CHAPTER 6

CHARACTERISING THE INFLUENCE OF ATMOSPHERIC INPUT

Traditionally, it has been assumed that local *in situ* mineral weathering represents the dominant source of heavy lithophile elements, like strontium, within the biosphere. However, strontium is also supplied to the biosphere by atmospheric deposition. Although solid rock formations and superficial geology can be mapped as discrete geographic units, weather systems are capable of transporting atmospheric aerosols over substantial distances, redistributing strontium across geological boundaries.

Atmospheric sources of strontium can be divided simplistically into dry and wet deposits. The dry deposition of atmospheric aerosols is driven both by gravitational settling, and by air turbulence and convention; particulate materials are also entrained by rainwater, both within clouds and below the cloud layer during precipitation (Kay-Berner and Berner 1987). Accordingly, wet deposits incorporate insoluble particulate matter, as well as soluble. Clearly, if a substantial proportion of the strontium cycled within a terrestrial ecosystem is of atmospheric origin, significant long-term geographic variation in the $^{87}Sr/^{86}Sr$ composition of atmospheric inputs may influence patterns of geographic biosphere variation.

Strontium is released from soils by various physical and chemical weathering processes. This is cycled though vegetation and animals, and ultimately enters the oceans as run-off in rivers. Numerous methods can be used to estimate the range of bioavailable $^{87}Sr/^{86}Sr$ values that are provided by soils and their parent materials. However, it is the composition of biologically-cycled strontium that is of most relevance to the archaeological applications of $^{87}Sr/^{86}Sr$ analysis. Although a comprehensive biosphere model would call for construction of regional, or even local cation budgets (Capo *et al.* 1998), data presented in Chapter 4 of this thesis suggest that – at least in lowland areas of the UK – geographic variation can be characterized by measuring vegetation or stream waters. The aim of this

chapter is to contribute to a 'first-order' understanding of the character of geographic variation in atmospheric deposition, and their immediate influence on the measurements that can be made to characterize biosphere variation within the UK. This Chapter reports the results of three experiments designed to assess the potential influence of variations in dry and wet deposition on biosphere values:

- Can we detect the effect of dust deposition in UK from volcanic eruptions in rainwater and vegetation?

- Does surface dust make a significant contribution to biosphere measurements under in normal conditions?

- What is the composition of rainwater over Britain?

6.1   The immediate impact of volcanic ash originating from the Eyjafjallajökull eruption (Iceland) in 2010

In 2010 volcanic ash produced by the Eyjafjallajökull eruptions on the south central coast of Iceland caused widespread and prolonged disruption to international air-traffic (2010). The explosive character of the eruptions, and atmospheric transport patterns over continental airspace contributed significantly to the response of the air authorities (Davies *et al.* 2010) and lead both the UK Health Protection Agency and the European Food Safety Authority to publish an advisory statements (EFSA 2010; HPA 2010). However, the eruptions themselves were by no means exceptional, in terms either of their duration or the volume of ash that they produced (Thordarson and Larsen 2007). Accordingly, it is not unreasonable to assume that such events could enhance the atmospheric deposition of strontium across the North-Atlantic region, and beyond.

On the 14th of April 2010 the eruption of the caldera beneath the Eyjafjallajökull ice cap resulted in the production of large quantities of very fine ash (Ilyinskaya *et al.* 2011). Ash production is thought to have peaked during the first week of activity and continued sporadically during the first two

weeks of May, but declined towards the end of the month (Petersen 2010). From April 14th–16th high pressure over the British Isles and low pressure over Scandinavia lead to the principal flow of the plume over central Europe in an SE direction from Iceland towards the Faroe Islands, and eastwards towards western Norway (Schleicher *et al.* 2012; Petersen 2010). The predicted patterns of dispersal suggested that ash was likely to be present across most of England, Scotland and Wales by 18:00 GMT on the 15th of April, moving approximately NE–SW (Met Office 2010). However, Devenish *et al.* (2012) report that the ash cloud was not detected above southern and SW England until the following day.

Iceland is a subaerial protrusion of the Mid-Atlantic ridge, formed by the continuous accretion of oceanic basalt. Siliceous volcanic dust derived from the primitive magma and re-worked Icelandic rocks may therefore have a low and highly characteristic $^{87}Sr/^{86}Sr$ composition. For example, biosphere $^{87}Sr/^{86}Sr$ values in the range of around 0.7060 have been reported from Iceland itself (Price and Gestsdóttir 2006). Strontium isotope compositions such as these would distinguish Icelandic volcanic ash from biosphere values associated with the majority of geological formations comprising the British Mainland (Evans *et al.* 2010b). Thus, the events of 2010 provided an opportunity to assess the impact of atmospheric dust on the biosphere. To take advantage of this, an experimental plot was established in the east midlands of England to measure the $^{87}Sr/^{86}Sr$ composition of rainwater and grass cuttings collected during and after the eruption in an attempt to ascertain whether a major dust contribution could be detected within UK.

6.1.1 Sample collection

On the 16th of April 2010 a 5 × 5 m experimental plot was established, in a location adjacent to the British Geological Survey weather station at the Kingsley Dunham Centre in Keyworth, Nottinghamshire (65 m OD, NGR: 462050, 331620); the grass growing in this area had not been cut since the previous year. Samples of grass were collected on a daily basis, between 10:00–11:00 GMT, from 16th of April to the 20th of March 2010. Using powder

free examination gloves, the leaves were picked (excluding roots) across the area to produce one composite vegetation sample for each day of the study. On each occasion sufficient material was collected to loosely fill one 125 × 250 mm Kraft paper sample bag and allow air circulation within. The samples were air-dried within each bag for 3–5 days before processed for analysis, following standard procedures (Chapter 3).

Throughout the same period, rainwater was collected in an acid leached one litre Nalgene™ FEP bottle fitted with a 15 cm diameter HDPE funnel. This was placed within the same experimental plot within which the grass samples were collected. Collected rainwater was removed from the bottle on a daily basis, again between 10:00–11:00 GMT (except if it was raining at the scheduled time of collection). If rainfall was on-going at this time, the collector was not emptied until rainfall either ceased, or until next dry day, whichever was the sooner. Six rainwater samples were obtained throughout the sampling period. When collecting rainwater, care was taken to avoid the transfer of exogenous material to the collector, minimise solar gain (and thus reduce evaporation the from the collection bottle), and reduce potential cross-contamination between rainwater samples.

The mouth of the rainwater collection funnel was located at 35 cm from the ground-level and shielded from back-splash using a modified plastic bucket and a skirt of polythene sheeting. The collection bottle was insulated using a block of polystyrene foam. Prior to being emptied the mouth of the funnel was covered with Parafilm™, and the collector transferred to clean conditions. The sample was then decanted into to an acid-leached, rinsed and dried HDPE Nalgene™ bottle of appropriate size. The samples were acidified with quartz distilled nitric acid (1 % w/w) and stored under refrigerated conditions. Unless it was raining, the collection apparatus (funnel and bottle) was rinsed thoroughly each day with deionised water and allowed to dry under clean conditions. Once reassembled under clean conditions, the mouth of the funnel covered until the collector was placed back in position.

6.1.2 Results

Figure 6.01 (overleaf) shows the $^{87}Sr/^{86}Sr$ composition of grass samples from the beginning (16/04/2010), middle (03/05/2010) and end (20/05/2010) of the collection period and their strontium concentrations. Two additional samples collected on 24/04/2010 and 13/05/10 were also analysed to bracket the period during which rainfall took place. To gain an indication of the $^{87}Sr/^{86}Sr$ of the strontium provided by wet deposition all six rainfall samples, collected from 25/04/2010–12/05/2010 were subject to analysis. Having achieved a successful $^{87}Sr/^{86}Sr$ measurement for the rainwater collected on 25/04/2010, the five remaining rainwater samples were spiked with a known quantity of a ^{84}Sr enriched tracer solution (Oak Ridge Dilute Sr) prior to dying-down, so that strontium concentrations could be obtained by isotope dilution. All samples (grass and rainwater) were prepared and analysed following the standard methods outlined in Chapter 3 and the results are fully documented in Appendix C.

Replicate analyses of the NIST SRM 1515 (Apple Leaves) by ID-TIMS (n = 20) has returned a relative standard deviation for the determination of for $^{87}Sr/^{86}Sr$ composition in vegetation samples that is equivalent to ± 0.00005 (2 RSD) across the range of biosphere $^{87}Sr/^{86}Sr$ values reported in this thesis (Chapter 3). On this basis, the difference in the $^{87}Sr/^{86}Sr$ compositions of consecutive samples grass does not exceed the best estimate of external precision available to the current study. However, there is a gradual increase in $^{87}Sr/^{86}Sr$ of the grass. The concentrations of strontium in the grass samples are consistent with those reported for samples of similar material provided by the GEMAS survey (Chapter 5), which ranged from 7.2–25 μg/g and provide a mean strontium concentration of 12 ± 9.7 μg/g (2 SD, n = 15). However, there is an apparent, decrease in the concentration over the experimental period.
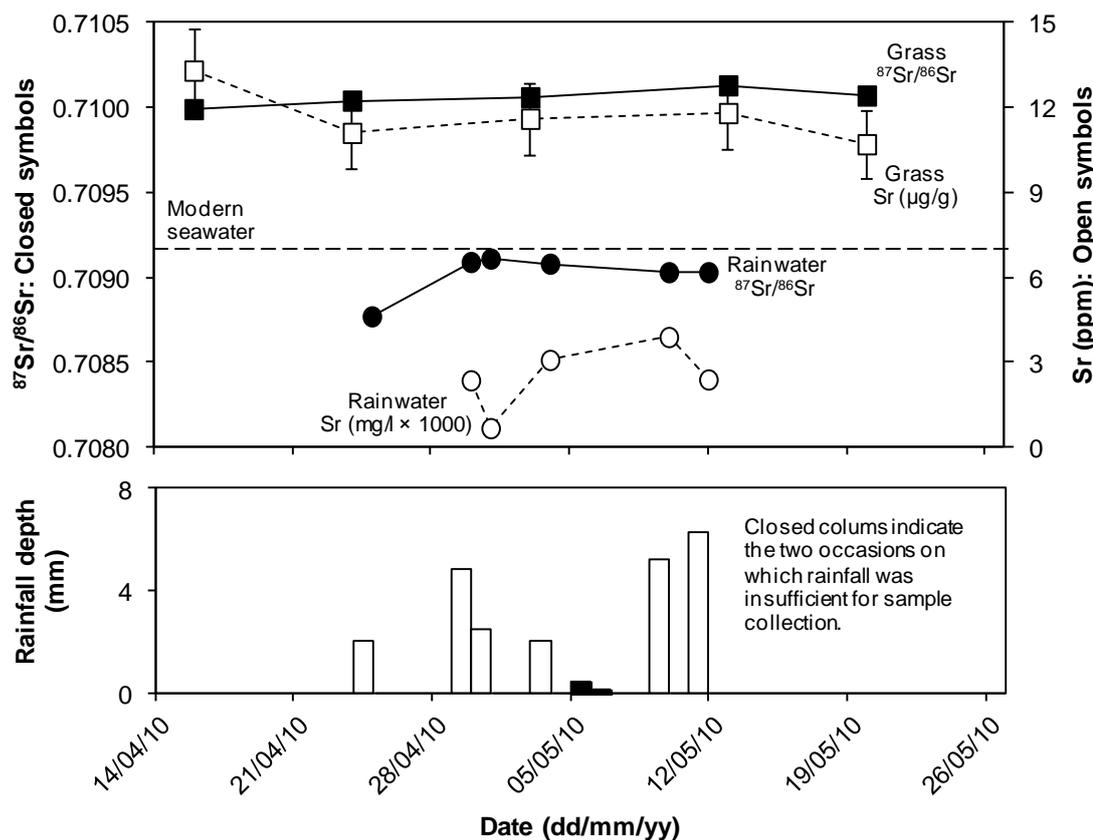
Figure shows the $^{87}Sr/^{86}Sr$ data for Grass and Rain samples on a time-related axis (collection date). Strontium concentrations are also plotted on a secondary y-axis. In grass these are shown in units of µg/g, and to fit the rainwater data on the same axis concentrations are shown as mg/l × 1000 (equivalent to µg/l). Rainfall depth (mm) over the experimental period is recorded in the form of a bar chart, using meteorological data provided by the British Geological Survey (Shepherd pers. comm.). Rainwater was collected on six occasions and the results of the $^{87}Sr/^{86}Sr$ analysis of grass and rainwater are documented fully in Appendix C.

Figure 6.01: Line and bar chart showing the results of the $^{87}Sr/^{86}Sr$ analysis of Grass and Rain samples collected from 25/04/2010–12/05/2010 (documented in Appendix C).

The $^{87}Sr/^{86}Sr$ compositions of all the rainwater samples fall below that of seawater, which is likely to represent a significant influence on rainwater chemistry within the British Isles. This suggests the inland wet deposits are influenced by non-marine sources of strontium, with a lower $^{87}Sr/^{86}Sr$ composition than that of seawater. Despite evidence of variation in strontium concentrations, rainwater collected after the 25/04/2010, appears to achieve some level of isotopic stability around a mean $^{87}Sr/^{86}Sr$ value of 0.7091 ± 0.0001 (2 SD, N = 5). Thus, there is no evidence of covariance between strontium concentration and $^{87}Sr/^{86}Sr$ composition. The first rainwater that was collected during the experimental period fell only shortly after the Eyjafjallajökull volcano had been at its most effusive, and the $^{87}Sr/^{86}Sr$ composition of this sample is significantly lower than any other.

However, a $^{87}Sr/^{86}Sr$ composition of 0.7088 is not low enough to rule out the influence of non-volcanic sources of strontium that are present within the UK, such as Mesozoic marine carbonates (Banner 2004).

6.1.3 Discussion

In the current study, un-washed grass samples were analysed in order to assess the influence of the deposition of atmospheric aerosols on leaf surfaces. Although atmospheric deposits of volcanic dust could elevate the exposure of herbivores to strontium, evidence gained from the study of radioactive fall-out suggests that particulate material can also be washed rapidly from fodder crops during periods of rainfall (Madoz-Escande *et al.* 2005). A potential upward trend in the $^{87}Sr/^{86}Sr$ composition of grass, from 0.7100–0.7101 between 16/04/2010–13/05/2010 could conceivably reflect the removal of volcanic dust that had been deposited following the most effusive period of the eruption, prior any rainfall (Figure 6.01). However, this represents a somewhat subtle inflection. The mean $^{87}Sr/^{86}Sr$ composition of grass samples analysed from the current study is 0.7101 (n = 5) with a 2σ interval of ± 0.0001 (2 SD). Similar numbers of samples (n = 3–6) collected above specific geological divisions of the biosphere, but at a wider geographic scale, have provided mean values with standard deviations 3–9 times greater in magnitude (Chapter 4).

At a national scale, based on the estimates of Evans *et al.* (2010b), biosphere $^{87}Sr/^{86}Sr$ values in the region in which the current study was undertaken are likely to vary across a relatively wide range, from approximately 0.7090–0.7100. However, the broad biosphere package presented by the authors (*ibid.*) comprises a range of variable geological formations. Evans *et al.* (2010a) cite stream water data collected from catchments, located largely above Triassic mudstones similar to those underlying the Keyworth site, with a mean $^{87}Sr/^{86}Sr$ composition of 0.7097 ± 0.0012 (2 SD, n = 29). Accordingly, in terms of regional and local biosphere $^{87}Sr/^{86}Sr$ values, the level of variation in grass composition (Figure 6.01) can be considered to be highly consistent.

The initial explosive character of the Eyjafjallajökull eruptions and the large quantities of very fine, powdery ash that were produced during the first week of activity were caused by the interaction of the magma with glacial melt-water (Ilyinskaya *et al.* 2011). Although it has been assumed that the ash is likely to have had a basalt-like $^{87}Sr/^{86}Sr$ signature, contact with melt-water may have resulted in a less distinctive ash $^{87}Sr/^{86}Sr$ composition. Gislason *et al.* (2011) report only small differences in strontium concentration between the ash produced during the initial phases of the Eyjafjallajökull eruption (330 mg/kg) and the later magmatic ash (328 mg/kg). However, to date it has not been possible to obtain an appropriate sample of ash from Iceland, or from the UK to use as an isotopic control. Therefore, in order to assess the range of $^{87}Sr/^{86}Sr$ values obtained from rainwater as part of the current study, it necessary to consider the wider patterns of long-range dust transport, which may contribute to baseline wet-deposition within the UK.

Globally, terrestrial dust accounts for around 1700 Tg/A of atmospherically transported material (Jickells *et al.* 2005). However, climate simulations indicate that global dust deposition varies geographically by over six orders of magnitude, and that – at a predicted 0.5–2.0 g/m^2/A – the British Isles are located at the lower limit of that range (Mahowald *et al.* 2006b). In contrast they fall within the highest end of the estimated global range for the terrestrial deposition of sea salts, at 10–50 g/m^2/A (Mahowald *et al.* 2006a). This is a function of the northerly latitude of the British Isles and the exposure of the archipelago to westerly Atlantic weather systems. Globally, atmospheric dust is dominated by African material derived from sources within the Sahara–Sahel 'dust corridor' (Koren *et al.* 2006 ; Moreno *et al.* 2006). This strongly influences the radiogenic North African 'dust domain' described by Grousset and Biscaye (2005). However, the necessary leaching process needed to obtain a distinctive carbonate-free $^{87}Sr/^{86}Sr$ dust fingerprint (Grousset *et al.* 1992 ; Rognon *et al.* 1996) also results in the removal of the exchangeable strontium prior to measurement (cf. Tessier *et al.* 1979).

Due to the low level of deposition of atmospherically transported dust from the continental dust-belt within the UK, the potential influence of seawater strontium and the manner in which atmospheric dust is 'fingerprinted', global dust provenance studies are of little value when attempting to characterise the influence of dust on the biosphere. However, rainwater data collected across France suggest that the $^{87}Sr/^{86}Sr$ compositions of wet deposits vary geographically on a sub-continental scale, in response to regional dust sources Négrel *et al.* (2007). The authors (*ibid.*) cite $^{87}Sr/^{86}Sr$ values for samples collected near Paris that range from 0.7085–0.7089: a region underlain by Mesozoic sediments similar to those present in southern and central England. Similar values have been shown to result in Israel (Herut *et al.* 1993) and other areas of the Mediterranean (Ben-Othman *et al.* 1997) from the influence of Mesozoic carbonates and seawater. Accordingly, although the rainwaters collected during the current study have $^{87}Sr/^{86}Sr$ compositions lower than that of modern seawater, it is not necessary to invoke a volcanic end-member.

6.1.4 Conclusions

Rainwater collected as part of the current study shows some level of short-term stability in $^{87}Sr/^{86}Sr$ composition over the collection period. However, the composition of these samples is not sufficiently low to confirm the presence of a volcanic end member. However, the ranges of values are consistent with those reported from other parts of the world where wet deposits may contain material derived from Mesozoic sediments and modern seawater. The $^{87}Sr/^{86}Sr$ composition of grass shows no evidence of co-variance with rainwater. Although, there is a slight upwards inflection in the $^{87}Sr/^{86}Sr$ composition of grass during the first four weeks of the study, this is not sufficiently great to rule out variation due to ambient heterogeneity, and cannot be considered to be significant in terms of the level of variation recorded in vegetation samples reported in Chapter 4.

6.2   Comparison of the isotopic composition of woody material and accompanying foliage

Wood was used in Chapter 4, to characterise biosphere $^{87}Sr/^{86}Sr$ variation across a range of geological formations. All of the outer surfaces were removed from these samples, so that only the bioavailable strontium incorporated either by root or foliar uptake was analysed (Chapter 3). In the Section 6.1 it was shown that, using the methods of bulk analysis reported within this thesis (Chapter 3), a one-off, dust-producing event that occurred in 2010 did not result in any immediate measurable effect on the bulk $^{87}Sr/^{86}Sr$ composition plant material. However, if atmospheric aerosols are able to accumulate on plant leaves over time, either as dried-down salts or particulate matter, the $^{87}Sr/^{86}Sr$ values associated with un-washed foliage may be different to those supplied by wood. Arguably, leaf material may make a more direct contribution than wood does, to the strontium that is cycled with the biosphere. That is, foliar strontium may be rapidly cycled, either through annual leaf-fall or through the consumption of foliage by animals, whereas the strontium that is sequestered by wood may represent a temporary loss from the system. Accordingly, the use of wood for biosphere characterisation could introduce a significant method-bias.

As described previously (Chapter 3), only a small proportion of the vegetation samples collected by G-BASE project in 2007 provided both woody material and foliage from the same sampling site. However, enough material was present within the sample archive to provide at least one pair of samples – woody material (Wood) and foliage (Leaf) – from a site within each of the seven geological divisions of the biosphere identified in Chapter 4. In this section, un-washed Leaf samples are used to assess whether exogenous deposits are likely to bias the analytical outcomes previously reported in this thesis. The additional samples were prepared and analysed following the standard methods outlined in Chapter 3. The resulting data make it possible to ascertain whether Wood and Leaf samples obtained from the same site might provide different isotope compositions due either to: A)

the presence of domains of differing ^{87}Sr/^{86}Sr composition within the structure of the plant tissues; B) exogenous surface deposits on leaves, such as local soil, fertilizer or exotic atmospheric aerosols.

6.2.1 Results

Table 6.01 shows the results of the analysis of the seven paired Wood and Leaf samples collected from sites underlain by a range of lithologies. The underlying outcrops include the Chalk, and the limestones and mudstones which fall within the seven chrono-stratigraphic groups identified within Chapter 4. Consistent with previously published data (e.g. Reimann *et al.* 2007a and 2007b) the Leaf samples contain strontium in substantially greater concentrations than the equivalent Wood sample from the same site. However, there is no correlation between strontium concentration and ^{87}Sr/^{86}Sr composition. Moreover, any small off-set in ^{87}Sr/^{86}Sr composition between Wood and Leaf does not reflect the magnitude of the differences in strontium concentration between the two sample media (Figure 6.02, overleaf).

Table 6.01: Results of ^{87}Sr/^{86}Sr analysis of paired Wood and Leaf samples presented in ascending order of Wood composition.

G-BASE number	Formation	Wood		Leaf		Difference
		^{87}Sr/^{86}Sr	Sr (µg/g)	^{87}Sr/^{86}Sr	Sr (µg/g)	^{87}Sr/^{86}Sr
461598	Gault formation	0.70790	10.5	0.70794	53.5	0.00006
461545	Lower Chalk*	0.70804	6.07	0.70810	38.0	0.00006
461492	Kimmeridge Clay	0.70873	3.68	0.70878	28.2	0.00005
461548	Purbeck Limestone	0.70875	18.2	0.70882	106	0.00007
461258	West Walton formation	0.70947	19.5	0.70955	117	0.00008
461084	Cornbrash (Great Oolite)	0.70924	3.28	0.70926	22.7	0.00002
461277	Oxford Clay (Peterborough member)	0.71040	10.1	0.71047	40.3	0.00007

*West Melbury, Marly Chalk formation (glauconitic marl).
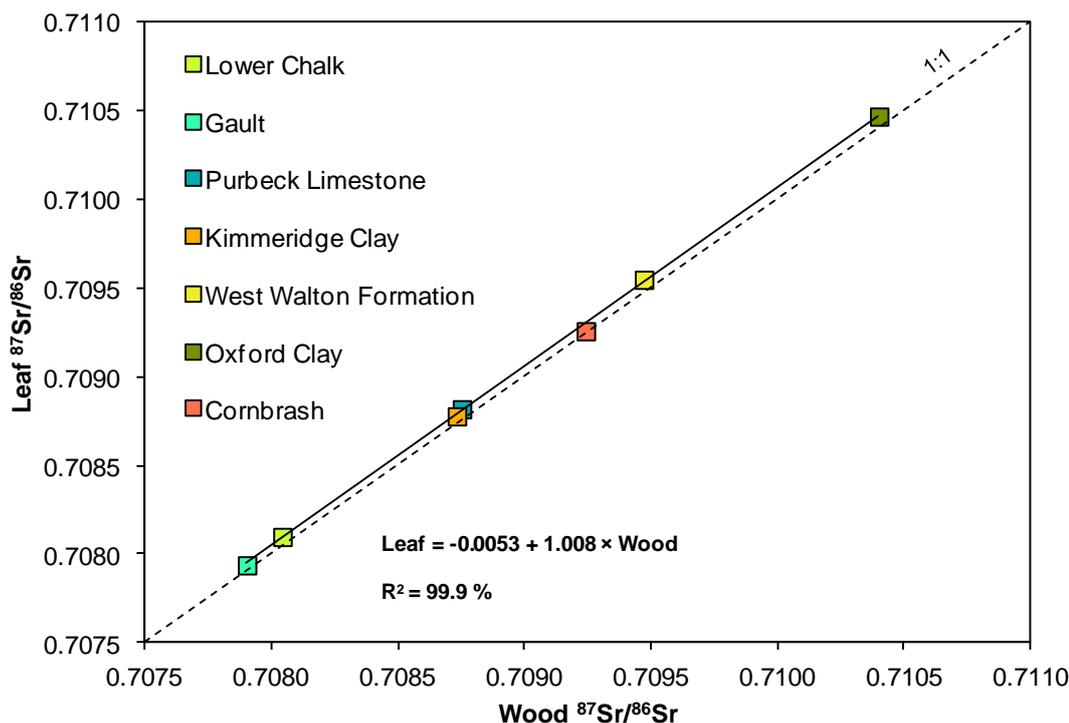
Estimated standard deviation (± 2 SD) in the ^{87}Sr/^{86}Sr composition of vegetation samples, based on replicate analysis (n = 20) of NIST SRM 1515 (Chapter 3), is approximately equivalent to the height of each symbol (see Chapter 3). Regression analysis was undertaken without error assignment.

Figure 6.02: Scatter plot showing the linear regression (ordinary least squares) of the ^{87}Sr/^{86}Sr composition of G-BASE Wood versus Leaf samples.

As reported in Chapter 3, replicate analyses of the NIST SRM 1515 (Apple Leaves) by ID-TIMS has returned a relative standard deviation for strontium concentration of approximately ± 11 % (2 RSD, n = 18), and a relative standard deviation for ^{87}Sr/^{86}Sr composition (2 RSD, n = 20) that is equivalent to ± 0.00005 across the range of values reported in Table 6.01. The level of variation in ^{87}Sr/^{86}Sr composition of the standard suggests some degree of heterogeneity is present even within this well-mixed sample. The difference in the ^{87}Sr/^{86}Sr compositions of the Wood and Leaf samples from each site cannot be considered to be significant. Linear regression analysis (ordinary least squares) of Leaf versus Wood confirms that the ^{87}Sr/^{86}Sr data provided by the two sample media are highly correlated (Figure 6.02). The slope of the regression line – calculated as 1.008 ± 0.010 (1 SE) – and the R^2 value of approximately 100 % show that the linear model fits the data exceptionally well. The value of the constant is -0.0053 ± 0.0072 (1 SE), which is not significantly different from zero.

6.2.2 Discussion

The $^{87}Sr/^{86}Sr$ compositions of Leaf and Wood samples are highly correlated (Figure 6.02). Given the level of variation between sample sites, the two sample media can be considered to be indistinguishable within error. As there is no evidence of any significant random or systematic difference between the $^{87}Sr/^{86}Sr$ composition of the Leaf and Wood samples, it can be assumed that the high strontium concentrations reported in Leaf samples with respect to Wood represent a metabolic difference between two sample media that draw strontium from the same source. As it is likely that the Leaf samples incorporate at least some exogenous material, these data suggest that within the limits of measurement:

A. The quantity of strontium provided by exogenous surface deposits is so small that that it has no significant influence of Leaf composition.

B. Exogenous surface deposits are dominated by local dust sources that are isotopically indistinguishable from locally biologically cycled strontium.

Trees and all other vascular plants transport nutrients from their roots to their leaves by the evaporative process of transpiration. Under natural conditions, positive root pressure frequently leads the appearance of drops of xylem sap on the tips or edges of the leaves (other than confers), due to positive root pressure (Pallardy 2008). This is referred to as guttation. Accordingly, even if exogenous strontium is able to accumulate on leaf surfaces, a mechanism exits which may be capable of diluting such material with the soluble strontium contained by plant fluids.

Although direct comparisons of the $^{87}Sr/^{86}Sr$ composition of un-washed foliage and internal plant tissues are not widely available in the literature, the chemical and isotopic contrast between 'throughfall' precipitation – collected under a tree canopy – and directly deposited rainwater is used to study nutrient cycles within mature forested watersheds (Capo *et al.* 1998). These data provide an indication of the provenance of the

strontium that is transferred to rainwater during foliar interception. Samples are collected in order to characterise of the rate of nutrient inputs and losses within what Åberg *et al.* (1989) refer to as the 'soil–water–vegetation system'. This work has largely been undertaken in base-depleted, upland environments that are sensitive to atmospheric influences, both in terms of the acidification of the soil environment and the input of atmospherically transported strontium.

Using samples collected over one year, Bailey *et al.* (1996) report that in mixed woodland in the White Mountain National Forest (New Hampshire, USA) the strontium in throughfall was derived largely from canopy leaching, rather than the removal of accumulated atmospheric deposits. That is, throughfall closely resembled biomass $^{87}Sr/^{86}Sr$ values – i.e. wood and foliage – rather than rainwater (*ibid.*). Stream waters also provided a consistent range of values throughout the year, which resembled those of wood and foliage. In a similar study undertaken over a shorter period, Graustein and Armstrong (1983) estimate the $^{87}Sr/^{86}Sr$ composition of the foliar contribution to throughfall, under the assumption that any increases in strontium concentration were caused by foliar transfer and not by evaporation. The data reported from a deciduous Aspen stand in the Rocky Mountains of New Mexico (USA) provide an estimated $^{87}Sr/^{86}Sr$ composition for foliar transfer that resembles Aspen wood.

In the granitic terrain of NE France (Vosges Mountains) Probst *et al.* (2000) found that throughfall $^{87}Sr/^{86}Sr$ values were more radiogenic than the rainwater collected in open field conditions. Although the authors (*ibid.*) do not report vegetation data, stream waters and soil pore-waters provided a consistent range of $^{87}Sr/^{86}Sr$ values that were substantially more radiogenic than those of throughfall. Other authors have shown that soil pore-waters may provide a similar range of $^{87}Sr/^{86}Sr$ values to those of vegetation (e.g. Graustein 1989). Although it is difficult to extrapolate from base-depleted, woodland ecosystems directly to lowland sites where open field conditions are predominant, the available data suggest that where deposits accumulate

on deciduous foliage they are likely to resemble locally bioavailable strontium. Within the limitations of the current study it is not possible to determine whether these represent locally transported materials with similar $^{87}Sr/^{86}Sr$ compositions to those of vegetation, or endogenous plant exudates.

In terms of the potential influence of surface deposits on dietary intake, non-local deposits on leaf material are unlikely to influence the range of biosphere $^{87}Sr/^{86}Sr$ values available to livestock, as grazing animals habitually ingest of significant quantities of soil (Underwood and Suttle 1999). Thornton and Abrahams (1983) suggest that soil may account for as much as 18 % and 30 % of the dry matter ingested respectively by cattle and by sheep. For sheep grazed on lowland pasture, Green *et al.* (1996) report mean values for soil ingestion as a proportion of monthly dry matter, typically of around 2 %; Fries *et al.* (1982) report levels for grazing cattle of around 1.4–2.4 %. Presumably, if particulate material is washed from leaves during periods of rainfall it is then subject to the same weathering and transport processes as other soil parent materials, and cannot be considered to be a discrete dietary component.

The reported Wood-Leaf comparison (Figure 6.02) does not indicate that there are no atmospheric inputs of bioavailable strontium into the study area. It is possible that some proportion of the strontium circulated within the soil–water–vegetation system could be derived from atmospheric deposits. However, these must compete with the labile strontium that is already circulating within the biosphere and, in the case of livestock, other soil-forming material already present in the surface environment. The biosphere data reported in Chapter 4 indicate that there is a significant level of geographic variation in the $^{87}Sr/^{86}Sr$ strontium that is actively cycled within the study area. As surface run-off, measured in stream water, broadly resembles the range of $^{87}Sr/^{86}Sr$ values measured in Wood and indicates a similar pattern of local variation, it is possible that some form of equilibrium has been established within the study area.

6.2.3 Conclusions

The $^{87}Sr/^{86}Sr$ compositions of the Wood samples reported within this thesis can be compared directly with those of plant foliage reported in the literature, and can be used interoperably to characterise biosphere values. Moreover, as well as supplying strontium to domestic livestock, plant-based foodstuffs may provide the majority of the strontium contained within the human diet (Wasserman *et al.* 1977 ; IAEA 2008). Accordingly, the Wood-Leaf comparisons undertaken in this study show that any atmospherically transported, exogenous particulate matter or dried-down salts that are inadvertently consumed with vegetable matter are unlikely to represent a distinctive source of bioavailable strontium within the food chain.

6.3   Evidence of regional variation in the $^{87}Sr/^{86}Sr$ composition of atmospheric inputs within the UK

Under temperate conditions, rainwater chemistry is strongly influenced by seawater input (Kay-Berner and Berner 1987). Moreover, sea-salt particles have an atmospheric residence time of around three days, allowing them to be transported for considerable distances over land (Junge 1972). Accordingly, it is often assumed that under the maritime climate of the British Isles, biosphere variation is moderated by atmospherically-deposited strontium with a characteristic long-term average composition equivalent to that of modern seawater. That is, approximately 0.70917 ± 0.00001 (Palmer and Edmond 1989 ; Hodell *et al.* 1990 ; Davis *et al.* 2003). It has been proposed that in coastal areas subject to high levels of rainfall and direct sea-spray, marine strontium may make a more substantial contribution to the biosphere than in inland areas subject to lower rainfall (Evans *et al.* 2010b), and that above the Chalk of eastern England – an otherwise well-constrained biosphere end-member – seawater strontium may constrain the upper limit of normal biosphere variation (Montgomery *et al.* 2007).

In the current study, rainwater samples and chemical data have been obtained from the Rural Heavy Metals Monitoring Network: an established

network of monitoring sites, operated by the Centre for Ecology and Hydrology (CEH). This comprises 15 collection sites that are used to demonstrate national compliance with European directives for ambient air quality (Figure 6.03). Excluding the site at Penallt – which monitors fall-out from the metal processing industry of Avonmouth and South Wales – the low-density network is designed to provide baseline data, and thus avoids collection sites that are influenced directly by major point-sources of airborne pollution (Fowler *et al.* 2006). The $^{87}Sr/^{86}Sr$ composition of a comprehensive suite of rainwater samples have been analysed within a narrow collection period, as well as multiple samples collected in the course of a year from one inland site (Wytham) that is located close to the study area detailed in Chapter 4. The former provides some indication of characteristics of national variation, whereas the latter are intended to indicate the degree of precision with which it may be possible to define longer-term local averages.
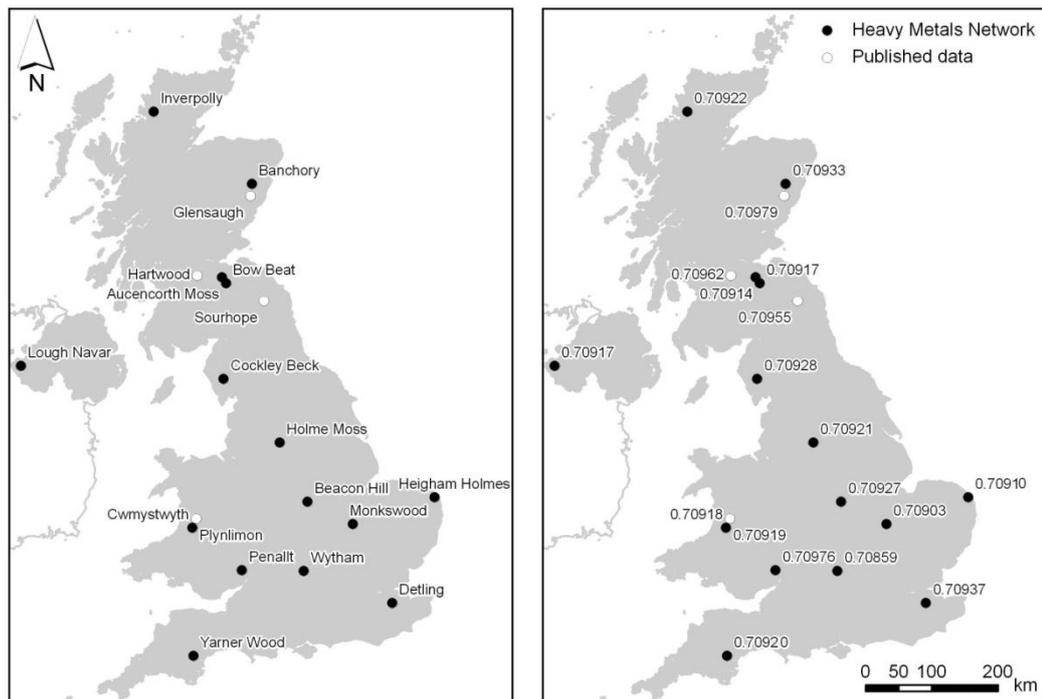
Based upon DiGMapGB-625, with the permission of the British Geological Survey.

Closed symbols (●) show location rainwater collection sites comprising the CEH Rural Heavy Metals Monitoring Network (this study: cf. Tables 6.02–6.04). Open symbols (○) show location of collection sites contributing published $^{87}Sr/^{86}Sr$ data: mean $^{87}Sr/^{86}Sr$ values are shown for Glensaugh, Hartwood and Sourhope (Bacon and Bain 1995) and Plynlimon (Shand *et al.* 2007).

Figure 6.03: Maps showing the location of the rainwater collection sites comprising the CEH Rural Heavy Metals Monitoring Network and the accompanying $^{87}Sr/^{86}Sr$ values reported in Table 6.04, together with the published rainwater data from the UK.

6.3.1 Results

Table 6.02 (overleaf) details the $^{87}Sr/^{86}Sr$ composition of 14 consecutive circum-monthly rainwater samples from the Wytham collection site located in central southern England (Oxfordshire). In addition, 15 samples were selected across the entire network from a high-rainfall period that would allow a narrow temporal range to be achieved (Guyatt pers. comm.). The selected samples were collected between 03/09/2008–20/10/2008 and consisted of six circum-weekly, and nine circum-monthly rainwater samples (Table 6.04, page 152). These were intended to provide a short-term snap-shot of strontium deposition across the British Isles. Collection and measurement protocols undertaken by CEH are designed to detect ultra-trace analytes (see Chapter 3), and typically ≥ 20 ml of rainwater was available for analysis. This material was analyzed following the standard methods outlined in Chapter 3. The isotope data are accompanied by selected trace element data, also provided by CEH (Malcolm pers. comm.).

The central tendencies of element concentrations in rainwater are often expressed as a weighted means, with rainfall depth (mm) as the weighting factor (Hawley *et al.* 1988); the annual weighted mean of the data from the Wytham collection site is 1.9 µg/l. Strontium-isotope data can be summarised following a similar approach (e.g. Négrel and Roy 1998) by using the fractional contribution of each sample to the annual budget to calculate an annual deposition-weighted mean (DWM). This represents an estimate of the $^{87}Sr/^{86}Sr$ composition of a mixture, comprising all strontium inputs during the experimental period. Thus, in the case of the complete-sampling exercise recorded in Table 6.02, the only source of differences between the true $^{87}Sr/^{86}Sr$ composition of an 'annual mixture' and the weighted sample mean (DWM) are the errors associated with the determination of strontium concentration, $^{87}Sr/^{86}Sr$ composition, and rainfall depth. However, as the DWM is calculated in respect of monthly weighting-factors rather than the number of samples, there is no direct analogue for the standard error of the mean (Gatz and Smith 1995a; 1995b).

Table 6.02: Details of the rainwater samples from the CEH Rural Heavy Metals Monitoring Network collection site in Oxfordshire (Wytham) collected during 2008, and results of ^{87}Sr/^{86}Sr analysis.

Sample ID	Collection period*		Rainfall*		Sr*	^{87}Sr/^{86}Sr
	Start	End	(mm)	(mm/day)	(µg/l)	
EF94708	26/11/2008	24/12/2008	42.5	1.5	6.5	0.70734
EF03918	09/07/2008	06/08/2008	100	3.6	0.57	0.70838
EF38716	01/10/2008	29/10/2008	39.1	1.4	1.3	0.70859
EF38513	03/09/2008	01/10/2008	62.7	2.2	0.85	0.70883
EF94919	24/12/2008	21/01/2009	20.5	0.7	2.5	0.70883
EF03705	11/06/2008	09/07/2008	64.3	2.6	0.98	0.70884
EF38301	06/08/2008	03/09/2008	72.4	2.3	0.74	0.70884
EF39102	29/10/2008	26/11/2008	74.2	2.7	1.0	0.70894
EF03322	14/05/2008	11/06/2008	142	5.1	0.84	0.70910
EE54921	19/03/2008	16/04/2008	18.7	0,7	3.4	0.70917
EE54612	20/02/2008	19/03/2008	68.9	2.5	1.5	0.70952
EE53406	27/12/2007	23/01/2008	98.1	3.6	1.5	0.70958
EF03107	16/04/2008	14/05/2008	51.1	1.8	8.9	0.70967
EE54024	23/01/2008	20/02/2008	13.2	0.5	4.1	0.70968

	Median	0.7089
	‡DWM	0.7090
	Mean	0.7090
	2 SD	0.0012

*Data provided by CEH Rural Heavy Metals Monitoring Network (Malcolm pers. comm.).

‡Deposition-weighted mean (DWM).

Table 6.03: Details of the rainwater samples from the CEH Rural Heavy Metals Monitoring Network selected for ^{87}Sr/^{86}Sr analysis, which provide coverage across the British Isles.

Sample ID	Site	Altitude	Collection period*		Rainfall*	
		(m OD)	Start	End	(mm)	(mm/day)
EF38705	Holme Moss	525	09/09/2008	23/10/2008	68.3	1.6
EF38710	Bow Beat	580	29/09/2008	27/10/2008	104.5	3.7
EF38715	Heigham Holmes	< 5	03/09/2008	24/10/2008	120.5	2.4
EF38716	Wytham	155	01/10/2008	29/10/2008	39.1	1.4
EF38717	Cockley Beck	225	26/10/2008	02/11/2008	9.2	1.3
EF38718	Monkswood	35	22/10/2008	29/10/2008	13.3	1.9
EF38719	Inverpolly	245	30/09/2008	03/11/2008	369.5	10.9
EF38720	Banchory	125	25/10/2008	04/11/2008	14.6	1.5
EF38723	Lough Navar	140	08/10/2008	04/11/2008	169.3	6.3
EF38902	Penallt	205	30/09/2008	04/11/2008	10.1	0.3
EF38903	Aucencorth Moss	265	15/10/2008	22/10/2008	29.7	4.2
EF38904	Beacon Hill	185	29/09/2008	06/11/2008	85.3	2.2
EF38909	Yarner Wood	100	28/10/2008	04/11/2008	23.4	3.3
EF38912	Cwmystwyth	230	06/11/2008	12/11/2008	37.9	6.3
EF38921	Detling	180	23/10/2008	20/11/2008	126.3	4.5

*Data provided by CEH Rural Heavy Metals Monitoring Network (Malcolm pers.comm.).

Table 6.04: Results of $^{87}Sr/^{86}Sr$ analysis of rainwater samples from the CEH Rural Heavy Metals Monitoring Network, which provide coverage across the British Isles.

Sample ID	Site	$^{87}Sr/^{86}Sr$	Cl (mg/l)	Na (mg/l)	Sr (ug/l)	Ba (ug/l)	Al (ug/l)
			Chemical data provided by CEH*				
EF38716	Wytham	0.70859	1.5	0.85	1.3	0.77	5.2
EF38718	Monkswood	0.70903	1.5	0.81	0.86	0.67	8.3
EF38715	Heigham Holmes	0.70910	4.0	2.2	2.0	0.69	2.7
EF38903	Aucencorth Moss	0.70914	3.1	1.7	1.2	0.11	1.4
EF38710	Bow Beat	0.70917	2.8	1.4	0.86	0.10	0.1
EF38723	Lough Navar	0.70917	5.8	2.7	1.8	0.04	—
EF38912	Cwmystwyth	0.70918	8.8	4.5	3.2	0.08	0.37
EF38909	Yarner Wood	0.70920	3.6	1.9	1.4	0.30	5.1
EF38705	Holme Moss	0.70921	3.6	2.0	1.5	0.84	4.5
EF38719	Inverpolly	0.70922	12	6.2	4.9	0.16	—
EF38904	Beacon Hill	0.70927	1.2	0.66	1.1	2.0	14
EF38717	Cockley Beck	0.70928	12	6.0	4.3	0.35	18
EF38720	Banchory	0.70933	12	6.2	4.6	0.36	7.2
EF38921	Detling	0.70937	4.1	2.2	2.6	2.11	38
EF38902	Penallt	0.70976	2.9	0.86	1.9	0.92	13

Median	0.7092	
Mean	0.7092	
2 SD	0.0005	

*Data provided by CEH Rural Heavy Metals Monitoring Network (Malcolm pers. comm.).

In terms of representative sampling, it difficult to estimate the level of uncertainty associated with the average $^{87}Sr/^{86}Sr$ of atmospheric inputs using a weighted model (DWM). Moreover, the DWM is sensitive to isotopic outliers that represent a disproportionately large fraction of the annual budget. Figure 6.04 (overleaf) shows the distribution of the annual circum-monthly data from Wytham (Table 6.03) summarised by weighted and by un-weighted methods. There is a peak in absolute deposition and the frequency of deposition between 0.7088–07092, but while most of the samples represent less than 10 % of the annual budget, approximately 45 % of the strontium was deposited in just two samples (EF94708 and EF03107). This results in a much more scattered distribution under the weighted model. As no information is available to indicate the residence time of water from any one rainfall event within the water–soil–vegetation system, the weighted model may not be intrinsically more accurate than frequency-based measures of central tendency and dispersion.

A: Depostion-weighted distribution

B: Frequency distibtion
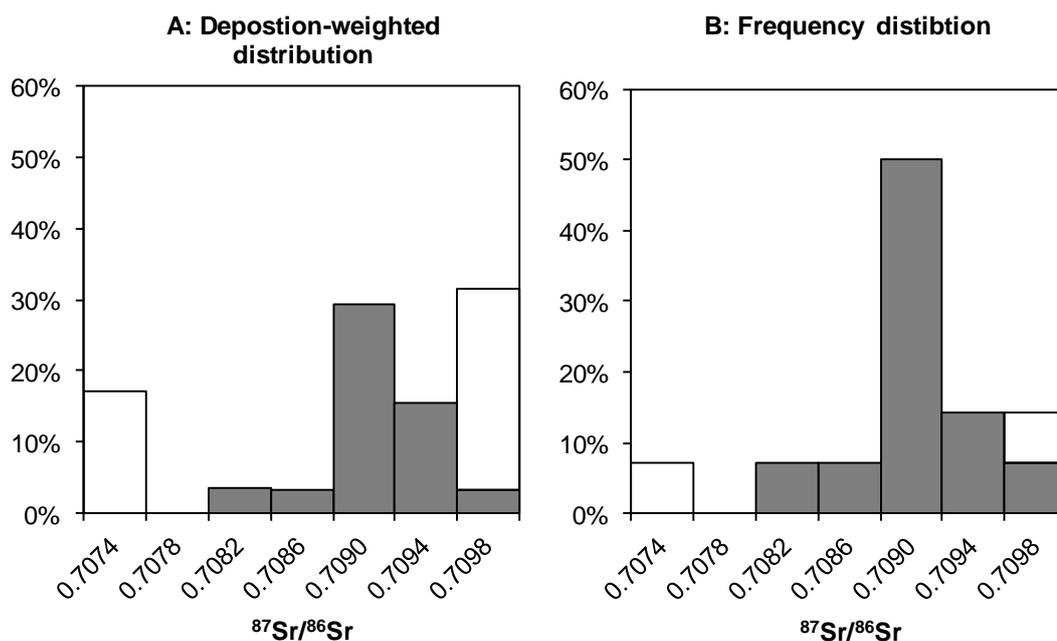
Open columns indicate rainfall events that, due to high strontium concentrations, supplied a disproportionally large fraction of the annual strontium budget (cf. Table 6.02).

Figure 6.04: Histograms of annual monthly rainwater $^{87}Sr/^{86}Sr$ composition formulated using deposition weightings (A) and frequency distribution (B).

Within the national data-set presented in Table 6.04 two samples with extreme $^{87}Sr/^{86}Sr$ compositions of 0.7086 and 0.7098 were collected respectively at Wytham and Penalt. The remaining 13 samples fall within one standard deviation of the mean of the data-set, which is close to the composition of modern seawater; often quoted as 0.70917 ± 0.00001 (Hodell *et al.* 1990; Davis *et al.* 2003). If the samples with outlying $^{87}Sr/^{86}Sr$ compositions are excluded, this has little effect on the mean value, returning 0.7092 ± 0.0002 (2 SD, n = 13). As the majority of sample achieved a level of analytical precision of ± 0.00002 or better (see Chapter 3), eight of the samples with $^{87}Sr/^{86}Sr$ compositions that fall outside an ± 0.00006 interval about the seawater value can be considered to have been affected significantly by a non-marine source of strontium. However, this does not mean that those samples falling with this interval are not influenced by non-marine strontium.

It is possible that the distinctive, radiogenic $^{87}Sr/^{86}Sr$ composition of the sample from Penalt (0.7098) is related to ore sources used in the local metal industry of Avonmouth (e.g. Geagea *et al.* 2007). However, in the

course of a year, circum-monthly samples with a similar composition were also collected at the Wytham site (Table 6.02). The ^{87}Sr/^{86}Sr composition of the sample collected at the Wytham site on the 29/10/2008, is exceptionally low compared to other samples collected during the same period (Table 6.04), and falls within the lower quartile of the annual data. However, given the degree of scatter in the Wytham data-set, it cannot necessarily be considered to be unusual for the site. Overall, Wytham shows a high degree of variation in the course of a year (2 SD = 0.0012, n = 14), which substantially exceeds that of rainwater collected at a wider geographic scale, but over a short period of time (Table 6.04).

6.3.2 Discussion

A substantial proportion of samples detailed in Table 6.04 (n = 7) do not diverge substantially from a seawater ^{87}Sr/^{86}Sr value of approximately 0.7092, suggesting that marine-influenced wet deposition may be widespread. Three of these samples provided ^{87}Sr/^{86}Sr compositions precisely resembling that of seawater. These were collected at sites located the Moorfoot Hills of east central Scotland, south of Edinburgh (Bow Beat); the Lough Navar Forest of north western County Fermanagh, in Northern Ireland (Lough Navar); and the Cambrian Mountains of western central Wales (Cwmystwyth). All three sites are located in remote areas subject to high annual rainfall, and experienced a relatively high intensity of rainfall during the respective collection periods, exceeding the median value for the sample suite of 2.4 mm/day (Table 6.02). Lough Navar represents the most westerly site within the sampling network. Likewise, Cwmystwyth lies within a region that is strongly influenced by westerly, Atlantic weather systems.

Two rainwater samples have previously been reported by Shand *et al.* (2007), which also display seawater ^{87}Sr/^{86}Sr compositions. These were collected at a site located at 580 m OD in the Cambrian Mountains of Wales, in close proximity to Cwmystwyth. Within 20 km to the west of both sites, the topography falls steeply to sea level. This leads to high levels of rainfall, as westerly weather systems make landfall and the air masses are forced to rise

(i.e. orographic precipitation). Long-term monitoring also suggests that the rainwater chemistry in this region is dominated by marine inputs (Durand *et al.* 1994 ; Wilkinson *et al.* 1997 ; Neal and Kirchner 2000 ; Neal *et al.* 2001). Accordingly, although the data from Wytham (Figure 6.04) suggest a high degree of variation in inland deposition, the $^{87}Sr/^{86}Sr$ data reported by Shand *et al.* (2007), together with the data from Cwmystwyth (Table 6.04), confirm the initial maritime composition of rainwater as it begins its landward trajectory across the British Isles.

Over two thirds of the samples from Wytham have a $^{87}Sr/^{86}Sr$ composition that is lower than that of seawater (Table 6.02), in contrast to the majority of the data presented in Table 6.04, and all the previously published data from British Isles (Bain and Bacon 1994 ; Bacon and Bain 1995 ; Shand *et al.* 2007). However, all of the samples fall within range of the biosphere $^{87}Sr/^{86}Sr$ values previously reported within the British Isles (Evans *et al.* 2010a) and cannot be regarded extreme, or in any way exotic. In Scotland, Bacon and Bain (1995) suggest that strontium derived from radiogenic Scottish rocks may be entrained within air masses, such that marine strontium constrains the lower limit of normal variation. The Wytham collection site is in central southern England, a region underlain by Mesozoic marine sediments (see Chapter 4). These include a number of substantial limestone outcrops, such as the Jurassic Great Oolite of the Cotswolds (to the NW), the Cretaceous Chalk of the Chilterns (to the SE), and the Jurassic Corallian formation (underlying the site). The marine isotope curve suggests that carbonates derived from these rocks may range in $^{87}Sr/^{86}Sr$ composition from around 0.7069–0.7078 (McArthur *et al.* 2001), which could account for the range of values reported in a substantial number of the samples.

If seawater represents a more significant proportion of atmospherically deposited strontium in some areas than in others, it is possible that there is geographic variation in both the central tendency associated with wet deposition, and in variance. In this respect, rainwater chemistry can provide complementary evidence concerning the provenance

of atmospheric inputs. Oceanic seawater has a highly consistent Na/Cl ratio 0.56 and a Sr/Cl ratio of 0.41×10^{-3} (Wilson 1975 ; Millero 2006). However, the majority of samples in the current study have Na/Cl values lower than 0.56, and a significant proportion of these have Sr/Cl values lower than that of seawater too. This suggests that, it is not appropriate to use seawater solute ratios to correct for non-marine strontium input, as other authors have done elsewhere (Herut *et al.* 1993). Although barium and aluminium are present at low trace levels in seawater (Brewer 1975) they are present at high levels within the upper continental crust (Rudnick and Gao 2004). If these non-marine elements are present at detectable in levels in rainwater, they can provide evidence of interaction with non-marine aerosols.

Overall, the rainwater strontium concentrations provided by the Rural Heavy Metals Monitoring Network (Tables 6.02 and 6.04) are consistent with values reported from the continent (*cf.* Négrel *et al.* 2007), which are typically of around 1–3 µg/l (i.e. a few ppb). Figure 6.05 (overleaf) shows the $^{87}Sr/^{86}Sr$ composition of the samples collected between 03/09/2008–20/10/2008 versus the reciprocal of strontium concentration (cf. Tables 6.03 and 6.04). This graph indicates that there is no simple relationship between strontium concentration and rainwater $^{87}Sr/^{86}Sr$ composition. That is, samples with high concentrations of strontium do not deviate further from the seawater $^{86}Sr/^{86}Sr$ reference line than those with lower concentrations. Figure 6.06 (overleaf) shows the relationship between $^{87}Sr/^{86}Sr$ composition the sum of the non-marine elements (Ba + Al), normalized to the sum of major marine elements (Na + Cl). This demonstrates that a significant component of the scatter in $^{86}Sr/^{86}Sr$ composition is associated with those samples displaying substantial enrichment in non-marine solutes (identified with square symbols). These samples deviate further from the seawater $^{87}Sr/^{86}Sr$ reference line than others with similar strontium concentrations (i.e. less than 4 µg/l).
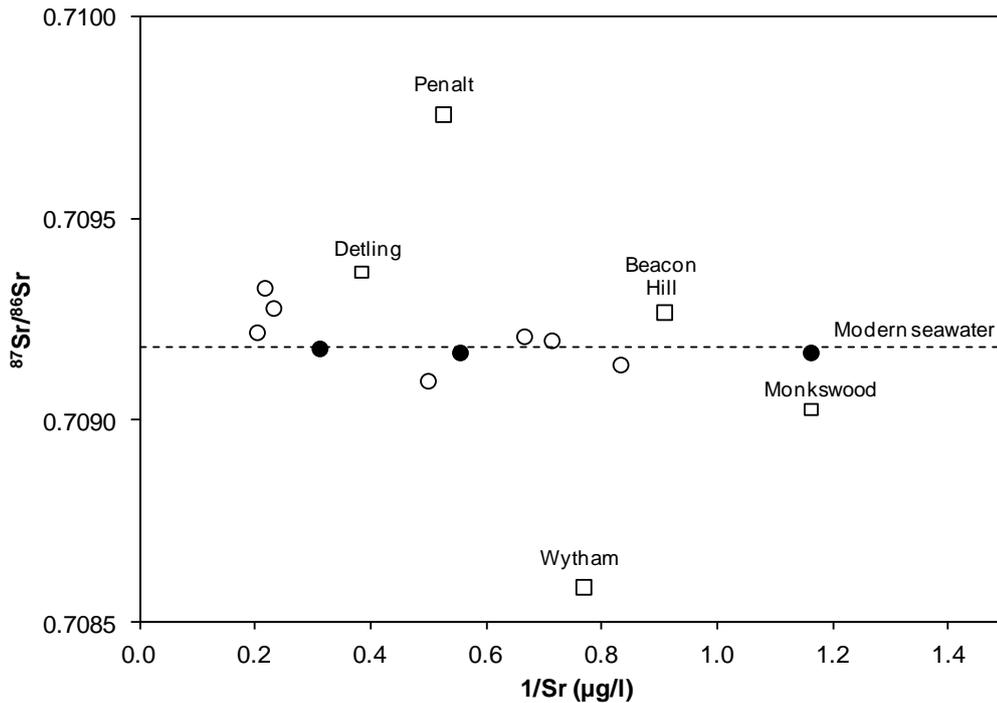
Samples with marine ⁸⁷Sr/⁸⁶Sr values falling on the seawater reference line (Bow Beat, Lough Navar, Cwmystwyth) are shown as closed circles (●); samples with low levels of enrichment in non-marine cations shown as open circles (○); samples with high levels of enrichment in non-marine cations identified with open squares (□) (cf. Figure 6.06).

Figure 6.05: Graph showing the relationship between rainwater ^{87}Sr/^{86}Sr composition and 1/Sr.
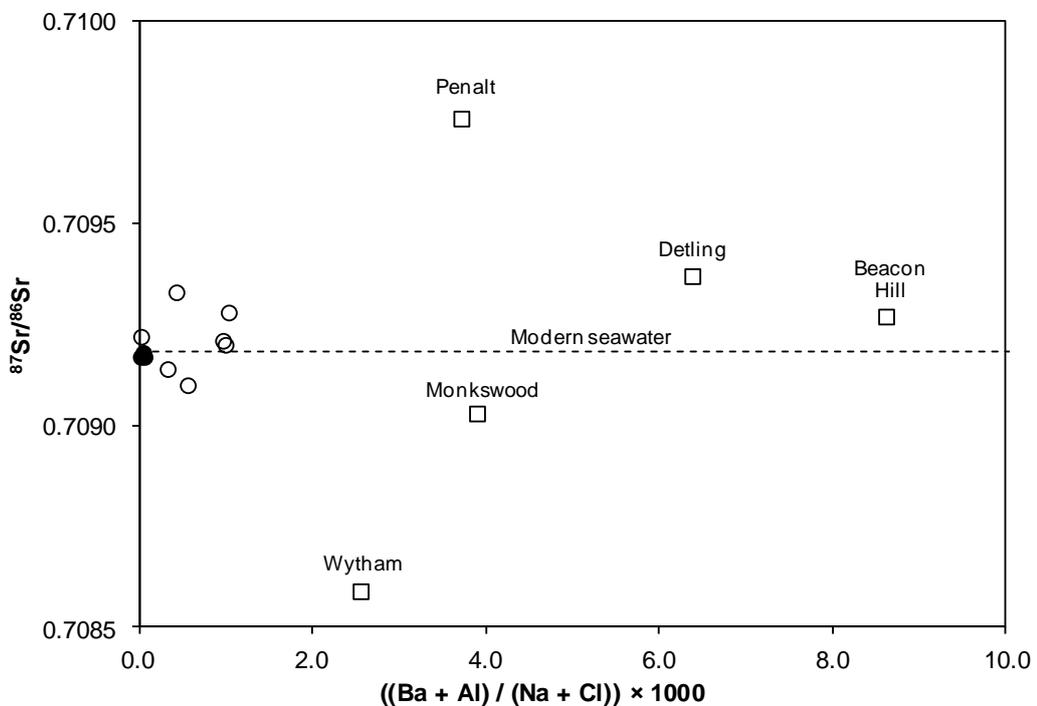
Samples with marine ⁸⁷Sr/⁸⁶Sr values falling on the seawater reference line (Bow Beat, Lough Navar, Cwmystwyth) are shown as closed circles (●); samples with low levels of enrichment in non-marine cations shown as open circles (○); samples with high levels of enrichment in non-marine cations identified with open squares (□).

Figure 6.06: Graph showing the relationship between rainwater ^{87}Sr/^{86}Sr composition and enrichment in non-marine cations (Ba and Al).

Those samples showing high levels of enrichment in non-marine cations (Figure 6.06) include the outlying samples identified on the basis of $^{86}Sr/^{86}Sr$, from central southern England (Wytham) and an industrial region of Wales (Penalt). They also include two samples from the English midlands (Monkswood and Beacon Hill) and one from eastern England (Detling). Rainwater collected from more northern latitudes and from sites closer to the coast (Figure 6.03) shows less evidence of non-marine enrichment and generally lies closer to the seawater $^{87}Sr/^{86}Sr$ line. Excluding Penalt, the samples with high solute concentrations (Inverpolly, Cockley Beck and Banchory) do not show substantial enrichment in non-marine cations and of these the least enriched sample (Inverpolly) lies closest to the seawater $^{87}Sr/^{86}Sr$ line. The snap-shot provided by the national data-set suggests that enrichment of rainwater in non-marine cations is associated with increased deviation from a seawater $^{87}Sr/^{86}Sr$ value.

The high degree of scatter shown by samples from the Wytham collection site casts some doubt on the feasibility placing realistic constraints on the $^{87}Sr/^{86}Sr$ composition of regional atmospheric deposits based on small numbers of samples. However, the distributions shown in Figure 6.04 are less variable than the annual circum-monthly data reported by Négrel and Roy (1998), with a mean of 0.7104 ± 0.0025 (2 SD, n = 13). Exclusion of the two outliers in the Wytham data-set (Table 6.02: EF94708 and EF03107) results in much reduced variance, returning a mean value of 0.7090 ± 0.0008 (2 SD, n = 12). This level of variation is comparable to that reported Bacon & Bain (1995) for rainwater collected in Scotland over a two-year period in the Cheviot hills, in Strathcylde and the in Grampian Highlands, which provided average $^{87}Sr/^{86}Sr$ values of 0.7096 ± 0.0005 (2 SD, n = 12), 0.7096 ± 0.0005 (2 SD n = 9), and 0.7098 ± 0.0009 (2 SD, n= 13) respectively.

The averages reported by Bacon & Bain (1995) are similar to one another, but contrast substantially with the central tendency of the Wytham data, suggesting that there may be regional differences in deposition across the British Isles. However, the published Scottish data (*ibid.*) were provided

by samples, which each representing a longer collection period than any one sample within the Wytham data-set. This may reduce the influence of short-term variations. For example, although obtained from an extreme and highly contrasting environment, a long-term record provided by ice-core data (Burton *et al.* 2006) shows a high degree of annual scatter – comparable to the standard deviation quoted by Négrel and Roy (1998) – but average values that are stable on a decadal, or possibly centennial time-scale. The direct applicability of these data to a lowland region of the UK is perhaps doubtful, but they do suggest that variable monthly and annual averages can contribute to a stable long-term pattern.

Graustein (1989) suggests that, where nutrient losses are greater than the inputs provided by soil-mineral weathering, ecosystems may be sustained by atmospheric deposits, which gradually become concentrated in the system through biomass recycling (e.g. Chadwick 1999). However, even under high levels of rainfall – ca. 2500 mm/A – this pattern is not universal (eg. Bern *et al.* 2005). Moreover, although the rapid transport of erosion products out of a watershed can lead to local atmospheric dependence (Bern et al. 2007), this can increase the supply of strontium from terrestrial sources to alluvial valley systems (Palmer *et al.* 2009). Given the limited range of rainwater ^{87}Sr/^{86}Sr values reported in Table 6.04 (0.7086–0.7098), the degree to which different ecosystems are dependent on atmospheric inputs may be at least as important a factor in determining geographic patterns of biosphere ^{87}Sr/^{86}Sr variation as the ^{87}Sr/^{86}Sr composition of those inputs.

Ecosystem atmospheric dependence has not been studied widely within the British Isles. However, stream and river waters have been investigated by Shand *et al.* (2007) in the Cambrian Mountains of Wales, providing a useful case study for comparison with the contrasting lowland zone of England (i.e. Chapters 4 and 5). Shand *et al.* (2007) show that atmospheric input provides between 7–50 % of the strontium in the waters of the River Severn and its upland tributaries; these have strontium concentrations of 4.2–20 µg/l, which plot on a mixing-line between

groundwater, with a $^{87}Sr/^{86}Sr$ composition of 0.7148 (330 µg/l), and rainwater with a composition of 0.7092 (2 µg/l). Minerogenic topsoil pore-waters were also analysed, with strontium concentrations of 13 µg/l and 12 µg/l, and respective $^{87}Sr/^{86}Sr$ compositions of 0.7112 and 0.7114. These two values are similar to the mean composition of 0.7111 ± 0.0026 (2 SD, n = 21) provided by vegetation collected above Lower Palaeozoic mudstones, comparable to those underlying Plynlimon (Evans et al. 2010a). Thus, despite containing high levels of atmospherically transported strontium, the Welsh biosphere maintains a significant contrast in $^{87}Sr/^{86}Sr$ composition with that of southern England (Evans *et al.* 2010b).

In central southern England the annual DWM strontium concentration in rainwater from the Wytham collection site (Table 6.02) is indistinguishable from the Plynlimon long-term average of 1.8 µg/l (Wilkinson *et al.* 1997). However, the strontium concentrations achieved within the upland catchment of the River Severn (Shand *et al.* 2007), are an order of magnitude lower than those commonly encountered in the lowland zone; for example, the G-BASE stream water strontium concentrations reported in Chapter 4 (Table 4.04) range from 0.36–1.3 mg/l. Soil pore-waters collected within the same region as the Wytham rainwater have been reported (Campbell *et al.* 1989; Kinniburgh and Miles 1983), which are also an order of magnitude higher than those reported by Shand *et al.* (2007). Moreover, UK Meteorological Office data (Met Office 2012) indicate that the average rainfall depth in southern England is 781.7 mm/A compared to 1435.9 mm/A in Wales. This suggests that, to achieve similar solute concentrations within the lowland zone, rainfall levels would need to be around 20 times higher than they are today. It is therefore unlikely that wet deposition has a significant immediate effect on biosphere values through the direct dilution of groundwater and soil pore-water.

6.3.3 Conclusions

Under some conditions it has been possible to show that a substantial proportion of the strontium cycled in some base-depleted ecosystems is of atmospheric origin (eg. Miller *et al.* 1993). However, any ability to resolve the respective sources of strontium is limited by the variability of the contributing environmental end-members (Capo *et al.* 1998). Sensitivity is increased in ecosystems that are subject to the influence isotopically distinct and narrowly constrained nutrient sources. If local sources of strontium, such as soils and exposed rock outcrops, provide a significant proportion of the strontium that is redistributed regionally by atmospheric transport, gross over-estimates may be made of the proportion of non-local strontium circulated within the system. Although it is likely that atmospherically deposited strontium is incorporated into the biosphere, the rainwater compositions reported in the current study (Tables 6.02–6.04) suggest that it may be difficult to achieve accurate estimates of the influence of atmospheric input within the British Isels.

It is possible that regionally or locally important rock outcrops have a significant influence on the atmospheric deposition of strontium. In this respect, the annual data from the Wytham collection site – in central southern England (Oxfordshire) – are consistent with the findings of other authors studying atmospheric deposition in Scotland (Bain and Bacon 1994 ; Bacon and Bain 1995), and in continental Europe (Négrel *et al.* 2007). That is, in a situation where geologically recent marine sediments dominate regional surface geology, modern marine strontium may represent the upper limit of normal $^{87}Sr/^{86}Sr$ variation. In contrast, higher $^{87}Sr/^{86}Sr$ ranges for European rainwater – consistently in excess of 0.7092 – have been reported from areas underlain by granitic rocks and gneisses: south central Sweden (Åberg *et al.* 1989); the Vosges mountains in France (Probst *et al.* 2000; Chabaux *et al.* 2005; Schmitt and Stille 2005); and the Massif Central (Négrel and Roy 1998).

Notably, rainwater collected in the Cambrian Mountains of Wales (Cwmstwyth) has an exact seawater $^{87}Sr/^{86}Sr$ signature, and shows little evidence of non-marine input (Figures 6.05 and 6.06). This is consistent with previously published work, which suggests that the composition of stream water in this region is controlled principally by mixing groundwater and recent surface run-off with a $^{87}Sr/^{86}Sr$ composition resembling that of seawater (Shand *et al.* 2007). As discussed in the BGS Geochemical Atlas of Wales (BGS 1999: 79), as a result of low levels of water-rock interaction, this region is characterized by nationally low stream water strontium concentrations, potentially making it sensitive to atmospheric inputs. Accordingly, underlying geology can influence the balance between the atmospherically deposited and locally weathered strontium that is circulated within the biosphere, as well as the $^{87}Sr/^{86}Sr$ composition of both potential end-members.

The $^{87}Sr/^{86}Sr$ composition of atmospheric input in upland areas exposed to westerly Atlantic weather systems, and subject to orographic precipitation, may be more tightly constrained around a seawater $^{87}Sr/^{86}Sr$ value than in lowland areas further inland. A conservative interpretation would be to suggest that atmospheric deposition becomes rapidly de-focused from a seawater value as air-masses move inland, potentially under different regional terrestrial influences. Variation in the $^{87}Sr/^{86}Sr$ composition of wet deposits in the lowland zone may be related to/modified by regional/local transport patterns, rather than a variable base-load provided by longer-range (continental) sources. Thus, it is likely that geographic variation in atmospheric deposition is superimposed on a baseline marine value. Potentially, beyond those areas affected by maritime precipitation, wet deposition within the British Isles should be considered as a regional homogenizer of biosphere $^{87}Sr/^{86}Sr$ values, rather than a distinctive biosphere end-member.