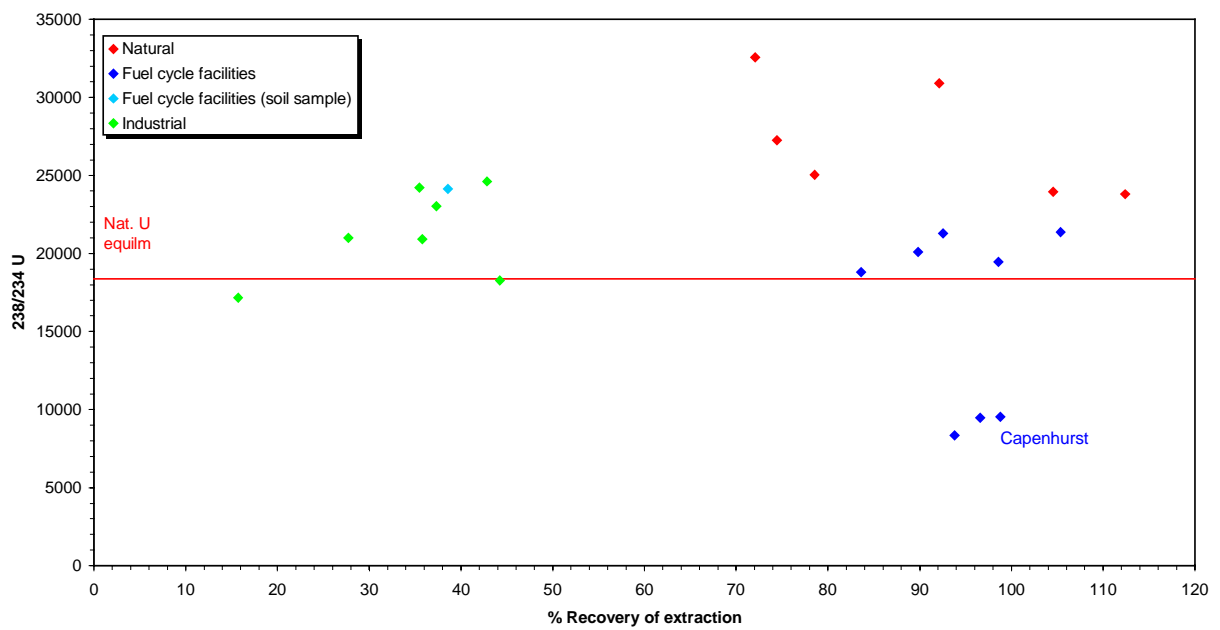


Figure 3:2 Plot of percentage uranium extracted by microwave digestion versus ²³⁸/₂₃₄U showing deviations from expected uranium isotope equilibrium

3.2 URANIUM ISOTOPE RATIOS IN G-BASE STREAM SEDIMENT AND SOIL SAMPLES

It should be noted that in Figure 3:3 the size of the data points is such that they are equivalent to twice the standard error of the mean (sem) internal measurements. The QC data on SDO-1 from Table 2:6 suggests that a 2 standard deviation (sd) external error based on full repeat digestion and analysis, is appropriate at the 0.5% confidence level for $^{238/235}\text{U}$ and the 3% confidence level for $^{238/234}\text{U}$. These errors will be improved in the samples containing anthropogenic fuel cycle uranium as the higher proportion of ^{235}U and ^{234}U will give rise to better counting statistics. However, in the samples with less than $10 \mu\text{g g}^{-1}$ extracted uranium (i.e. the “industrial” samples, Capenhurst soil sample and one of the Forest of Bowland samples (353169)), these errors will increase due to less than optimal counting statistics.

The $^{238/235}\text{U}$ is plotted against $^{238/234}\text{U}$ in Figure 3:3 where it is observed that the samples fall primarily into two groups: those with a constant $^{238/235}\text{U}$ ratio but variable $^{238/234}\text{U}$ ratio; and those falling along an apparent mixing trend with declining $^{238/235}\text{U}$ and $^{238/234}\text{U}$ ratios. Inspection of Table 3:1 shows that this division is wholly reflected in the origin of the samples. Those samples lying along the trend where $^{238/235}\text{U}$ is fixed and $^{238/234}\text{U}$ varies (Figure 3:3), from the “natural”, as expected, and “industrial” sites. Those samples which lie upon the apparent mixing trend between natural isotopic compositions and those modified by nuclear fuel industry processing, are all geographically associated with nuclear fuel industrial complexes. This suggests a varying degree of accumulation of uranium by these stream sediment samples from nuclear industry discharges. These factors will be discussed further in the subsequent sections of this report.

It should be noted that data from the study of the Crich area (Table 3:2) (Chenery et al., 2002, in prep.) has been included in Figure 3:3 for comparison with the data acquired in this study. These Crich stream sediment data are entirely consistent with wholly naturally derived uranium.

Table 3:1 Mean measured $^{238/235}\text{U}$ and $^{238/234}\text{U}$ isotope ratios and uranium concentrations in samples, with associated precision data

GBASE Sample	Sampling date	Location	Sample	$^{238/235}\text{U}$			$^{238/234}\text{U}$			U Concentration (ppm)		
				Mean	Std Dev	2sem	Mean	Std Dev	2sem	ICP-QMS found	XRFS total (expected)	% Recovery
357075	89/07/31	Capenhurst	Mean of 357075	54.8	0.7	0.03	8346	438	18	6.7	7.1	94
357040	89/07/31	Capenhurst	Mean of 357040dup	62.8	1.1	0.05	9471	366	15	11	11.6	97
357040	89/07/31	Capenhurst	Mean of 357040	63.0	3.2	0.13	9533	348	14	11	11.6	99
354578	89/06/21	Springfields sub-sample	Mean of 354578	114.0	2.3	0.09	18796	1039	42	57	67.8	84
354581	89/06/21	Springfields	Mean of 354581	118.5	0.9	0.03	19455	1141	46	67	67.8	99
323394	79/08/03	Drigg Beach	Mean of 323394	122.8	3.1	0.13	20091	1353	54	43	47.7	90
354576	89/06/21	Springfields	Mean of 354576	125.1	0.4	0.02	21303	1336	53	63	67.8	93
354586	89/06/21	Springfields sub-sample	Mean of 354586	125.4	1.3	0.05	21376	1297	52	71	67.8	105
357016	89/07/31	Capenhurst (soil)	Mean of 357016	131.7	1.2	0.05	24154	6131	245	0.8	2.1	39
356871	89/07/31	next to Shrops Union Canal	Mean of 356871	137.5	3.7	0.15	17162	2653	106	1.1	6.7	16
357300	89/08/21	Clatterbridge Hosp., Bebbington	Mean of 357300	137.6	0.9	0.03	20993	2957	118	1.7	6	28
357248	89/08/21	nr Irby, Wirral	Mean of 357248	137.8	1.2	0.05	24626	4466	179	1.5	3.4	43
356629	89/07/25	Keckwick Brook	Mean of 356629	137.9	0.8	0.03	20919	3312	132	1.8	5	36
356608	89/07/25	Preston Brook	Mean of 356608dup	138.2	1.3	0.05	24232	6230	249	1.4	4	35
356608	89/07/25	Preston Brook	Mean of 356608	138.3	4.0	0.16	23026	4675	187	1.5	4	37
356686	89/07/25	Keckwick Brook	Mean of 356686	139.3	0.4	0.02	18268	4920	197	2.2	5	44
323898	80/09/03	Cow Green	Mean of 323898	137.7	1.3	0.05	23811	1498	60	664	591	112
323898	80/09/03	Cow Green	Mean of 323898dup	137.8	6.2	0.25	23954	1498	60	618	591	105
353130	88/08/03	Forest of Bowland	Mean of 353130	137.8	1.4	0.05	27259	2098	84	8.3	11.2	74
352979	88/08/01	Forest of Bowland	Mean of 352979	137.9	0.8	0.03	32575	3550	142	7.8	10.8	72
352959	88/08/01	Forest of Bowland	Mean of 352959	138.0	0.9	0.03	30909	2288	92	15	16.7	92
353169	88/08/01	Forest of Bowland	Mean of 353169	138.1	3.1	0.12	25054	1844	74	7.5	9.5	79

Dup = duplicate digestion and determination

Table 3:2 Crich samples summary chemical and isotopic data.

GBASE Sample	Sampling date	Location	Sample	Mean	Std Dev	2sem	Mean	Std Dev	2sem	U Concentration (ppm)		
				U238/U235	U238/U235	U238/U235	U238/U234	U238/U234	U238/U234	ICP-QMS found	XRFS total (expected)	% Recovery
407703	01/07/96	Crich	407703	137.6	0.7	0.2	18218	1078	305	3.4	2.9	116
407719	01/07/96	Crich	407719	137.3	0.9	0.2	19064	1294	366	3.4	2.3	147
407727	01/07/96	Crich	407727	137.0	0.9	0.2	18128	1344	380	3.2	3.0	107
407729	04/07/96	Crich	407729	137.3	0.9	0.3	17867	1279	362	3.3	2.2	151
407778	04/07/96	Crich	407778	137.3	0.7	0.2	18078	1192	337	3.7	3.0	123
407796	01/07/96	Crich	407796	137.4	0.9	0.3	18222	1254	355	4.2	2.0	210
407950	01/07/96	Crich	407950	138.0	0.8	0.2	18288	1324	375	5.9	0.3	2372
407977	01/07/96	Crich	407977	137.7	0.7	0.2	18385	1490	421	5.4	5.0	108

Data from (Chenery et al., 2002, in prep.). Duplicate analyses have been averaged for presentation in this table.

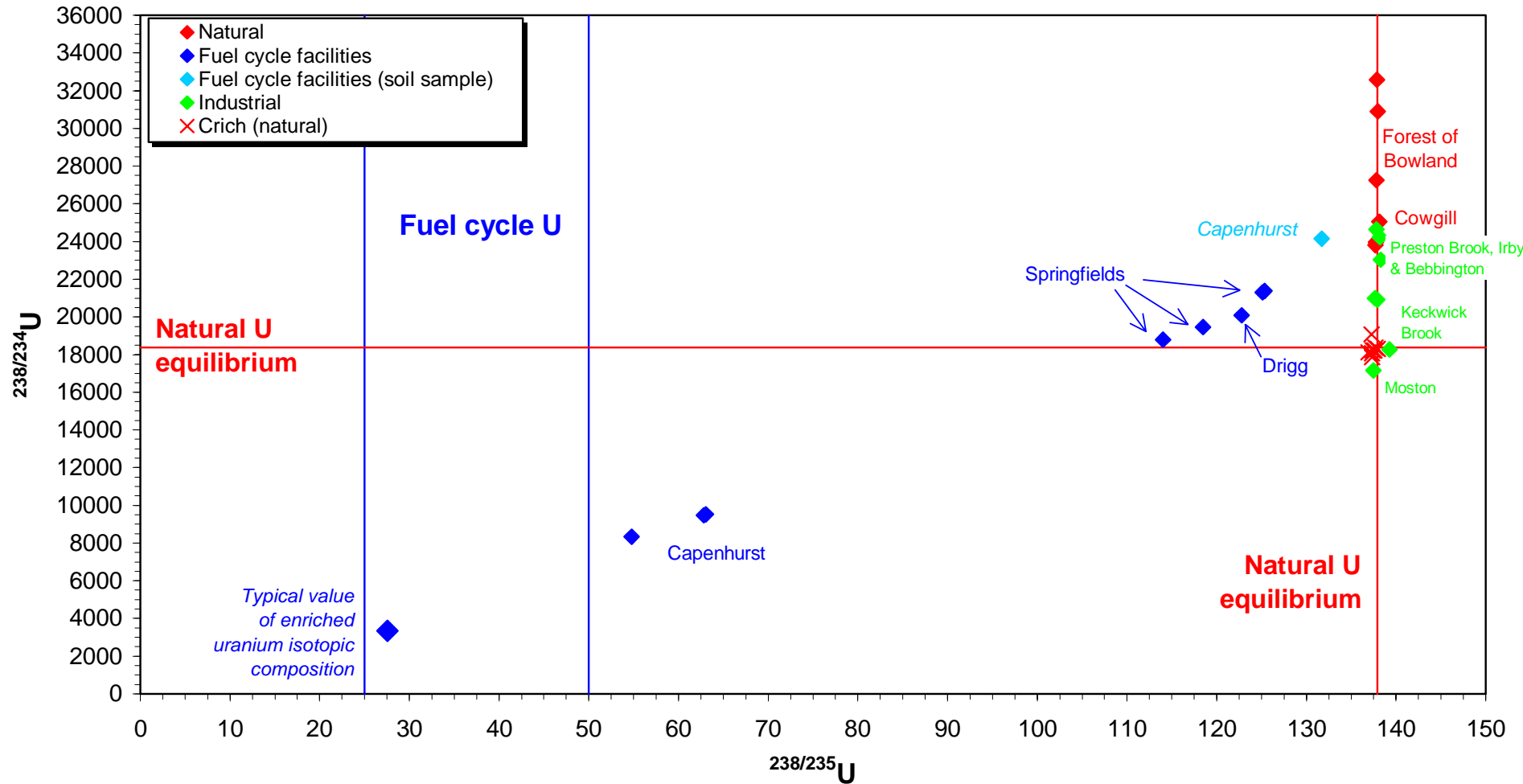


Figure 3:3 Uranium isotope data, measured during this study, for natural, industrial and nuclear fuel cycle associated sediment samples.

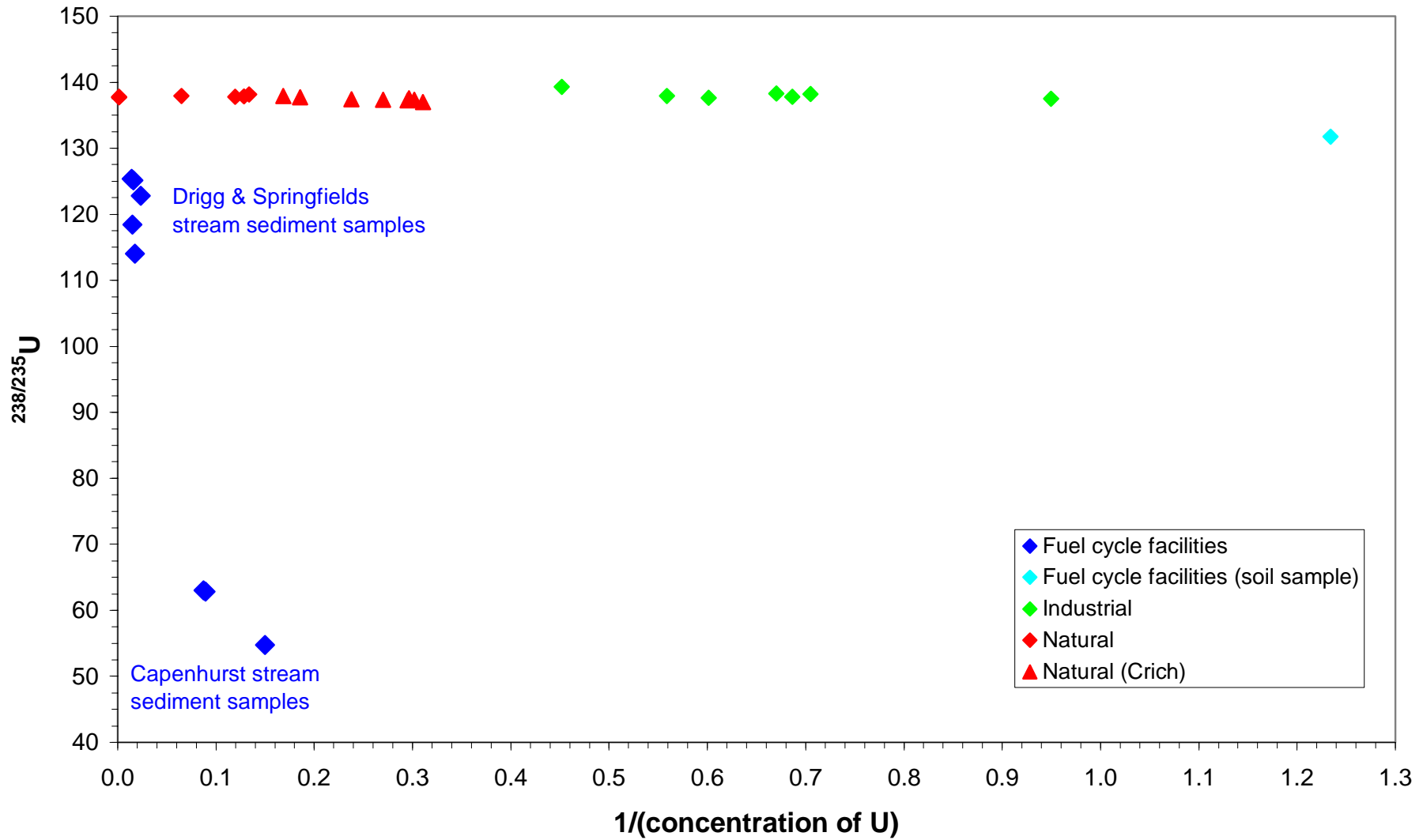


Figure 3:4 The reciprocal of uranium concentration plotted against the $^{238/235}\text{U}$ ratio.

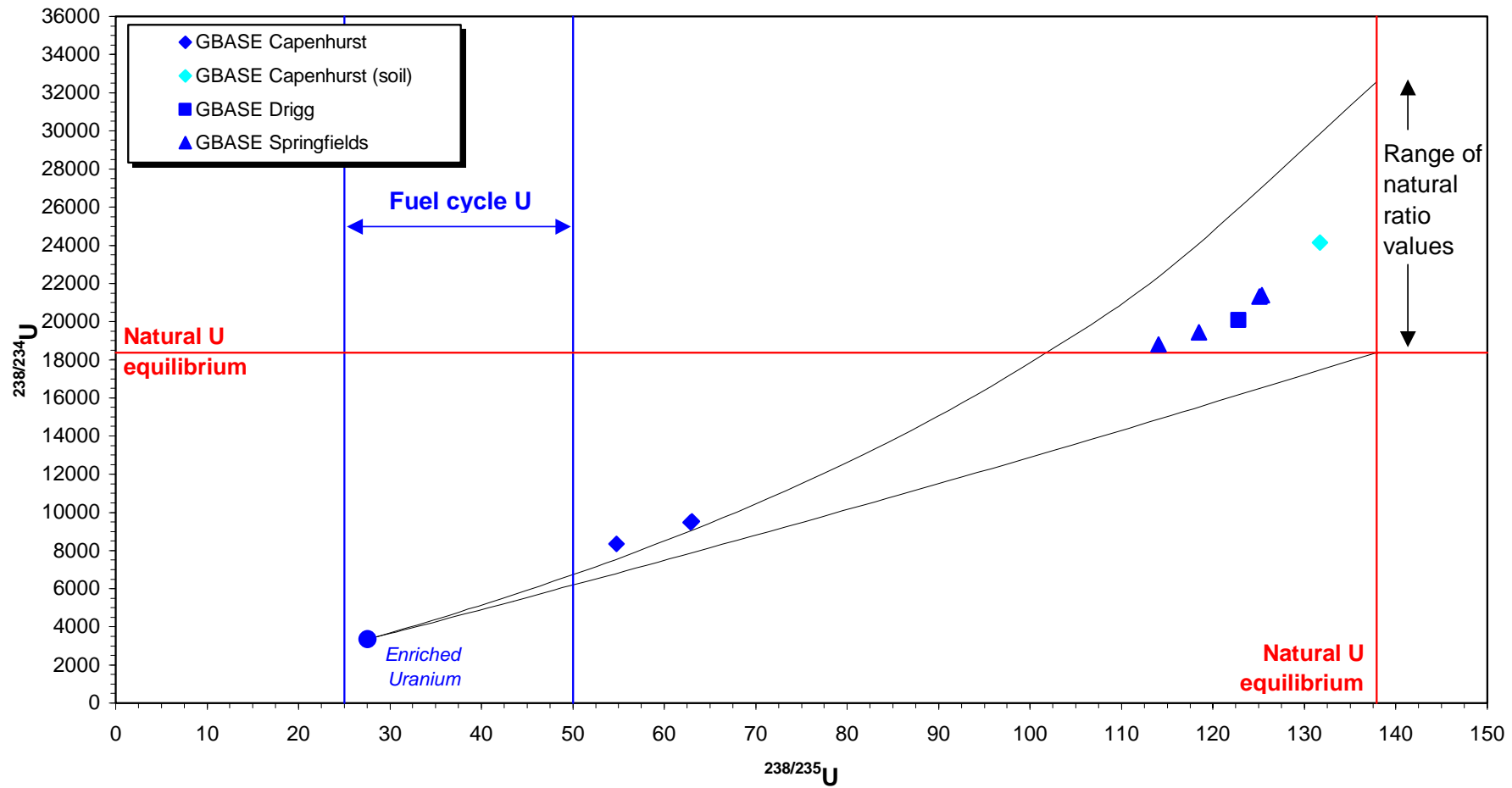


Figure 3:5 Theoretical mixing lines between enriched uranium and natural end-member compositions.

The two theoretical mixing lines representing the mixing of a suggested value for the composition of enriched uranium (WHO, 2001) with the maximum and equilibrium $^{238/234}\text{U}$ ratios measured in this study.

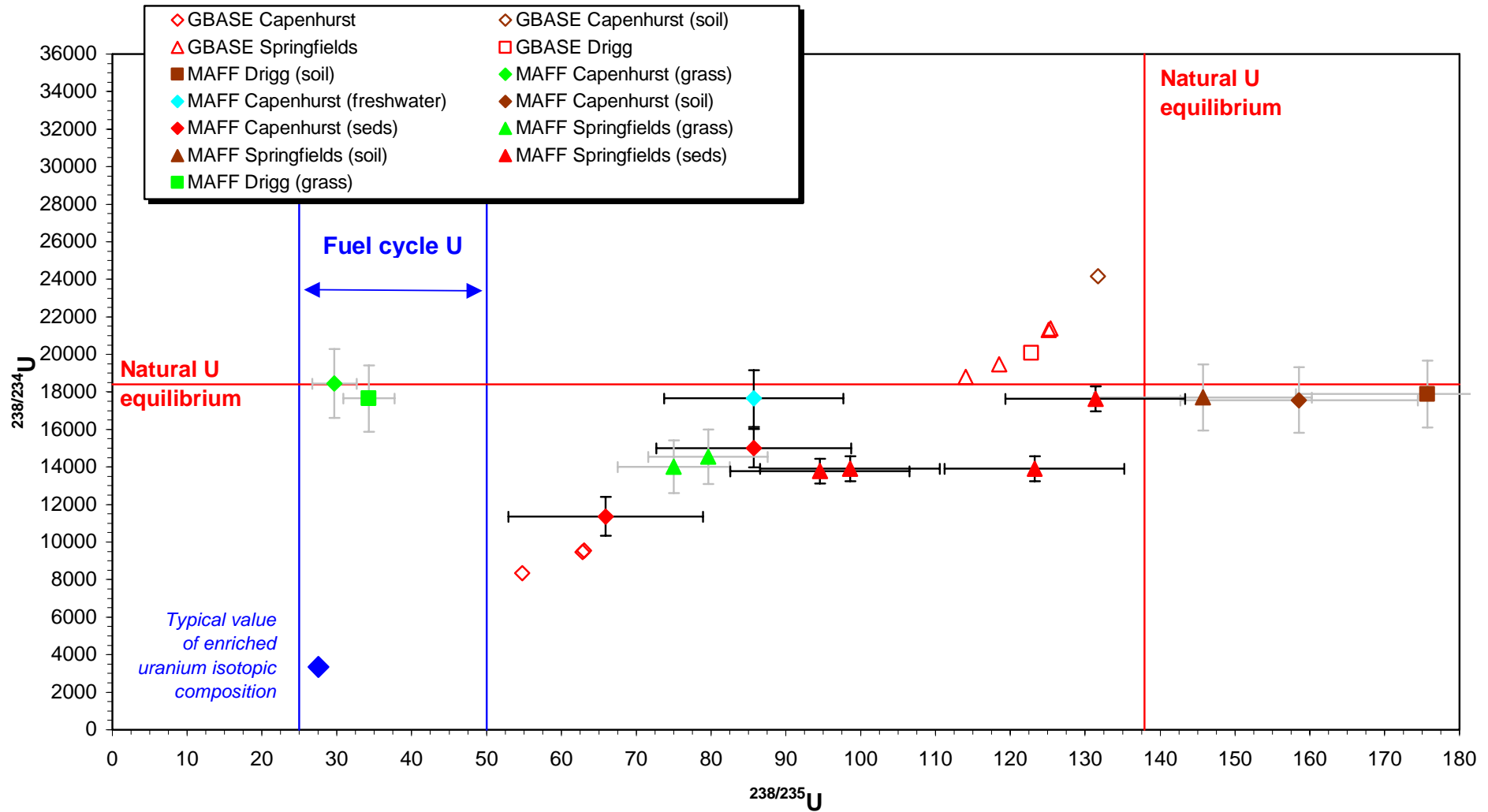


Figure 3:6 Comparison of G-BASE data with previously published environmental data

The black error bars show the reported analytical precision which appears to be approximately 10% of the reported mean. Thus, the data reported without such information have been assumed to have comparable errors (as the analytical techniques are constant) and are shown as grey error bars.

3.3 THE NATURAL VARIATION IN RATIOS $^{238/234}\text{U}$ AND $^{238/235}\text{U}$.

The variation in $^{238/234}\text{U}$ ratios, in particular for the “natural” samples, requires some explanation. ^{234}U is a daughter product of ^{238}U decay and from half-life data, in an undisturbed system, secular equilibrium should be reached within approximately 1 Ma. The resultant $^{238/234}\text{U}$ ratio is 18383. However, unlike $^{238/235}\text{U}$, this ratio varies in nature. As early as 1955 Russian scientists (Cherdyntsev and with Chalov P.I. et al., 1955) had proposed a leaching mechanism from damaged sites in crystal lattices (defects) to explain an excess of ^{234}U in river waters compared to ^{238}U . This ‘Szilard-Chalmers’ effect of preferential leaching was then demonstrated in laboratory experiments (Baranov et al., 1958). By 1962, this work had been confirmed by Thurber, (1962) who observed a small but significant excess of ^{234}U in seawater. The conventional explanation of this is that production of ^{234}U from ^{238}U produces lattice damage in host minerals by an alpha recoil effect. The ^{234}U sited in these produced defects preferentially, compared to ^{238}U , can then be liberated from the host mineral by fluids. The result of this process is reflected in $^{238/234}\text{U}$ ratios in water of less than 18383, and thus values greater than 18383 in the leached solids. Many of the control samples in this study display this effect, although it is not the case for the samples from Crich, which show no measurable enhancement in ^{234}U concentrations and are at secular equilibrium.

In a review of the chemistry of uranium and thorium series nuclides in rivers, Scott (1982) compiled a list of published $^{234/238}\text{U}$ activity ratios for river waters, suspended and bottom sediments (Table 1:1). This review demonstrated the range of $^{238/234}\text{U}$ activity ratios which may be found, and recent studies have shown that $^{238/234}\text{U}$ can be used diagnostically to distinguish differing sources of water in a catchment (Riotte and Chabaux, 1999) or to deduce sources of uranium contamination in an aqueous system (Zielinski et al., 2000).

3.4 THE PRESENCE OF FUEL CYCLE URANIUM IN G-BASE SAMPLES

The trend exhibited by the stream sediment samples associated with the nuclear fuel cycle facilities in Figure 3:3, can be seen to be consistent with mixing between natural and a hypothetical fuel cycle composition. In isotope geoscience it is conventional to show this type of relationship by displaying a selected ratio against the inverse of the sample concentration. This is presented in Figure 3:4 for the data collected during this study. Unlike the geochemical situation frequently encountered in such studies, where the end-members have both fixed ratio and fixed concentration values, which results in simple straight line relationships. Data in this study is more complex, e.g. Figure 3:4. Samples apparently affected by nuclear fuel processing lie on a trend, where those with the highest concentrations of uranium (Drigg & Springfields) have the lowest contribution of enriched uranium (EU), whilst those from Capenhurst (lower concentrations of uranium) have a greater influence from enriched uranium.

The use of isotopes for the calculation of the proportions of different sources of an element present in a sample is well established. This has been particularly widely used in source apportionment calculations of lead associated with mining (Whitehead et al., 1997), industrial and petrol (Monna et al., 1997) sources. Whitehead et al. (1997) and Monna et al. (1997) use simple calculations which were investigated in this study for application to the uranium isotope system, in addition to simple mixing based on a plot of $^{238/234}\text{U}$ versus $^{238/235}\text{U}$.

In seeking to undertake more quantitative modelling, using the results of this study to assess the contribution of fuel cycle waste products, several knowledge gaps combine to cause such fundamental difficulties as to make full quantitative modelling impossible. Although it is possible to construct simple mixing lines between the end-members (using a plausible, but theoretical enriched uranium end-member), as is shown in Figure 3:5. However, in doing this consideration must be given to the uncertainties associated with such simplistic modelling. Figure 3:5 reconfirms that it is reasonable to consider the stream sediment and soil samples

shown to contain a proportion of uranium which is associated with fuel cycle wastes, and that it may be desirable to use these lines to assess the contribution of such materials to the total uranium concentration.

To calculate the contribution of isotopically differing components within a system, information about each end-members isotopic composition is required. Whilst this study has provided information on the likely range of natural $^{238/234}\text{U}$ ratios in the stream sediments geographically associated with fuel processing facilities, information is not available on the nature of the waste stream source term (which would be required for each site, and with temporal variations recorded). The fuel used in different reactor systems will be of a differing degree of enrichment in ^{235}U , according to the original ore, the processing undertaken, and the final product. The fuel enrichment (percentage ^{235}U present) varies between 0.72% (natural abundance for Magnox reactor fuel) to 2% (Advanced Gas Cooled reactor) and 3% for a Pressurised Water Reactor (Greenwood and Earnshaw, 1997). Specific information for the sites close to G-BASE sample locations is not available to the authors, and included in the factors listed above affecting the composition of enriched uranium, will be any mixing (spatially and temporally) of various waste streams at processing, handling and storage sites prior to licenced discharge. This will introduce additional uncertainty in resolving the proportion of natural and anthropogenically modified uranium present in any sample.

For these reasons fully quantitative estimates of the proportion of fuel cycle uranium in the samples investigated in this study are not presented.

3.5 COMPARISON OF THE RESULTS WITH FUEL CYCLE ENVIRONMENTAL MONITORING DATA

3.5.1 RIFE data

The Radioactivity in Food and the Environment (RIFE) publication series (e.g. MAFF, 1989; 1996; 1999) were previously published by MAFF; they now fall under the auspices of DEFRA. These publications summarise the data collected as part of the ongoing monitoring programme around establishments within the research, industrial and defence nuclear industry (including disposal sites). The nuclear fuel facilities around which this study has determined uranium isotope ratios, all fall under the remit of the RIFE programme. There are several factors which need to be taken into account when comparing RIFE data with those of this study.

The RIFE results are quoted as “mean” or “max” values. Whilst the (arithmetic) mean results are shown to be related to specific numbers of samples in the results tables, inspection of the brief description in the analytical section, and of the footnotes to the table of results, would appear to suggest that where multiple samples have been collected they have often been bulked prior to analysis. The geographical distributions of these samples are shown in Figure 2:2, and the extent of their separation would suggest that comparing the data arising from these bulked samples with that generated by this study is not possible, other than in the most qualitative sense. Notwithstanding these comments, comparison has been attempted, as the RIFE data is the only nationally published dataset available of comparable sample media.

3.5.2 Comparison of RIFE data with this study

The comparison of G-BASE samples with those published in the annual MAFF reports is shown in Figure 3:6, for two selected years. Unfortunately, the data in the two reports used (MAFF, 1996; 1999) does not exactly correspond between years, with some sample types or locations not occurring in both publications. Additionally, it should be noted that they were collected in different years to the G-BASE samples selected for this study.

Conversion of the RIFE data, from the published activity ratios to atom ratios, allows its presentation in conjunction with the G-BASE samples apparently containing an enriched uranium component (Figure 3:6). It should be noted that the analytical errors associated with the RIFE data are far greater than those of the data produced for this study. Despite the larger errors (Figure 3:6), it may be observed that much of the RIFE data appears to lie along the same trend as that found for the G-BASE samples. Due to the difficulty in ascertaining the exact location of the samples from which the RIFE results are obtained (Figure 2:2), no numerical comparison between the RIFE samples and the results of this study has been attempted. Figure 3:6 shows that grass samples from Drigg and Capenhurst lie well off the trend of much of the data. No explanation can be offered for this, and it would be desirable to check for any reporting errors prior to producing an explanation of this apparent anomaly.

4 Conclusions and Recommendations For Possible Future Work

4.1 CONCLUSIONS OF THE CURRENT STUDY

The two aims of the current study have been successfully achieved. (i) It has been possible, using uranium isotope ratios, to observe anthropogenic uranium contamination of G-BASE stream sediments around known uranium fuel cycle facilities and expected natural values resulting from natural uranium 'hotspots'. (ii) These measurements were made using the BGS ICP-QMS facility in a 'fit for purpose' and cost-effective manner. Having achieved these aims, extension of this study would be both feasible and desirable.

It is accepted that data of a higher quality could have been produced using the NIGL-BGS multi-collector instruments, but it is unlikely that this could have been achieved in such a timely and cost effective manner. It should be noted that if BGS were to acquire a single collector magnetic sector ICP-MS system, higher quality data would be achievable, allowing samples with very small amounts of contamination to be identified but in similar timely and cost effective manner as this study.

4.2 POTENTIAL FUTURE WORK

This pilot study could be extended in a number of directions to increase our understanding of anthropogenic versus natural inputs. These are listed below in no particular order of priority.

- 1) Measure more of the G-BASE sample set from the geographical areas considered here, and try to discriminate the extent of anthropogenic contamination around the uranium processing facilities.
- 2) Extend the sample set to include River Mersey sediments collected as part of the BGS Estuarine Contamination project, close to the inflow of Rivacre Brook, draining the Capenhurst facility. The project also holds material from the River Ribble and its estuary sediments, which could be used to investigate the hypothesised accumulation of uranium in organic and clay rich sediments of that area (section 2.1).
- 3) Re-sample sites to determine whether the uranium concentration and isotopic profile has changed since the original sampling.
- 4) Further investigation of the samples used in this study:
 - (a) identification and mineralogical analysis of 'hot' particles contributing uranium;
 - (b) establish mineral phases or size fractions the anthropogenic uranium is associated with;
 - (c) assessment of the bio-accessibility of the uranium through PBET type tests;
 - (d) dissolution of the residual fractions where the uranium isotope ratio is anomalous, to study whether the residual fraction is acting as a sink / future source of the uranium in the system;
 - (e) investigation of other nucleogenic elements and isotopes that might be associated with the anomalous fuel cycle enriched samples.

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