THE UNIVERSITY *of* EDINBURGH

Edinburgh Research Explorer

Investigation of the concentration and isotopic composition of inputs and outputs of Pb in waters at an upland catchment in NE Scotland

Citation for published version:
Vinogradoff, SI, Graham, MC, Thornton, GJP, Dunn, SM, Bacon, JR & Farmer, JG 2005, 'Investigation of the concentration and isotopic composition of inputs and outputs of Pb in waters at an upland catchment in NE Scotland' Journal of Environmental Monitoring, vol 7, no. 5, pp. 431-444., 10.1039/b415642k

Digital Object Identifier (DOI):
10.1039/b415642k

Link:
Link to publication record in Edinburgh Research Explorer

Document Version:
Publisher final version (usually the publisher pdf)

Published In:
Journal of Environmental Monitoring

Publisher Rights Statement:
Published in the Journal of Environmental Monitoring by the Royal Society of Chemistry (2005)

OPEN ACCESS

Investigation of the concentration and isotopic composition of inputs and outputs of Pb in waters at an upland catchment in NE Scotland†

Susan I. Vinogradoff,[a] Margaret C. Graham,*[a] Gareth J. P. Thornton,[a] Sarah M. Dunn,[b] Jeffrey R. Bacon[b] and John G. Farmer[a]

[a] School of GeoSciences, The University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ. E-mail: Margaret.Graham@ed.ac.uk; Fax: +44 131 6504757; Tel: +44 131 6504767
[b] The Macaulay Institute, Craigiebuckler, Aberdeen, UK AB15 8QH

As a consequence of the accumulation of anthropogenic Pb in upland catchments, there has been much recent concern about the potential mobilisation and transport of Pb from the soils to receiving waters and also the possible harmful effects that this might have on aquatic biota. This paper presents the findings of a two-year study of Pb behaviour in an organic-rich upland catchment at Glensaugh in NE Scotland. Pb inputs to the catchment were characterised by direct measurements of Pb concentration and $^{206}Pb/^{207}Pb$ ratios in rain water and interception. Pb outputs from the catchment were calculated from measurements on stream water samples taken from the two main streams, the Cairn Burn and Birnie Burn. The relative contribution of Pb from groundwater and throughflow, under different flow conditions (base flow and high flow), to stream waters was investigated *via* analysis of springs sourced from groundwater and of waters flowing through the various soil horizons (S (surface), A, B, C, and D), respectively. The outcome of intensive sampling and analysis over the two-year time period was that, even with marked reduction in Pb inputs over the past two decades, the catchment was still acting as a net sink for the current atmospheric deposition. Although the Pb isotopic signature for stream water is very similar to that for the contemporaneous rain water ($^{206}Pb/^{207}Pb \sim 1.15$–1.16), only a small portion of the rain water is transferred directly to stream water. Instead, the Pb input is transferred to the stream waters mainly *via* groundwater and it was also confirmed that the latter had a similar Pb isotopic signature. From the Pb isotopic measurements on throughflow waters, however, Pb being removed *via* the streams contained some previously deposited Pb, *i.e.* mobilisation of a small portion of soil-derived anthropogenic Pb was occurring. These findings are important not only with respect to the source/sink status of the catchment but also for calculation of the extent of retention of the current atmospheric Pb inputs, which must take account of the release of previously deposited Pb from the catchment soils, a process occurring mainly under high flow conditions.

Introduction

Since the onset of the Industrial Revolution some 250 years ago, soils and aquatic sediments have become highly contaminated with heavy metals. Under appropriate environmental conditions, such sinks can be transformed into sources, with the potential for release of possibly deleterious chemical entities.[1] It has even been suggested that these accumulations should be viewed as 'chemical time bombs', liable to significant transformation over a relatively short time period by appropriate environmental triggers.[2,3]

There is particular interest at present in the nature and extent of release of anthropogenic Pb from soils, given the pervasive contamination of the Earth's surface by this potentially harmful, non-essential element. Miller and Friedland[4] claimed that analysis of Pb transit times in mineral soil horizons in northeastern US forests indicated that the large pulse of anthropogenic Pb deposited after 1960 may begin to be released to upland streams from the middle of the 21st century. In contrast, Wang et al.[5,6] concluded that mineral soil horizons adsorb Pb^{2+} ions and colloidal Pb, acting as the net sink for atmospheric Pb as it passes through forested ecosystems, and that stream Pb contributed by soil percolates is virtually nil. Johnson et al.[7] however, commented that the stability of the soil Pb pool and the long-term implications of

mineral soil Pb accumulation are unknown. On the basis of modelling studies, Wang and Benoit[8] later claimed that Pb output from the mineral soil has been increasing since the 1970s. In a study of the temporal variability of trace metals in New Jersey Pinelands streams, Sherrell and Ross[9] reported that upper soil reservoirs of Cd, Cu and Pb could supply riverine dissolved metals for many years, even if atmospheric inputs were curtailed. In recent years, the feasibility of using Pb isotopic ratios (*e.g.* $^{206}Pb/^{207}Pb$) to investigate the possible migration of anthropogenic Pb in soils and the transport of Pb through soils into the hydrocycle has been demonstrated at several locations around the world.[10–18]

We have for some time been engaged in the determination of current and past variations in the isotopic signature (*e.g.* $^{206}Pb/^{207}Pb$ ratio) of Pb released to the environment as a consequence of human activities, *e.g.* smelting, coal combustion, car exhaust emissions.[19–30] The $^{206}Pb/^{207}Pb$ ratio (1.06–1.09) of alkyl lead additives, used in UK petrol until the complete ban upon their use in January 2000, reflected the strong influence of older Australian Pb ($^{206}Pb/^{207}Pb = 1.04$), mixed with British Columbian Pb ($^{206}Pb/^{207}Pb = 1.16$).[22,27] The $^{206}Pb/^{207}Pb$ ratios of most significant indigenous Pb ore deposits in the UK (~ 1.16–1.18) and British coals (1.182 ± 0.009) were considerably higher.[22,26] The influence of imported low $^{206}Pb/^{207}Pb$ ratio Australian Pb and therefore, to some extent, car exhaust emissions can be seen in the decline of the $^{206}Pb/^{207}Pb$ ratio of anthropogenic Pb from ~ 1.17 during the 19th and early 20th centuries to values of ~ 1.12 in the surface layers (*ca.* 1975–

† Electronic supplementary information (ESI) available: Figs. A1–A14. See http://www.rsc.org/suppdata/em/b4/b415642k/

1990) of freshwater lake sediments and peat bogs in central Scotland[24,25,30] and in Scottish archival moss.[28] Subsequent to the reduced use of leaded petrol since the 1980s, there was an increase in the average $^{206}Pb/^{207}Pb$ ratio of rainfall and atmospheric particulates in Scotland and, indeed, elsewhere in western Europe from ~ 1.10[22,23,31] to 1.12–1.14 by the late 1990s.[27,28,32,33]

Even allowing for the highly significant, if recently diminishing, input of petrol-derived Pb since the 1920s, however, there is considerable evidence from lake sediment and peat core profiles to suggest that atmospheric inputs of Pb from other sources prior to the introduction of leaded petrol were quite substantial.[24,25,30] Furthermore, Bacon *et al.*[19] found concentrations in surface soils from remote upland areas of Scotland, such as the catchment of this study, in the late 1980s–early 1990s to be as high as 500 mg kg^{-1} and with a $^{206}Pb/^{207}Pb$ ratio much higher than the petrol-Pb-dominated atmospheric deposition of the time, indicating the significant contribution of non-petrol sources of Pb in the past.

This relatively high accumulation of Pb in surface soils in the upland areas of Scotland, such as Glensaugh, makes it important to investigate the extent and process of transfer of this potentially harmful element from the soil to freshwaters. Accordingly, having previously generated useful but sporadic data for Pb in various components of the catchment at different times during the 1990s,[19,20,23,27,33] we embarked upon a major comprehensive study of the concentrations, distribution, associations, behaviour and isotopic composition of Pb in the catchment, including atmospheric input and stream output, over a two-year period from the autumn of 2001 to the autumn of 2003. This paper, which focuses primarily upon the aqueous components (rain water, groundwater, soil throughflow, soil porewaters and stream waters), seeks, in conjunction with other papers on the history of Pb deposition,[34] the associations of Pb with different solid phases of soil,[35] the influence of major storm events[36] and the hydrology of the catchment,[37] to quantify the extent of Pb contamination and the magnitude and relative contributions of the different sources and pathways of current Pb input, throughput and output, as well as identify the processes controlling retention and release of Pb in the catchment.

Materials and methods

Catchment location

The catchment used in this study is part of the Glensaugh Research Station (OS Grid Reference 365000E 775000N), an upland area of Scotland which lies about 40 km southwest of Aberdeen in the Grampian foothills (Fig. 1). The elevation at the upper boundary of the catchment is ~ 410–440 m whilst that at the lower boundary is ~ 220–230 m. The catchment includes two main streams, the Cairn and Birnie Burns, which converge just below the lower boundary. The total catchment area of about 1.76 km^2 can be split into sub-catchment zones on the basis of drainage into the two streams above each of the sampling points (CB1, CB2 and CB3 on the Cairn Burn; BB1, BB2 and BB3 on the Birnie Burn). The sub-catchment zones for CB3 and BB3 are the areas within the dotted lines in Fig. 1. The areas of the zones are 0.32 (CB1), 0.23 (BB1), 0.90 (CB2), 0.50 (BB2), 0.99 (CB3) and 0.77 (BB3) km^2. Thus the area of 0.99 km^2 draining into the Cairn Burn at CB3 is equal to 56% of the total catchment area.

The catchment geology is predominantly quartz mica schists of the Dalradian age. The depth of overlying glacial deposits varies with topography with generally deeper deposits downslope and thinner, stonier amounts on higher ground.[38] The soils which have developed on the glacial drifts are mainly of the Strichen Association and include hill peat, gleys and podzols. In the uppermost parts of the catchment (*e.g.* Thorter Hill), the soils are mainly hill peat derived from *Sphagnum* spp.
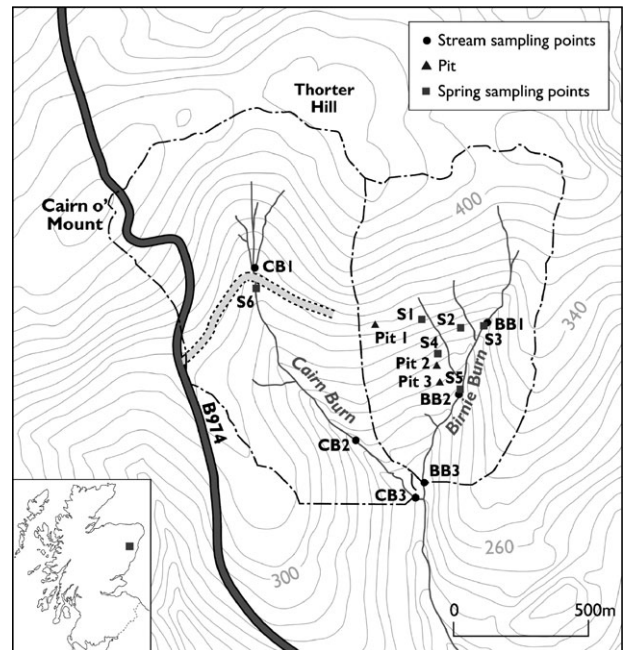
Fig. 1 Map of the catchment at Glensaugh, NE Scotland, showing the locations of stream water (CB1–CB3 and BB1–BB3), spring water (S1–S6) and soil throughflow pit (Pits 1–3) sampling sites. The inset map shows the location of Glensaugh within Scotland.

and *Eriophorum vaginatum*. Soils in the vicinity of the upper parts of the Cairn and Birnie Burns are of the Hythie Series.[35,38,39] These are poorly drained flushed gleys, *i.e.* a peaty loam topsoil overlying a mineral horizon which overlies grey stony sandy silt loams (umbric gleysol). In the middle of the catchment, peaty podzols of the Gaerlie Series have developed and the vegetation is dominated by *Calluna vulgaris*.[38,40] These are often characterised by the presence of an iron pan. At the lower altitudes, soils are often freely drained humus iron podzols (dystric cambisols) of the Strichen Series and are covered by *Calluna vulgaris* and *Vaccinium myrtillus*.[40]

Sample collection

Rain water, interception, spring water sourced from groundwater, soil throughflow water, deep spring water, soil porewater and stream water samples were collected from the catchment between October 2001 and August 2003.

Rain water

Rain water was collected over two-week periods at the location of two of the three soil throughflow pit sites (see below), Pit 1 and Pit 2 (Fig. 1). To ensure the reliability of the rain water data set, collection from two sites rather than one was considered to be necessary. The collection apparatus at each site consisted of eight plastic funnels (inner diameter 168 mm) held at the ends and midpoints of each of four arms of a horizontal wooden cross which was supported on a wooden stake at a height of ~ 2 m. Plastic tubing connected the funnels to a covered 5 l collection bucket. A 250 ml aliquot of the accumulated rain water was taken at the end of each two-week period and any remainder discarded.

Interception

Interception gauges are designed to capture not only rainfall but also air particulates, mist, fog and cloud, thus providing a sample that might reflect the atmospheric components intercepted by vegetation.[27,41] Interception gauges were attached to the same wooden stakes as the rain water gauges at Pit 1 and Pit 2 (Fig. 1) and consisted of four cylinders of polyethylene-coated wire mesh supported vertically above plastic funnels.

Spring waters

A characteristic of the hydrology of the catchment was the presence of areas of flush on the hill-slopes. Water emerging from the ground *via* springs resulted in the formation of small surface flows which connected with the streams. Spot samples from six spring flows, S1 (366079E 780251N), S2 (366220E 780216N), S3 (366312E 780227N), S4 (366132E 780122N), S5 (366201E 779977N) and S6 (365472E 780396N) (Fig. 1), were collected in 250 ml polypropylene bottles every two weeks. Chemical analysis of these samples indicated that they had the hydrochemical characteristics of groundwater.[37] Thus the spring water samples could be used to establish the importance of Pb transport *via* groundwater into the streams.

Soil throughflow water

The collection of throughflow waters was carried out so that the importance of vertical and lateral flow through different soil horizons with respect to Pb transport could be established. The locations of the three pit sites were as follows: Pit 1 (365904E 780238N), Pit 2 (366126E 780074N) and Pit 3 (366137E 780014N) (Fig. 1).

The soils at Pit 1 were similar to the hill peat in the most elevated parts of the catchment and those at Pits 2 and 3 to the Gaerlie Series.[38,41] The depths of the soil horizons at each of the three soil pits were as follows. At Pit 1, the S (surface), A, B, and C horizons corresponded to depths of 0–2, 2–8, 8–52 and 52–84 cm, respectively. At Pit 2, the S, A, B, C, and D horizons were found at depths of 0–2, 2–37, 37–61, 61–85 and 85–145 cm, respectively. The S, A, B, and C horizons at Pit 3 were defined by depth intervals of 0–2, 2–48, 48–93 and 93–135 cm, respectively. Base rock in Pits 1, 2 and 3 was encountered at depths of 84, 145 and 135 cm, respectively.

Water flowing through the soil horizons was channelled through plastic tubing to 5 l plastic collection buckets. A detailed account of the soil throughflow sampling equipment set-up, similar to that adopted in this study, has been published by Miller *et al.*[42] A 250 ml aliquot of the accumulated soil throughflow water from each horizon was sampled every two weeks and any excess discarded.

Deep spring water (groundwater)

A spot sample of water emerging at a depth of 135 cm from a deep spring just below the site of Pit 3 was collected (250 ml) in a polypropylene bottle every two weeks.

Soil porewaters

Soil porewaters were collected over two-week periods near each of the six stream water sampling sites (Fig. 1). Prenart Super Quartz suction cup lysimeters (Prenart Equipment ApS, Frederiksberg, Denmark) were placed at depths of 0–5 and 15–20 cm at each site. Each lysimeter was connected by plastic tubing to a 1 l polypropylene collecting bottle. Vacuum ($\sim$750 mbar) was applied to the lysimeter–collecting bottle system using a portable vacuum pump. A 250 ml aliquot of the accumulated soil porewater was sampled every two weeks. Excess porewater was discarded, the collecting bottle was re-installed and the vacuum was then re-applied to the system. These samples were collected at sites close to the streams for comparison with the soil throughflow waters from the pits which were located more centrally within the catchment.

Stream water

Stream water was collected daily in 600 ml polyethylene bottles using Rock & Taylor 48 Interval Samplers (Rock & Taylor Ltd, Warley, West Midlands, UK) at stream sites CB1 (365465E 780486N), CB3 (366035E 779575N), BB1 (366320E 780234N) and BB3 (366067E 779631N) (Fig. 1) and in 575 ml polyethylene bottles using Xian 1000 samplers (Bühler Montec Group Limited, Salford, Manchester, UK) at stream sites CB2 (365834E 779575N) and BB2 (366203E 779965N) (Fig. 1). During storm event conditions the raised water levels of the streams triggered two-hourly sample collection at stream sites CB3 and BB3. Some of the daily samples were collected during the storm events and are included in the stream water data presented herein but a detailed description and discussion of storm event samples is considered separately in Graham *et al.*[36]

Sample preparation

Aliquots ($\sim$250 ml) of all collected samples were acidified with 0.5 ml nitric acid (Aristar nitric acid, 15.55 M, VWR International Ltd, Poole, UK) and then concentrated ten-fold by evaporation on a hot plate to reduce volume. The resultant concentrated samples were $\sim$2% v/v (0.31 M) nitric acid. 'Sample blanks' of 250 ml were similarly acidified and reduced in volume on a hot plate alongside the samples. The concentrated sample blanks were also $\sim$2% v/v nitric acid.

Sample analysis

Pb concentration. All samples were analysed by graphite furnace-atomic absorption spectrometry (GF-AAS) using a PE 1100B spectrometer and HGA 700 graphite furnace (Perkin Elmer, Seer Green, UK). The four-step furnace temperature program for drying, ashing, atomisation and purging of sample was 140 °C (60 s, ramp time 5 s), 500 °C (20 s, ramp time 3 s), 1700 °C (3 s) and 2500 °C (2 s, ramp time 1 s), respectively. The injection temperature was 30 °C. The argon gas flow was 300 ml min^{-1} for all steps, except for the atomisation step when there was no flow. The spectrometer settings were as follows: lamp current 7 mA, D_2 arc background correction, wavelength 283.3 nm, slit 0.7 nm, peak area signal processing, integration time 3 s, read delay 0 s. Samples with high Pb concentration ($>$40 µg l^{-1}) were analysed by flame-atomic absorption spectrometry (F-AAS) using a Solaar 929 AA spectrometer (ATI Unicam, Cambridge, UK).

Samples were analysed in three replicate runs. Calibration standards of 1, 2, 3, 4, 5, 10, 20, 30 and 40 µg l^{-1} Pb were prepared from a 1000 mg l^{-1} stock solution of Pb in 1 M nitric acid (Fisher Scientific UK, Loughborough, Leicestershire, UK) by dilution with 2% v/v nitric acid. Water used in the preparation of 2% v/v nitric acid was deionized and purified by reverse osmosis and ion exchange to $\sim$18 MΩ cm quality using a Milli-RO 15 and Milli-Q SP system (Millipore, Watford, UK). Natural water reference materials (Certified Reference Material LGC6019, LGC Middlesex, UK and Standard Reference Material SRM1640, National Institute of Standards & Technology, Maryland, USA) were used for quality control. For LGC6019 (certified Pb concentration 5.2 $\pm$ 0.3 µg l^{-1}), the mean value obtained by GF-AAS was 4.3 $\pm$ 0.7 µg l^{-1}. For SRM1640 (certified Pb concentration 27.89 $\pm$ 2.91 µg l^{-1}), the mean value obtained by GF-AAS was 30.6 $\pm$ 2.9 µg l^{-1}. Mean analytical precision (relative standard deviation) on the measured Pb concentrations for the different types of samples was $\pm$4% (range $\pm$2.8–4.4%).

Pb isotope ratios. All samples were analysed by inductively coupled plasma-mass spectrometry (ICP-MS) using a Plasma-Quad (PQ) 3 instrument (VG Elemental, Winsford, UK) with nickel sampler and skimmer cones, a Meinhard nebulizer, Gilson autosampler and Gilson Minipuls 3 peristaltic pump (Anachem, Luton, UK). Details of the instrument operation were described in Farmer *et al.*[27] A Pb isotopic reference material (Standard Reference Material 981, National Institute of Standards & Technology, Maryland, USA) was used for mass bias correction. Sample counts were corrected by sub-

traction of the counts obtained for 2% v/v nitric acid. Mean analytical precision (relative standard deviation) on the measured $^{206}Pb/^{207}Pb$ ratios was ±0.27% (range ±0.15–0.47%). Of the 3927 samples analysed by ICP-MS, Pb isotope ratio data for only 14 were discounted as outliers.

Other measurements

Rainfall. Rainfall was recorded on a two-weekly basis at the UK Environmental Change Network (ECN) station situated close to BB3. The overall error (arising from spatial variability and altitude enhancement) associated with the rainfall measurements was estimated at ±15%.[37]

Stream flow. Stage height measurements were obtained at 15-minute intervals from the ECN sampling station[43] situated close to BB3. The stage height-discharge relationship was used to convert these measurements to flow rate and averaging of the 15-minute values gave mean daily flow data for the ECN station during the time period October 2001–August 2003. On the basis of salt dilution gauging of stream flow (carried out monthly during 2002 and two-weekly during 2003), the relationship between flow at the three sampling points on each stream and that at the ECN station was established. This enabled the calculation of the daily flow rate at each of the six stream sampling sites. The overall error associated with stream flow measurements was estimated at ±15%.[37]

Results

The overall data set obtained during the two-year period of study was extremely large and has therefore been represented in the following ways. The individual time series trends in Pb concentration and $^{206}Pb/^{207}Pb$ ratio have been shown for rainwater, interception and stream water samples. Summary tables showing the range, the mean and median concentration and isotope ratio values, however, enable direct comparison of the data sets for all of the different sample types. In addition, the data were not always normally distributed about a mean value,

and histograms have been constructed for more detailed considerations. These histograms are contained in an accompanying data file (ESI†). The time series trends in Pb concentration and $^{206}Pb/^{207}Pb$ ratio for spring waters, soil throughflow and soil porewaters are also contained in the ESI.†

Rain water

The two-weekly data for rainfall, rain water Pb concentration and rain water $^{206}Pb/^{207}Pb$ ratio at Pits 1 and 2 are shown in Fig. 2. For the period October 2001–August 2003, the mean Pb concentrations in Pits 1 and 2 rain water were in good agreement at 1.21 ± 0.88 and 1.09 ± 0.87 µg l^{-1}, respectively. The range of values was from <0.1 µg l^{-1} to 4.1 µg l^{-1} (Table 1) but more than 60% of the values were in the range 0.5–2 µg l^{-1} at both Pits 1 and 2 (see ESI,† Fig. A1a).

Over the same time period, the mean $^{206}Pb/^{207}Pb$ ratio for Pit 1 rain water was 1.153 ± 0.007 whilst that for Pit 2 was slightly higher at 1.158 ± 0.008 (Table 1). Comparing the two data sets, there was a flatter distribution of isotope ratio values in the range 1.145–1.170 and a larger proportion (43% compared with 15% at Pit 1) of values greater than 1.160 for Pit 2 (ESI,† Fig. A1b).

Interception

The two-weekly data for rainfall, interception Pb concentration and interception $^{206}Pb/^{207}Pb$ ratio at Pits 1 and 2 are shown in Fig. 3. For the period May 2002–August 2003, interception Pb concentrations were typically higher than those in rain water as illustrated by mean concentrations of 4.69 ± 4.69 and 3.00 ± 4.22 µg l^{-1} at Pits 1 and 2, respectively (Table 1). The range of values was also much wider (0.1–22.9 µg l^{-1}). Compared with Pit 2, the higher mean concentration at the more elevated Pit 1 reflected the greater number of samples (28% compared with 12.5%) with concentrations >5 µg l^{-1} (ESI,† Fig. A1a).

The mean $^{206}Pb/^{207}Pb$ ratios for interception were 1.151 ± 0.005 at Pit 1 and 1.150 ± 0.005 at Pit 2 (Table 1). As might be

Pit 1   Pit 2
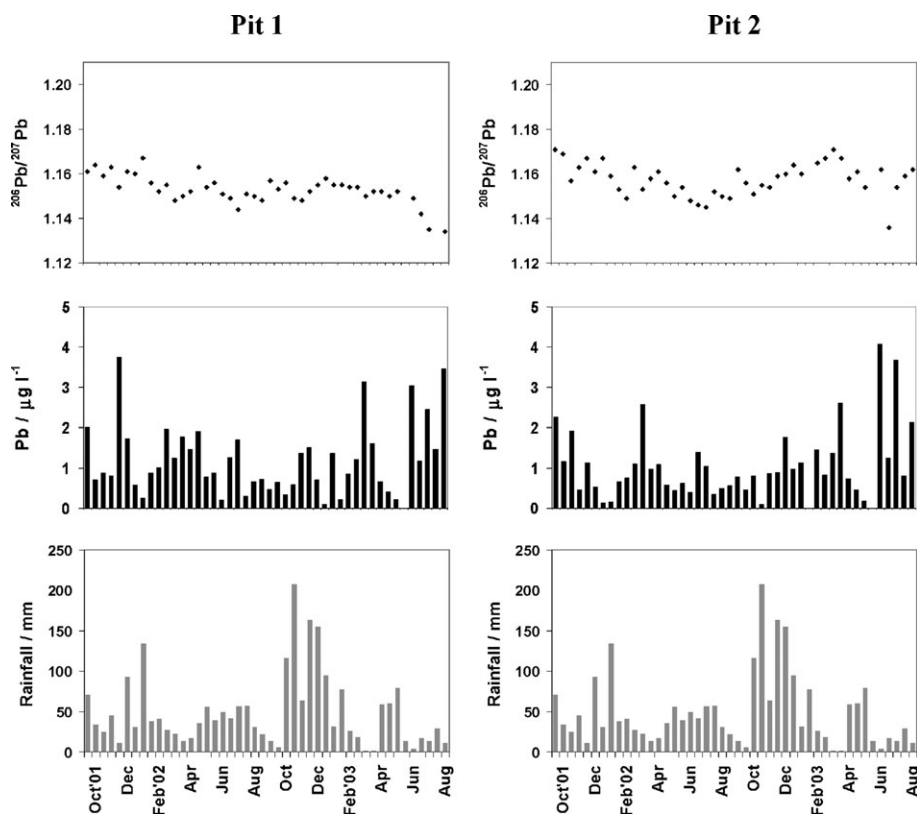
Fig. 2 Rain water $^{206}Pb/^{207}Pb$ ratios (typical error ±0.004) and Pb concentrations at Pits 1 and 2 along with the rainfall at the ECN station for two-weekly intervals during the period October 2001–August 2003 at Glensaugh.

Table 1 Pb concentration and $^{206}Pb/^{207}Pb$ ratio in rain water and interception collected over two-week periods at Pits 1 and 2

| Location | Sample type | Time period | n | Pb concentration/μg l^{-1} | | | $^{206}Pb/^{207}Pb$ ratio | | |
				Range[a]	Mean	Median	Range	Mean	Median
Pit 1	Rain	Oct 01–Aug 03	45	0.10–3.75	1.21 ± 0.88	0.88	1.134–1.167	1.153 ± 0.007	1.153
	Interception[b]	May 02–Aug 03	32	0.20–21.0	4.69 ± 4.69	3.66	1.137–1.161	1.151 ± 0.005	1.151
Pit 2	Rain	Oct 01–Aug 03	44	<0.10–4.07	1.09 ± 0.87	0.85	1.136–1.171	1.158 ± 0.007	1.159
	Interception[b]	May 02–Aug 03	31	0.10–22.9	3.00 ± 4.22	1.59	1.138–1.164	1.150 ± 0.005	1.150

[a] "Less than values": concentrations below the detection limit (a lower limit of 1 μg l^{-1} in the analysed solutions gave detection limits of ~0.09–0.10 μg l^{-1} in the original water samples); for the purposes of calculation of mean and median values, however, the one sample with a Pb concentration below the limit of detection was assigned a concentration equal to the detection limit. [b] No data before May 2002.

expected on the basis of the mean values, the distribution of the isotope ratio data for each site was very similar (ESI,† Fig. A1b). The mean interception $^{206}Pb/^{207}Pb$ ratio value was closer to the mean rain water value at Pit 1, there being fewer high values (*i.e.* >1.160) for rain water at Pit 1 relative to Pit 2 (ESI,† Fig. A1b).

Spring waters (sourced from groundwater)

Table 2 summarises the time series data ($^{206}Pb/^{207}Pb$ ratio and Pb concentration) for springs S1–S6. Apart from S5 and S6, which had low mean Pb concentrations of ~0.4–0.5 μg l^{-1}, the mean values (~1.1–2.7 μg l^{-1}) for the spring waters (Table 2) were generally slightly higher than those for rain water (Table 1). This was generally attributable to a small number of spring water samples containing elevated concentrations of Pb (up to ~32 μg l^{-1}; ESI,† Fig. A2) as reflected in the lower median (0.25–1.35 μg l^{-1}) relative to the mean values (Table 2). Indeed up to 50% of the samples at each site had concentrations in the range 0.07–0.3 μg l^{-1} (ESI,† Fig. A3). This was significantly greater than the ~10% of rain water samples that had Pb concentrations in the same range (ESI,† Fig. A1a).

The mean $^{206}Pb/^{207}Pb$ ratios of 1.158 ± 0.006, 1.155 ± 0.004, 1.158 ± 0.005 and 1.157 ± 0.005 for S1, S2, S4 and S5, respectively (Table 2), were very similar and close to the mean values for Pit 1 and 2 rain water (Table 1). In contrast to the

spread of Pb concentration data, that of the isotope ratio data was very small, with 77–94% of the isotope ratio data at each of S1, S2, S4 and S5 falling within the range 1.150–1.165 (ESI,† Fig. A4). The mean ratio for S3 samples was 1.164 ± 0.004 (Table 2), reflecting a higher proportion (76%) of data in the range 1.160–1.170 (ESI,† Fig. A4). In contrast, S6, the only one of the six spring flows entering the Cairn Burn, had a lower mean ratio value of 1.151 ± 0.004, identical to the median value, and 67% of the data in the range 1.145–1.155 (ESI,† Fig. A4).

Soil throughflow

Table 2 contains the summary data for the $^{206}Pb/^{207}Pb$ ratio and Pb concentration time series data for each horizon from all three pits. Excluding the deep spring (0.4 μg l^{-1}) at Pit 3, the mean Pb concentrations for the throughflow waters varied from 1.0 to 2.9 μg l^{-1} (Table 2). Investigation of vertical concentration profiles at each pit revealed that the mean Pb concentrations were greatest for the A and C horizons at Pit 1 and for the A and D horizons at Pit 2 (Table 2). Higher concentrations were generally observed in the S and A horizons compared with the C horizon at Pit 3 (Table 2). Although the mean concentrations were influenced by a small number of high values, the same horizons at each pit generally also had

Pit 1   Pit 2
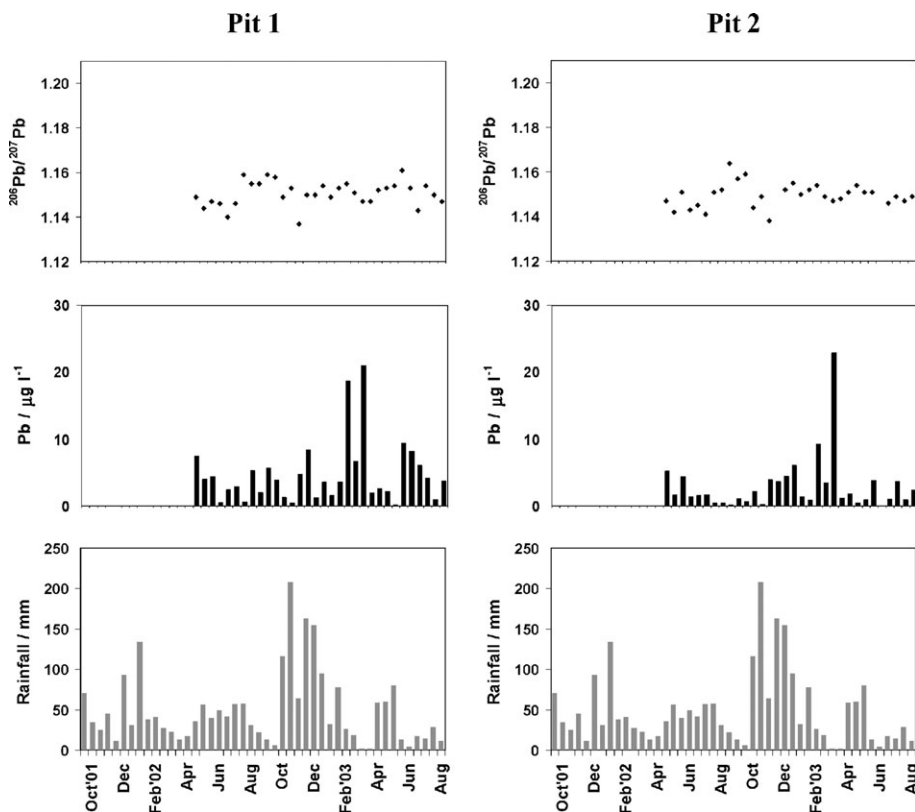
Fig. 3 Interception $^{206}Pb/^{207}Pb$ ratios (typical error ±0.004) and Pb concentrations at Pits 1 and 2 along with the rainfall at the ECN station for two-weekly intervals during the period October 2001–August 2003 at Glensaugh.

Table 2 Pb concentration and $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in spring flows, throughflow (Pits 1–3) and soil porewaters for the catchment

Sample type	Label	Time period	n	Pb concentration/µg l⁻¹			$^{206}\text{Pb}/^{207}\text{Pb}$ ratio		
				Range[a]	Mean	Median	Range	Mean	Median
Spring flow[b]	S1	May 02–Aug 03	31	<0.09–17.9	1.42 ± 3.51	0.25	1.142–1.169	1.158 ± 0.006	1.157
	S2	May 02–Aug 03	31	<0.12–32.2	2.66 ± 5.68	1.35	1.147–1.162	1.155 ± 0.004	1.154
	S3	May 02–Aug 03	33	<0.09–6.20	1.46 ± 1.37	1.00	1.156–1.172	1.164 ± 0.004	1.164
	S4	May 02–Aug 03	33	<0.09–12.2	1.11 ± 2.18	0.53	1.145–1.164	1.158 ± 0.005	1.159
	S5	May 02–Aug 03	32	<0.10–1.40	0.42 ± 0.36	0.29	1.143–1.170	1.157 ± 0.005	1.156
	S6	May 02–Aug 03	25	0.07–2.43	0.46 ± 0.58	0.26	1.144–1.162	1.151 ± 0.004	1.151
Soil throughflow at Pit 1	S horizon	Oct 01–Aug 03	30	0.11–7.30	1.82 ± 1.78	1.11	1.139–1.160	1.145 ± 0.005	1.144
	A horizon	Oct 01–Aug 03	38	0.26–14.4	2.85 ± 3.32	1.50	1.149–1.167	1.160 ± 0.004	1.160
	B horizon	Oct 01–Aug 03	36	0.18–8.92	1.76 ± 1.78	1.15	1.153–1.172	1.162 ± 0.003	1.162
	C horizon	Oct 01–Aug 03	39	0.13–13.6	2.69 ± 3.21	1.49	1.138–1.168	1.158 ± 0.006	1.159
Soil throughflow at Pit 2	S horizon	Oct 01–Aug 03	20	0.20–2.84	1.27 ± 0.89	1.05	1.135–1.166	1.155 ± 0.007	1.155
	A horizon	Oct 01–Aug 03	34	0.19–6.86	1.80 ± 1.38	1.56	1.154–1.172	1.164 ± 0.004	1.165
	B horizon	Oct 01–Aug 03	13	<0.09–2.02	0.96 ± 0.62	1.07	1.149–1.172	1.155 ± 0.006	1.155
	C horizon	Oct 01–Aug 03	37	<0.10–4.39	1.02 ± 0.92	0.84	1.158–1.177	1.167 ± 0.005	1.167
	D horizon	Oct 01–Aug 03	29	0.11–10.2	1.61 ± 1.96	1.04	1.151–1.211	1.174 ± 0.016	1.172
Soil throughflow at Pit 3[c]	S horizon	Oct 01–Aug 03	17	<0.09–14.9	2.50 ± 4.37	0.85	1.158–1.169	1.163 ± 0.003	1.163
	A horizon	Oct 01–Aug 03	6	<0.10–9.31	2.80 ± 3.62	1.10	1.139–1.164	1.153 ± 0.012	1.157
	B horizon	Oct 01–Aug 03	—	—	—	—	—	—	—
	C horizon	Oct 01–Aug 03	28	<0.10–4.64	1.31 ± 1.19	0.95	1.154–1.204	1.174 ± 0.018	1.173
	Deep Spring	Oct 01–Aug 03	46	<0.09–4.29	0.42 ± 0.68	0.20	1.136–1.182	1.154 ± 0.009	1.155
Soil porewater at CB1	CB1 surface	Oct 01–Aug 03	14	0.62–2.41	1.42 ± 0.55	1.35	1.152–1.171	1.163 ± 0.005	1.164
	CB1 depth	Oct 01–Aug 03	30	0.09–6.35	0.93 ± 1.13	0.63	1.157–1.179	1.170 ± 0.005	1.172
Soil porewater at CB2	CB2 surface	Oct 01–Aug 03	35	<0.10–17.1	5.57 ± 4.50	5.39	1.154–1.168	1.161 ± 0.004	1.161
	CB2 depth	Oct 01–Aug 03	37	<0.09–5.99	1.45 ± 1.55	1.00	1.137–1.175	1.163 ± 0.007	1.163
Soil porewater at CB3[d]	CB3 surface	Oct 01–Aug 03	—	—	—	—	—	—	—
	CB3 depth	Oct 01–Aug 03	5	<0.09–7.33	2.11 ± 3.01	1.00	1.168–1.183	1.179 ± 0.006	1.181
Soil porewater at BB1	BB1 surface	Oct 01–Aug 03	30	0.57–8.37	3.08 ± 1.62	2.81	1.158–1.182	1.174 ± 0.006	1.176
	BB1 depth	Oct 01–Aug 03	41	<0.09–2.45	0.31 ± 0.40	0.18	1.146–1.183	1.167 ± 0.008	1.167
Soil porewater at BB2	BB2 surface	Oct 01–Aug 03	30	<0.09–1.64	0.49 ± 0.47	0.27	1.140–1.178	1.161 ± 0.010	1.161
	BB2 depth	Oct 01–Aug 03	37	<0.09–1.30	0.30 ± 0.33	0.16	1.136–1.181	1.157 ± 0.010	1.157
Soil porewater at BB3	BB3 surface	Oct 01–Aug 03	36	<0.10–6.60	1.18 ± 1.15	0.96	1.154–1.179	1.170 ± 0.006	1.171
	BB3 depth	Oct 01–Aug 03	39	<0.09–3.03	0.44 ± 0.56	0.24	1.149–1.178	1.162 ± 0.006	1.163

[a] "Less than values": concentrations below the detection limit (a lower limit of 1 µg l⁻¹ in the analysed solutions gave detection limits of ~0.09–0.12 µg l⁻¹ in the original water samples). [b] No data before May 2002. [c] No data for Pit 3 B horizon. [d] No data for CB3 surface.

the greater median values (Table 2). The mean Pb concentrations in throughflow were, on average, one and a half times higher but the range of values was a factor of two smaller (0.09–14.9 µg l⁻¹) than the corresponding values for the spring flows (Table 2; ESI,† Figs. A2 and A5). In the main, more than 60% of the Pb concentrations in samples from individual throughflows were in the range 0.4–3 µg l⁻¹ (ESI,† Fig. A6). In contrast, the deep spring just below Pit 3, from which large volumes of water emerged (average flow rate = 0.41 l s⁻¹), had a mean Pb concentration of only 0.4 ± 0.7 µg l⁻¹ (Table 2) and 51% of values were in the range <0.09–0.3 µg l⁻¹ (ESI,† Fig. A6).

Variations in the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio were most clearly illustrated by plotting the mean ratio value (± 1 σ) against depth (Fig. 4). The value of 1.145 ± 0.005 obtained for S horizon throughflow at Pit 1 was statistically significantly (e.g. for S and A horizons, $|t| = 13.84$; critical value for 66 degrees of freedom is 2.58; 99% confidence interval) lower than the mean values for all underlying horizons at this site (Table 2 and Fig. 4). There was no significant difference (e.g. for A and B horizons, $|t| = 2.09 <$ critical value of 2.58 for 72 degrees of freedom; 99% confidence interval) between the mean values (~1.16) for throughflow from the A, B and C horizons (Table 2; ESI,† Fig. A7). At Pit 2, there was a non-uniform increase in $^{206}\text{Pb}/^{207}\text{Pb}$ ratio from 1.155 ± 0.007 (S) to 1.174 ± 0.016 (D) with increasing depth (Table 2 and Fig. 4). At Pit 3, however, there was no consistent vertical trend but, in contrast with Pits 1 and 2, the mean value of 1.163 ± 0.003 for the S horizon was higher than that of 1.153 ± 0.012 for the A horizon throughflow waters (Table 2 and Fig. 4). The deep spring emerging from just below Pit 3 had a lower, but not statistically significant, mean $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of 1.154 ± 0.009 compared

to a mean value of 1.174 ± 0.018 for the C horizon (Table 2 and Fig. 4). The median values of 1.155 and 1.173 for the deep spring and the C horizon, respectively, were in good agreement with the mean values.

Soil porewaters (Prenarts)

The $^{206}\text{Pb}/^{207}\text{Pb}$ ratio and Pb concentration time series data, respectively, for soil porewaters collected at both depths from the Prenart samplers at all six sites adjacent to the streams are summarised in Table 2 (ESI,† Figs. A8 and A9). The surface Prenart samplers were positioned at 0–5 cm, similar to the depth of the S horizon in the pits (0–2 cm), whilst the deeper samplers were located at 15–20 cm depth, more analogous to the A horizon at the pits (or the B horizon at Pit 1). The overall range of values, 0.09–17.1 µg l⁻¹, was closer to that of throughflow than of the spring flows (Table 2; ESI,† Figs. A3, A6 and A10). The mean Pb concentrations for the surface (0–5 cm) samples ranged from 0.5 (BB2) to 5.6 (CB2) µg l⁻¹, in every case higher than the mean concentrations (0.3–2.1 µg l⁻¹) for the deeper (15–20 cm) samples at the same site (Table 2). No data are reported for the surface sampler at CB3 as no samples were obtained during the sampling period.

The mean $^{206}\text{Pb}/^{207}\text{Pb}$ ratios for the surface (0–5 cm) soil porewaters were 1.163 ± 0.005 and 1.161 ± 0.004 at CB1 and CB2, and 1.174 ± 0.006, 1.161 ± 0.010 and 1.170 ± 0.006 at BB1, BB2 and BB3, respectively (Table 2). These were significantly higher than the values of 1.145 ± 0.005 and 1.155 ± 0.004 for the S horizons at Pits 1 and 2, respectively, but were closer to the value of 1.163 ± 0.003 observed for the S horizon at Pit 3 (Table 2; ESI,† Figs. A4, A7 and A11). The mean ratio

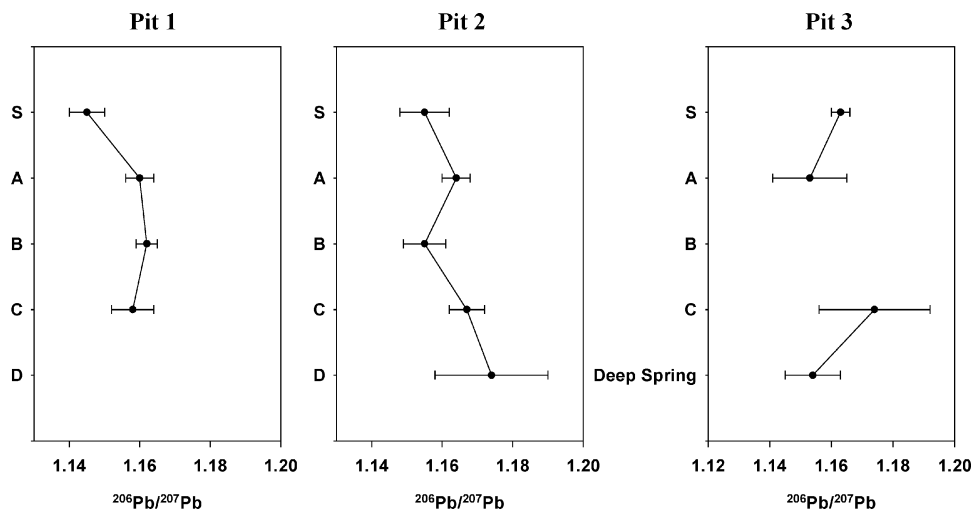**Fig. 4** Mean $^{206}Pb/^{207}Pb$ ratios for soil throughflow waters from Pits 1–3 during the period October 2001–August 2003 at Glensaugh.

values for the deeper (15–20 cm) Prenart samples on the banks of the Birnie Burn were in the range 1.157 ± 0.010–1.167 ± 0.008, *i.e.* close to those observed for the A horizons at Pits 1 and 2, but those for Cairn Burn soil porewaters ranged from 1.163 ± 0.007 to 1.179 ± 0.006 and were significantly higher than the Pits 1–3 A horizon values (Table 2). Thus, contrasting vertical trends were observed for the soil porewaters at Birnie Burn and Cairn Burn, the $^{206}Pb/^{207}Pb$ ratio decreasing with increasing depth for the former whilst increasing with increasing depth for the latter.

Stream waters

The daily data for stream flow, Pb concentration and $^{206}Pb/^{207}Pb$ ratio at CB1–CB3 (Cairn Burn) and BB1–BB3 (Birnie Burn) are shown in Figs. 5 and 6, respectively.

Cairn Burn

The flow rates at each site were approximately proportional to the relative catchment areas draining to each point on the stream, although flows for CB1 were slightly enhanced. The mean baseflow flow rates were 0.005, 0.010 and 0.011 $m^3 s^{-1}$ whilst the highest flow rates were ~ 0.15, 0.40 and 0.45 $m^3 s^{-1}$ at CB1, CB2 and CB3, respectively (Fig. 5).

Stream water Pb concentrations on the Cairn Burn ranged from <0.08 to 17.1 $\mu g\,l^{-1}$, with mean values of ~ 0.6–1.1 $\mu g\,l^{-1}$ (Table 3). The highest daily values were found at CB2, which also had the highest mean value of 1.1 ± 1.7 $\mu g\,l^{-1}$ (Fig. 5 and Table 3). The median values of 0.36, 0.49 and 0.35 $\mu g\,l^{-1}$ were lower than the respective mean values. At all three sites, the distribution of concentration data was bimodal, with one peak centred around <0.1–0.2 $\mu g\,l^{-1}$ and the other around 0.5–2.0 $\mu g\,l^{-1}$ (ESI,† Fig. A12a). Correspondingly, 25–33% of the concentration data was <0.2 $\mu g\,l^{-1}$ whilst 33–35% was in the range 0.5–2.0 $\mu g\,l^{-1}$ (ESI,† Fig. A12a).

The mean $^{206}Pb/^{207}Pb$ isotope ratios were 1.156 ± 0.006, 1.159 ± 0.006 and 1.152 ± 0.006 at CB1, CB2 and CB3, respectively (Table 3). Although the differences in the mean values were small, ratios for the upper sampling sites, CB1 and CB2, were higher than that for CB3 (ESI,† Fig. A12b). In all cases, the median values were similar to the mean values.

Birnie Burn

The flow rates were approximately proportional to the sub-catchment drainage areas. The mean baseflow flow rates were 0.002, 0.004 and 0.006 $m^3 s^{-1}$ and the maximum flow rates were ~ 0.10, 0.25 and 0.40 $m^3 s^{-1}$ for BB1, BB2 and BB3, respectively (Fig. 6).
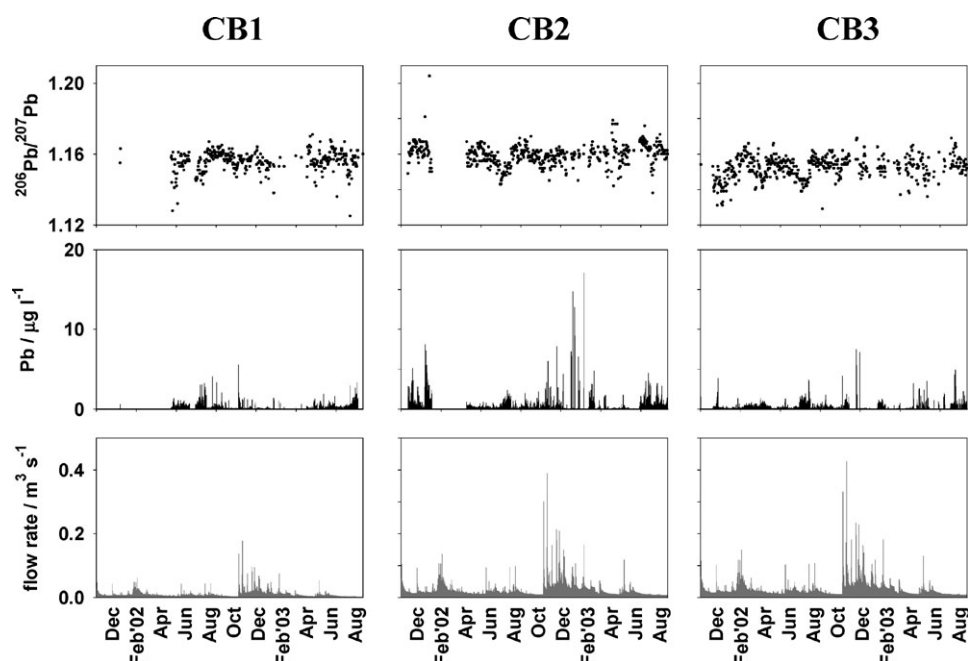

Fig. 5 Daily $^{206}Pb/^{207}Pb$ ratios, Pb concentrations and stream flows for CB1–CB3 during the period October 2001–August 2003 at Glensaugh.
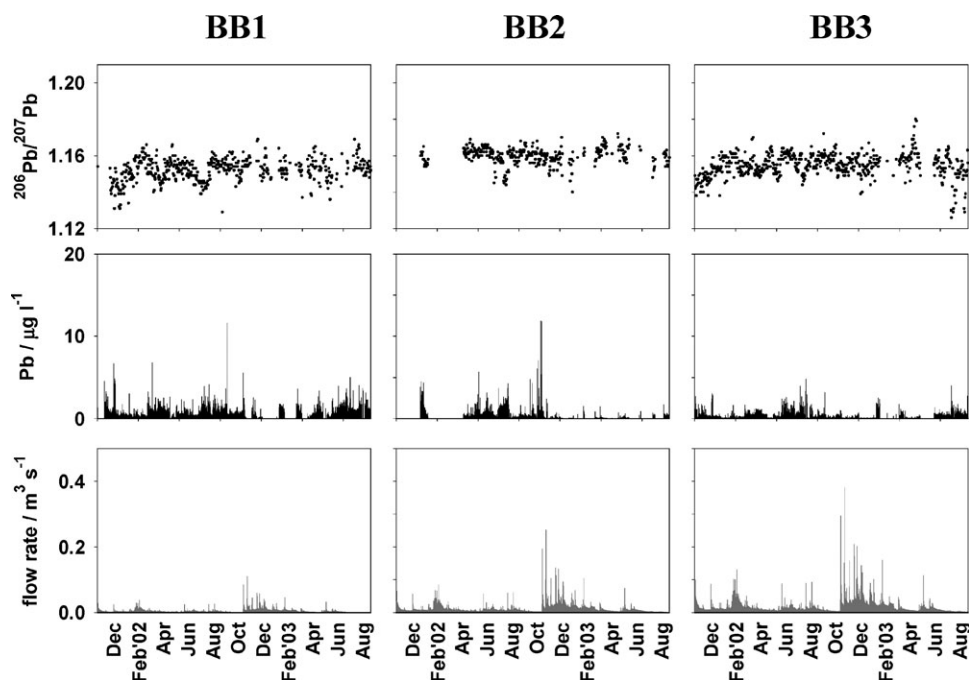
Fig. 6 Daily $^{206}Pb/^{207}Pb$ ratios, Pb concentrations and stream flows for BB1–BB3 during the period October 2001–August 2003 at Glensaugh.

Although the Pb concentration range of 0.08–11.9 µg l^{-1} was slightly narrower than that for the Cairn Burn, the mean values of ~0.6–1.2 µg l^{-1} for the Birnie Burn were quite similar to those obtained for the Cairn Burn stream waters (Table 3). Higher daily values (~3–~12 µg l^{-1}) were more frequently found at BB1 and BB2 in comparison with BB3 (Fig. 6). From BB1 to BB3, there was also an increase in the number of samples with Pb concentrations <0.5 µg l^{-1} (ESI,† Fig. A12a). These two factors clearly influenced the mean values, which decreased from BB1 to BB3 (Table 3).

The mean $^{206}Pb/^{207}Pb$ isotope ratios for BB1, BB2 and BB3 were 1.158 ± 0.004, 1.160 ± 0.005 and 1.155 ± 0.006, respectively (Table 3). As with the Cairn Burn stream waters, there were only small differences between the sites on the Birnie Burn but, again, there were slightly higher mean values at the upper sampling sites, BB1 and BB2 (ESI,† Fig. A12b).

Discussion

Rain water and interception Pb concentrations

Table 4 shows the change in rain water Pb concentrations at Glensaugh during the period 1989–2003. Compared with the present study, rain water Pb concentrations during the period 1989–1991 were significantly higher at up to 18.38 µg l^{-1} and with a mean value of 4.92 ± 5.47 µg l^{-1} (n = 19).[23] Other, unpublished, data showed that there had been only a small decrease from a mean value of 2.27 ± 3.16 µg l^{-1} (n = 12) in 1993 to 1.34 ± 0.71 µg l^{-1} (n = 10) in 2000.[27,44] The mean rain

water Pb concentrations of 1.21 ± 0.88 µg l^{-1} (Pit 1) and 1.09 ± 0.87 µg l^{-1} (Pit 2) obtained in this study during the period October 2001–August 2003 (Table 1) confirmed that, following the marked decrease observed towards the mid-1990s, there has been little subsequent change in rain water Pb concentrations at Glensaugh.

Rain water Pb concentrations recorded at Banchory, 16 km northeast of Glensaugh, decreased from ~10 µg l^{-1} in 1987 to ~2 µg l^{-1} in 1995.[45] Those reported for Lochnagar, 42 km to the west of Glensaugh, were in the range 0.24–3.75 µg l^{-1}, with a mean value of 1.11 µg l^{-1} during 1997–1998.[46] In 2000, values at Lochnagar were in the range 0.02–1.30 µg l^{-1}, with a mean value of 0.35 µg l^{-1}. Taken in conjunction with the Glensaugh data, the general trends for northern Scotland appear to have been a rapid decrease in Pb concentration towards the mid-1990s followed by a more gradual change towards the present. This is broadly consistent with the documented changes in atmospheric emissions of Pb in recent years.[47] For the UK as a whole, atmospheric emissions of Pb decreased by 80% from 1990 to 1999 but have not changed significantly from 2000 to 2002.[47]

In addition to the longer-term trends above, this study has revealed important information about variations over shorter time periods. Although not immediately apparent from the two-weekly time series data (Fig. 2), there was often an inverse relationship between concentration of Pb and rainfall (ESI,† Fig. A13), indicating that washout (decrease in metal concentration with increasing rainfall) was an important process influencing rain water Pb concentration. This has also been reported in several other studies elsewhere (e.g. Landing

Table 3 Pb concentration and $^{206}Pb/^{207}Pb$ ratio in stream waters CB1–BB3 and BB1–BB3 for the catchment

Location	Sample	Time period	n	Pb concentration/µg l^{-1}			$^{206}Pb/^{207}Pb$ ratio		
				Range	Mean	Median	Range	Mean	Median
Cairn Burn[a]	CB1	Oct 01–Aug 03	354	<0.09–5.59	0.57 ± 0.66	0.36	1.125–1.171	1.156 ± 0.006	1.157
	CB2	Oct 01–Aug 03	479	<0.08–17.1	1.06 ± 1.69	0.49	1.138–1.204	1.159 ± 0.006	1.160
	CB3	Oct 01–Aug 03	497	<0.08–7.53	0.58 ± 0.80	0.35	1.129–1.169	1.152 ± 0.006	1.153
Birnie Burn	BB1	Oct 01–Aug 03	558	<0.08–11.6	1.20 ± 1.02	1.00	1.131–1.167	1.158 ± 0.004	1.159
	BB2	Oct 01–Aug 03	358	<0.08–11.9	0.89 ± 1.32	0.47	1.140–1.172	1.160 ± 0.005	1.160
	BB3	Oct 01–Aug 03	584	<0.09–4.80	0.61 ± 0.63	0.43	1.126–1.180	1.155 ± 0.006	1.155

[a] More periods for which samples, and thus data, were not available.

Table 4 Concentration of Pb in rain water and stream water from the catchment during the period 1989–2003

| Time Period | n | Rain water Pb concentrations | | n | Stream water Pb concentrations | | Source |
		Range/µg l^{-1}	Mean/µg l^{-1}		Range/µg l^{-1}	Mean/µg l^{-1}	
1989–1991	19	0.25–18.38	4.92 ± 5.47	39	0.25–5.98	1.56 ± 1.53	Bacon and Bain[23]
1992–1993	25	0.2–13.20	3.07 ± 3.34				Bacon and Bain[23]
1993	12	0.15–11.28	2.27 ± 3.16				Farmer[44]
1994	9	0.45–4.93	1.94 ± 1.60				Farmer[44]
1995	3	0.58–3.45	1.54 ± 1.65				Farmer[44]
1997	3	1.50–4.10	2.88 ± 1.23				Farmer et al.[27]
1998	23	0.40–6.10	1.54 ± 1.34				Farmer et al.[27]
1999	12	0.18–6.44	1.88 ± 1.95	20	0.20–6.20	2.40 ± 1.40	Farmer[44]
2000	10	0.40–2.40	1.34 ± 0.71				Farmer[44]
2001–2003	44 (Pit 1)	0.10–3.75	1.21 ± 0.88	1081 (CB3 and BB3)	0.08–7.53	0.60 ± 0.71	This study

et al.,[48] Lawson and Mason[49]). The extent of this influence upon input of Pb to the catchment is explored later.

The inverse relationship between Pb concentration and rainfall was also observed for interception at Glensaugh. Interception Pb concentrations were approximately a factor of three higher than rain water concentrations (Table 1), a finding which will be used later to help provide an upper estimate of current Pb deposition for the catchment.

Rain water and interception $^{206}Pb/^{207}Pb$ ratios

Fig. 7 shows $^{206}Pb/^{207}Pb$ ratio data for rain water from Glensaugh previously reported in Bacon and Bain[23] and Farmer et al.[27] as well as other unpublished data[44] and the data from this study period, October 2001–August 2003. The rain water $^{206}Pb/^{207}Pb$ ratio has increased from ~1.12 at the beginning of the 1990s to ~1.14–1.16 by the late 1990s. The rate of subsequent change has been much slower and there has been very little, if any, increase in $^{206}Pb/^{207}Pb$ ratio during the period October 2001–August 2003.

For 1989–1991, the mean $^{206}Pb/^{207}Pb$ ratio for rain water collected at three long-term monitoring stations (Glensaugh; Hartwood, 10 km east of Motherwell, central Scotland; Sourhope, 18 km southeast of Kelso, southeast Scotland) was 1.120 ± 0.016.[23] Some unpublished data for rain water collected at Hartwood showed a change from 1.137 ± 0.014 in 1993 (n = 11) to 1.167 ± 0.012 in 1999 (n = 12) and, at Sourhope, a change from 1.126 ± 0.007 in 1993 (n = 10) to 1.155 ± 0.024 (n = 12) in 1999.[44] Thus a similar direction of change in the $^{206}Pb/^{207}Pb$ ratio in rain water collected from other rural locations in Scotland was observed over a similar time period. The results for rain water are also consistent with those obtained for grass samples collected at Glensaugh during the period 1989–2001.[33] This general picture showing co-occurrence of the increase in $^{206}Pb/^{207}Pb$ ratio and the decrease in Pb concentration is most likely a consequence of the introduction and increasing use of unleaded petrol, which commenced in the UK in 1986.[27]

Consideration of the two-weekly isotope ratio values for October 2001–August 2003 at Glensaugh revealed only small variations in $^{206}Pb/^{207}Pb$ ratio (Fig. 2). Lower values were found during summer months (e.g. 1.144–1.149 in July 2002 and 1.135–1.142 in July 2003) but a convincing seasonal trend was not apparent (Fig. 2). The higher values (1.158–1.171) during February–May 2003 in rain water samples collected at Pit 2 were not observed for those collected at Pit 1 but the effect on the mean ratio for the overall sampling period was small (Table 1). Analysis of the rain water from two sites was clearly important as typical values for the catchment could be established with greater confidence.

Additionally, from the two-weekly data (Fig. 2), there was little evidence of a relationship ($r^2 = 0.02$) between $^{206}Pb/^{207}Pb$ ratio and Pb concentration and so washout, which influenced Pb concentration, had no effect on the isotopic signature of Pb entering the catchment. This is supported by the good agreement between the weighted and unweighted mean isotope ratios for the entire sampling period (Table 1) and for the one-year period May 2002–April 2003 (Table 5). The isotope ratio data for interception (Fig. 3) again gave a very consistent signature for Pb input and was also unaffected by Pb concentration.

Stream water Pb concentrations

Table 4 presents the stream water Pb concentrations at Glensaugh during the period 1989–2003. Although the maximum values have increased slightly with time, the decrease in mean values from the 1990s to the present time was broadly in line with that described for rain water, suggesting that the input from rainfall has an influence (direct or indirect) on stream water Pb concentrations. A more detailed examination of the daily stream water (CB3 and BB3) and two-weekly rain water (Pit 1) data from the current study, however, showed that mean (0.60 ± 0.71 µg l^{-1}) and median (0.40 µg l^{-1}) concentrations in the stream water output (CB3 and BB3) from the catchment were lower (|t| = 5.59; 1124 degrees of freedom) than those (1.21 ± 0.88 µg l^{-1}; 0.88 µg l^{-1}) observed in current rain water (Table 1). Further consideration of the relationship between the input of Pb to the catchment and output of Pb from the catchment, taking account of the volumes of rain and stream water, is discussed under budget calculations.

From the time series data in Figs. 5 and 6, it was evident that higher stream water Pb concentrations sometimes correlated with high flow rates whilst, on other occasions, higher concentrations occurred during periods of low flow. Thus the inverse relationship observed between rain water Pb concentration and rainfall was not strongly evident for stream water Pb concentration and flow rate. The higher Pb concentrations in stream waters during prolonged drier periods (low flow) could arise from stream water evaporation but the partial correlation of high concentrations with high flow suggested
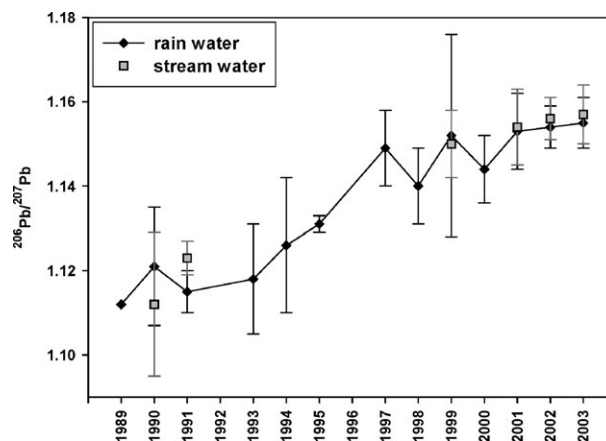
Fig. 7 Variation in $^{206}Pb/^{207}Pb$ ratio in rain water and stream water at Glensaugh during the period 1989–2003.[23,27,44]

Table 5 Rain water and interception Pb concentration, weighted $^{206}Pb/^{207}Pb$ ratio and calculated Pb inputs for the catchment during the period May 2002–April 2003

Location	Sample	Time period	Mean Pb concentration/μg l^{-1}	Weighted $^{206}Pb/^{207}Pb$ ratio	Rainfall/× 10^3 m^3	Pb input/g y^{-1}
Pit 1	Rain	May 02–Apr 03	0.97 ± 0.69	1.152	2492	1983 ± 316
Pit 2	Rain	May 02–Apr 03	0.90 ± 0.55	1.157	2492	1897 ± 302
Pit 1	Interception	May 02–Apr 03	4.79 ± 5.12	1.150	—	8515 ± 1357[a]
Pit 2	Interception	May 02–Apr 03	3.33 ± 4.71	1.149	—	6467 ± 1031[a]

[a] These Pb input values, derived from the two-weekly interception Pb concentrations, the two-weekly rainfall data and the catchment area, represent the interception-enhanced input to the catchment and include the input based on rainfall alone.

that interactions of input waters (*i.e.* rain water) with the catchment must contribute at least in part to the daily variations in Pb concentration in stream water.

Stream water $^{206}Pb/^{207}Pb$ ratios

Fig. 7 shows the variations in the mean $^{206}Pb/^{207}Pb$ ratio for stream water from Glensaugh during the period 1989–2003. A mean value of 1.114 ± 0.016 ($n = 10$) was recorded for the period 1989–1991 by Bacon and Bain.[23] By 1999, the mean value had increased to 1.150 ± 0.008 ($n = 18$).[44] During this current study, mean values were 1.154 ± 0.009 ($n = 236$), 1.156 ± 0.005 ($n = 2053$) and 1.157 ± 0.007 ($n = 541$) for 2001, 2002 and 2003, respectively. The overall pattern of change was very similar to that observed for rain water over the same time period, more convincingly showing that atmospheric inputs of Pb influenced the stream water outputs from the catchment.

A mean $^{206}Pb/^{207}Pb$ ratio of 1.129 ± 0.018 ($n = 8$) for stream water at Sourhope during the period 1989–1991 was reported by Bacon and Bain.[23] Although no recent data are available for comparison, the low mean stream water value was consistent with the mean rain water value of 1.120 ± 0.016 for all three long-term monitoring stations during the same time period.

There was no significant correlation ($r^2 \leq 0.01$) between the daily $^{206}Pb/^{207}Pb$ ratio data and either concentration or flow rate. As with rain water, lower ratio values were observed in July 2002 and July 2003, suggesting, at these times during the sampling period, a direct influence of the rain water input on the Pb isotopic signature of the stream water output from the catchment. Closer examination of the isotope ratio data for stream water samples with high Pb concentrations (> 5 μg l^{-1}), however, revealed that the associated isotope ratios were frequently higher than the mean values for stream water and, more significantly, for rain water. Indeed the mean $^{206}Pb/^{207}Pb$ value for these stream water samples was 1.162 ± 0.006 and 79% of the values ($n = 29$) were in the range 1.160–1.169 (ESI,† Fig. A14). The higher Pb concentrations together with the higher isotope ratio values strongly suggests that, at certain times during the sampling period, another source of Pb, specifically catchment-derived as distinct from contemporaneously atmospheric-deposited, was contributing to stream water outputs of Pb from the catchment. The stream flow rates corresponding to these daily samples ($n = 29$) ranged from 0.001 to 0.196 m^3 s^{-1} with a mean value of 0.039 ± 0.05 m^3 s^{-1}. Although the mean value suggested that high output typically occurred under high flow conditions (> 0.03 m^3 s^{-1}), there was no statistically significant correlation between mean daily stream flow rate and daily stream water Pb concentration. On the basis of the mean value, however, it could be hypothesised that catchment-derived Pb is being removed during high energy storm events. More thorough consideration of this hypothesis is beyond the scope of this paper but is instead the main focus of the work described in Graham *et al.*[36]

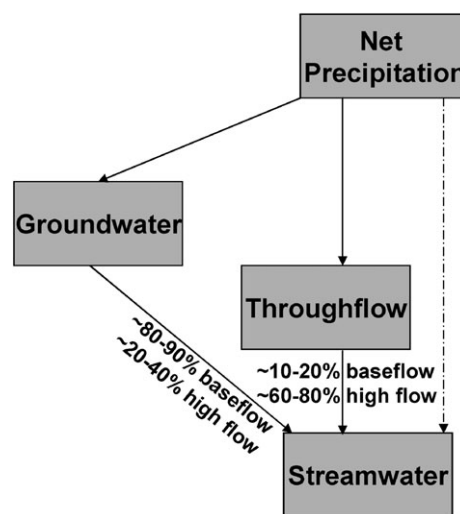### Contribution of throughflow and groundwater to stream water

A simple schematic representation of water flow through the catchment, based on a hydrological model,[37] is shown in Scheme 1. As a consequence of the relative surface areas, the majority of rain water falls on the catchment rather than directly enters the streams. Following deposition, rain water entering the streams *via* the catchment has been categorised into two types, namely groundwater (emerging springs) and throughflow (pit horizons). The flow contributions of each type to stream water and the implications for Pb transport will be considered in turn.

Spring flow (sourced from groundwater) Pb concentrations and $^{206}Pb/^{207}Pb$ ratios

For several of the springs (S1, S4, S5 and S6) the median Pb concentrations (Table 2) were lower than those for rain water (Table 1) whilst the mean $^{206}Pb/^{207}Pb$ ratios were similar to those for rain water (Tables 1 and 2). From hydrological modelling, groundwater has been shown to be the main contributor (80–90%) to stream water under baseflow conditions.[37] Thus groundwater is the means by which rain water falling on the catchment is most frequently transported to the streams. The slightly lower Pb concentrations in springs are attributable to retention of Pb by the catchment. There has been no effect, however, on the Pb isotopic signature and so spring flow water entering the streams is isotopically indistinguishable from rain water directly entering the streams. This interpretation, based on the hydrological model,[37] would be consistent with the stream water data set, which showed that the isotopic signature of stream water Pb (~ 1.15–1.16) was very similar to that of contemporaneous rain water.

Under high flow conditions (resulting from heavy and prolonged rainfall), however, only about 20–40% of stream water is derived from groundwater.[37] Indeed, the annual volumetric contribution of throughflow to stream water is about 35–40%[37] and so the characteristics of the throughflow waters are important.

Scheme 1 Schematic representation of contribution of water flows to stream water for the Glensaugh catchment based on hydrological modelling.[37]

Throughflow (and Prenart soil porewater) Pb concentrations and $^{206}Pb/^{207}Pb$ ratios

The more prolonged contact with catchment soils was manifested by the generally slightly higher mean and median Pb concentrations for throughflow from all horizons compared with those for both groundwater and rain water (Tables 1 and 2). A fairly consistent feature of the time series data (ESI,† Fig. A5) was the build up of Pb concentrations during summer periods (e.g. June–August 2002 and June–August 2003). Concentrations in, for example, throughflow for all horizons at Pit 1, then decreased rapidly during the period of heavy rainfall during October 2002–January 2003. This would be consistent with the flushing out of the soil waters and the increased contribution of throughflow waters to stream waters during heavy and prolonged rainfall (leading to high flow conditions) as predicted by the hydrological model.[37]

Importantly, the concentration data for Pit 1 (ESI,† Fig. A5) suggest that throughflow Pb could be flushed out from all of the soil horizons. The $^{206}Pb/^{207}Pb$ ratios were therefore particularly useful in characterising throughflow waters from the different horizons and in elucidating Pb transport processes. Some of the observed trends were site-specific and so are discussed separately.

Pit 1. The $^{206}Pb/^{207}Pb$ ratio values for waters (mean 1.145 ± 0.005) flowing through the S horizon at Pit 1 were consistently lower than those for rain water (mean 1.153 ± 0.007 at Pit 1 and 1.158 ± 0.007 at Pit 2) whilst those for waters flowing through the A (1.160 ± 0.004) and B (1.162 ± 0.003) horizons were very slightly higher than the rain water values. For the C horizon, a mean value of 1.158 ± 0.006 was obtained. The vertical $^{206}Pb/^{207}Pb$ ratio profile for throughflow waters at Pit 1 (Fig. 4) was quite similar to that observed for the solid phase in the more elevated parts of the catchment.[34] The pattern of decreasing isotope ratio towards the surface has also been found in other UK soils, sediments and peat bogs.[24,25,30] It has been attributed to the contribution of car-exhaust emissions of Pb (arising from the use of Australian Pb of low $^{206}Pb/^{207}Pb$ ratio (= 1.04) in the manufacture of alkyl lead additives for leaded petrol ($^{206}Pb/^{207}Pb$ ratio = 1.06–1.09) to deposited anthropogenic Pb during the period ∼1930–∼1990. The observation of a similar vertical trend in throughflow waters is significant because it suggests that (i) soil-derived Pb is potentially mobile but (ii) vertical transport of Pb with a low isotopic signature from surface to deeper throughflow waters is minimal. Other soil studies have also found very little evidence to support downwards migration of Pb. More recently, for example, Pb concentration and Pb isotope ratio data showed that <0.1% of the potentially mobile pool of Pb migrated downward out of the first 25 cm of Versaille soils.[17] As a consequence of such low vertical mobility at Glensaugh, lateral water flow through surface horizons would lead to transport of Pb with a highly characteristic isotopic signature distinguishable from that of Pb flowing through deeper horizons and indeed from current rain water inputs of Pb to the catchment.

Pit 2. Although the S horizon throughflow water also had a lower mean $^{206}Pb/^{207}Pb$ ratio than the waters from the underlying horizons, the mean value is not distinguishable from that for current rain water. From studies of soils in the less elevated parts of the catchment,[35] however, the decrease in solid phase $^{206}Pb/^{207}Pb$ ratio towards the soil surface was not as great as for the upper catchment soils[34] and so the throughflow $^{206}Pb/^{207}Pb$ ratio profile at Pit 2 may reflect the specific solid phase profile in the lower parts of the catchment. The general increase in the ratio (to 1.174 ± 0.016) with increasing soil depth suggests that "older" anthropogenic and/or geogenic, rather than current atmospherically derived, sources of Pb are predominantly present in these deeper throughflow waters.

Pit 3. In spite of their close proximity, there were some obvious differences between Pits 2 and 3 which may be attributable to variations in topography and soil accumulation rates, even over relatively small areas. The lowest mean $^{206}Pb/^{207}Pb$ ratio of 1.153 ± 0.012 was found in the A horizon throughflow waters. The S horizon (0–2 cm) waters were characterised by a mean ratio of 1.163 ± 0.003 (Table 2). In some recent soil and sediment studies of Pb concentration and $^{206}Pb/^{207}Pb$ ratio, slightly increasing values of the latter towards the surface resulting from the phasing out of leaded petrol have been observed.[30] The higher mean value of 1.174 ± 0.018 for the D horizon, almost identical to that found for the Pit 2 C horizon, would again be most consistent with coal/smelting-derived and/or geogenic sources of Pb.[22,26]

Deep spring (Pit 3). In comparison with the overlying C horizon at Pit 3, a generally lower $^{206}Pb/^{207}Pb$ ratio was observed for the deep spring waters. This does not necessarily imply downwards migration of near-surface anthropogenic Pb with a low isotopic ratio. The mean $^{206}Pb/^{207}Pb$ ratio of 1.154 ± 0.009 for the deep spring was similar to that of rainfall during the sampling period. The water from the deep spring is thought to comprise groundwater that does not come from the directly overlying catchment and may have been deposited at higher elevations with a lag time before emergence at the site of the deep spring. Evidence to support this was obtained from measurement of oxygen isotopes and water chemistry. Compared with the C horizon, the deep spring had typically higher pH, higher Ca concentrations, generally lower TOC concentrations[37] and an almost constant $\delta^{18}O$ signature of ∼−8.5‰.[50] The last of these characteristics in particular strongly suggested that the spring water was not influenced by direct rainfall since the waters from the overlying horizons and rain water all exhibited more positive $\delta^{18}O$ values of ∼−3 to −4‰ during July 2003.[50] The deep spring is thus categorised, along with the spring flows, as groundwater on the basis of the typically high flow rates, low Pb concentrations and similar $^{206}Pb/^{207}Pb$ isotopic ratio to that of rain water.

In summary, the transport of Pb via throughflow waters to stream waters is important under high flow conditions and clearly a proportion of the Pb is derived from the catchment soils. In the main, Pb transport from the upper horizons has a lower $^{206}Pb/^{207}Pb$ ratio than that from the lower horizons, a finding that can be useful in the further deconvolution of pathways of Pb transport to stream water.[36]

Prenarts. Soil porewaters from the Prenart samplers located close to each of the stream water sampling sites also appeared to have characteristic isotope ratio profiles. For the Cairn Burn sites, the pattern of increasing $^{206}Pb/^{207}Pb$ isotope ratio with increasing soil depth was consistent in the main with the results from the soil throughflow pits. In contrast, the lower mean ratio values for the 15–20 cm compared with the 0–5 cm porewaters from the Birnie Burn sites requires further explanation. These sites were prone to flooding and it is probable that waters, perhaps deriving from groundwater (on the basis of the low Pb concentrations as well as the lower $^{206}Pb/^{207}Pb$ ratio), may have been sampled rather than "true" soil porewaters. Thus the results from the soil porewaters, at least from the Birnie Burn, should not be compared with those from the pit throughflow waters.

Pb budget calculations

The Pb budget calculations have been based on the data for May 2002–April 2003, the 12-month period over which the data set for all sample types was most complete.

Calculation of Pb input to the catchment

The two-weekly rain water Pb concentration data for Pits 1 and 2 were used in conjunction with the two-weekly ECN rainfall values and the catchment area of 1.76 km^2 to give two-weekly Pb input values (in g) for the entire catchment (Fig. 8). Over the time period May 2002–April 2003, there was reasonably good agreement between the inputs calculated from the concentration data for Pits 1 and 2 (Table 5). During the period May 2002–April 2003, the Pb input to the catchment based on rain water alone was calculated to be 1983 ± 316 g and 1897 ± 302 g from Pit 1 and Pit 2 data, respectively. The associated error on each of these values was obtained by using the typical relative standard deviation on the Pb input data of 2%, an error of 15% on the measurement of rainfall and an error of 5% on the measurement of the catchment area, giving an overall error of 15.9%. The input based on rainfall alone, however, will underestimate Pb input to the catchment. An upper estimate of Pb input was obtained using the interception Pb concentration data as interception represents the Pb deposition from air particulates, mist, fog and cloud as well as from rainfall. The mean value (±1 σ) for the interception Pb input was calculated to be 7.5 ± 1.4 kg using the data for Pits 1 and 2 (Table 5). An overall error value of 26% was obtained by inclusion of associated errors on Pb concentration, rainfall measurement and catchment area. Thus the final estimate for interception Pb input to the catchment was 7.5 ± 2 kg. This is in good agreement with an independently determined value of 6.3 kg obtained using an average depositional flux of 3.6 mg m^{-2} y^{-1} derived for mid-2001–late-2002 from a ^{210}Pb-dated peat soil core at 426 m altitude.[34] This value is a good indicator of the maximum atmospheric input as it was obtained using data for soil from the most elevated part of the catchment.

A weighted ^{206}Pb/^{207}Pb ratio for rain water for May 2002–April 2003 was obtained by multiplying each ratio by the amount of Pb deposited in the same two-week period, summing these values and then dividing by the total amount of Pb deposited in the one year period. The overall error on the weighted mean isotopic ratio was taken to be the typical error on the two-weekly measured values. Thus the weighted ^{206}Pb/^{207}Pb ratio for May 2002–April 2003 was 1.152 ± 0.004 at Pit 1 and 1.157 ± 0.004 at Pit 2. These were in good agreement with the unweighted values for the same time period (1.152 ± 0.003 and 1.157 ± 0.007, respectively) and indeed for the overall sampling period (Table 1) at these sites. Similarly, the weighted
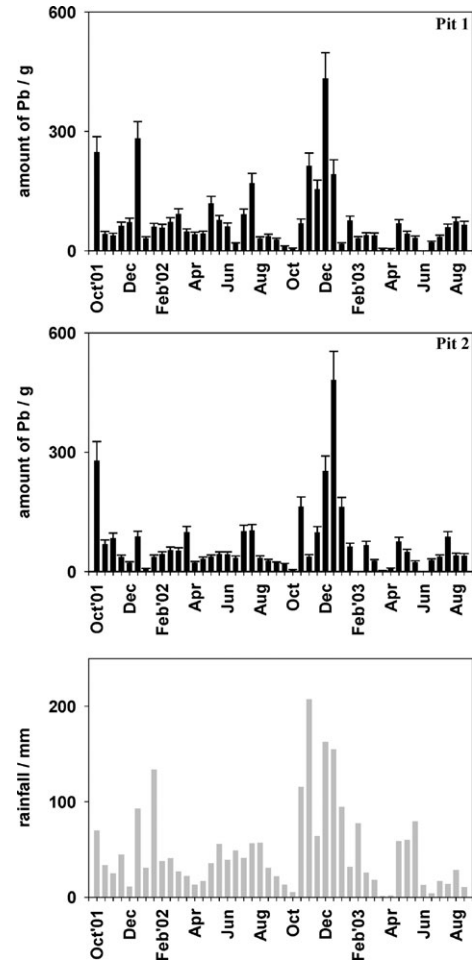

Fig. 8 Two-weekly input of Pb (in g) in rainfall calculated using the Pb concentration data for Pits 1 and 2 and the two-weekly rainfall at the ECN station at Glensaugh.

and unweighted values for the ^{206}Pb/^{207}Pb ratio for interception were in good agreement (Table 5).

Calculation of Pb output from the catchment

Daily stream water Pb concentration data were converted to daily Pb output values by using the daily flow data. These
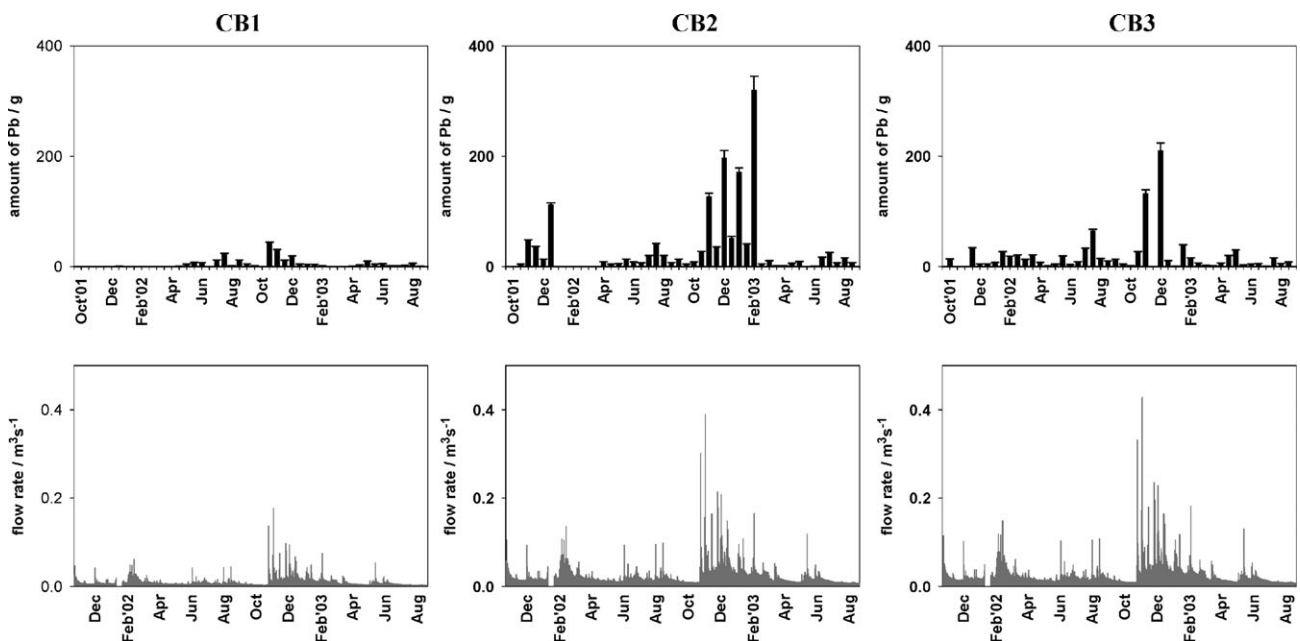

Fig. 9 Two-weekly Pb output (in g) and flow rate at CB1–CB3 for the catchment at Glensaugh.
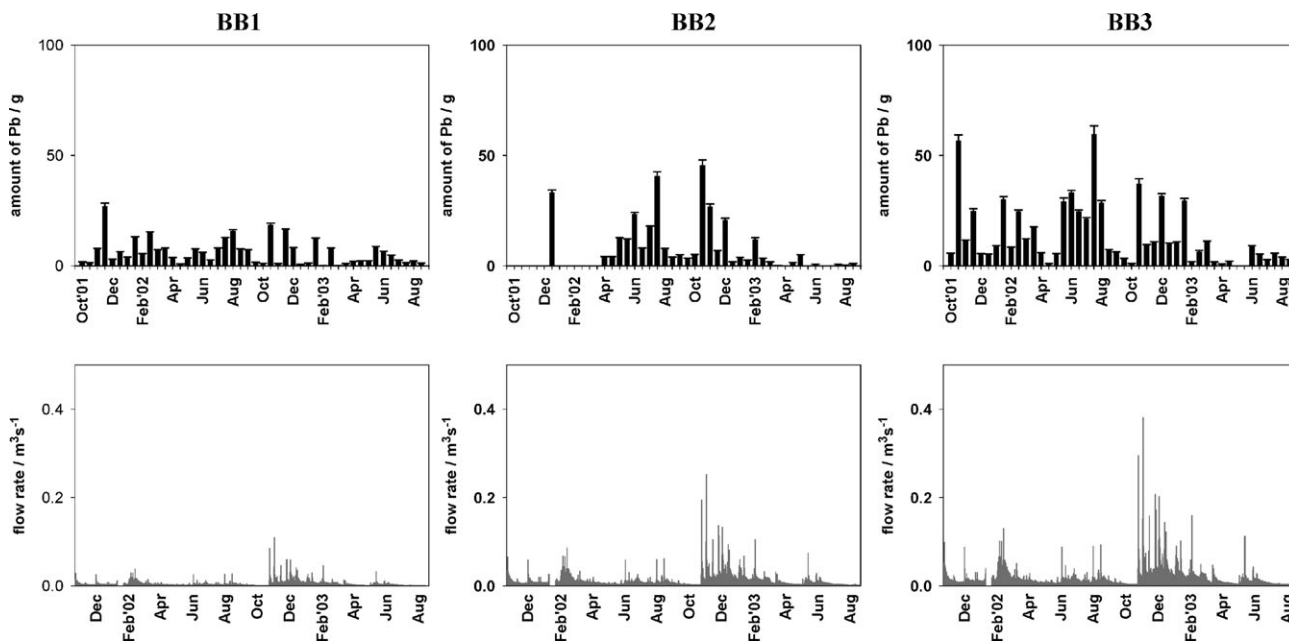
Fig. 10 Two-weekly Pb output (in g) and flow rate at BB1–BB3 for the catchment at Glensaugh.

values were then summed to give two-weekly Pb output values which were calculated for all stream sampling sites (Figs. 9 and 10). CB3 and BB3, representing the outflow from each of the two streams, were used in overall budget calculations (Table 6). The annual Pb output from the two streams, based on the daily stream water data, was 1263 ± 151 g in total (Table 6). From work on storm events, using higher frequency sampling, it was clear that this was an underestimate of the total annual output from the catchment, which was found to be 2 ± 1 kg.[36] The output, however, is still considerably lower than the upper estimate of the annual input of ~7.5 kg, suggesting that the catchment is still acting as a sink for a large proportion of current atmospherically deposited Pb. Furthermore, the annual output corresponds to <0.05% of the inventory of anthropogenic Pb to a depth of 10 cm over the catchment.[34]

A weighted stream water $^{206}Pb/^{207}Pb$ ratio for May 2002–April 2003 was obtained by multiplying each ratio by the amount of Pb released in the same daily period, summing these values and then dividing by the total amount of Pb released in the one year period. The overall error on the weighted mean isotopic ratio was taken to be the typical error on the daily measured values. Thus the weighted $^{206}Pb/^{207}Pb$ ratio for May 2002–April 2003 was 1.158 ± 0.004 at CB3 and 1.157 ± 0.004 at BB3. As expected, these values were in very good agreement with the mean weighted $^{206}Pb/^{207}Pb$ ratios for rain water during the same time period.

Temporal variability in rain water input of Pb to the catchment and stream water output of Pb from the catchment

From the two-weekly rain water input data, it was evident that a disproportionately large amount of Pb was deposited during October–December 2002 (Fig. 8). From Pit 1 data, for example, summing the two-weekly amounts gave 1153 g deposited

compared with a yearly amount of 1983 g for May 2002–April 2003, i.e. 58% of the annual input was deposited in this three-month period. There was clearly a strong correlation between rainfall and amount of Pb being deposited on the catchment (Fig. 8). The Pb concentrations were not, however, elevated during October–December 2002 (Fig. 2) and so it was the high volume of rain that was the main factor responsible for the large amounts of Pb deposited at that time.

From the stream water flow data (Figs. 9 and 10), high flow conditions coincided with the periods of heaviest rainfall (Fig. 8). The highest stream water outputs of Pb also occurred during these periods at the Cairn Burn sites (particularly CB2 and CB3), with some 56% of the annual output from CB3 being released during October–December 2002. For the Birnie Burn sites, however, the temporal pattern was more complicated as enhanced Pb output (e.g. during June–August 2002) coincided with periods of typically lower stream flow as well as with the periods of highest flow (October–December 2002). The importance of enhanced particle-transport of Pb, particularly during rain events occurring after prolonged dry periods, is discussed further in Graham et al.[36]

Conclusions

From the direct measurements during October 2001–August 2003, the lower limit for the annual input of Pb to the catchment via atmospheric deposition was 1.9 ± 0.3 kg. This was based only on Pb input via rainfall. An upper limit, based on Pb input via interception, was estimated at 7.5 ± 2 kg. The $^{206}Pb/^{207}Pb$ ratio for the input Pb was ~1.15–1.16. The annual Pb output via streams (~1.3 kg using the daily flow data; upper limit of 2 ± 1 kg[36] including storm events) was considerably lower. On the basis of these results, this upland catchment must be considered a continuing sink for anthro-

Table 6 Stream water Pb concentration, weighted $^{206}Pb/^{207}Pb$ ratio and calculated Pb outputs for the catchment during the period May 2002–April 2003[a]

Location	Sample	Time period	Mean Pb concentration/µg l^{-1}	Weighted $^{206}Pb/^{207}Pb$ ratio	Stream flow / × 10^3 m^3	Pb output/g y^{-1}
Cairn Burn	CB3	May 02–Apr 03	0.59 ± 0.89	1.158	1096	808 ± 132
Birnie Burn	BB3	May 02–Apr 03	0.58 ± 0.69	1.157	844	455 ± 74

[a] An average value of 0.5 µg l^{-1} has been used for days when samples were not available.

pogenic Pb. For the period October 2001–August 2003, the mean isotopic signature of stream water Pb was close to that of the rain water. In addition, the Pb isotopic measurements on the daily stream water values did not reveal any difference between samples collected during baseflow and high flow conditions. This is partly a consequence of the sampling frequency as high flow conditions sometimes occurred for only a few hours or the time of collection may not have coincided with, for example, the onset of high flow conditions (*i.e.* the beginning of an event). These issues are addressed in Graham *et al.*,[36] which considers higher frequency sampling under the high flow conditions of storm events in more detail. Pb isotopic analysis of groundwater samples, however, showed that the mean values were typically very close not only to those for rain water but also those for stream water and thus the direct measurements were consistent with the hydrological model predictions. Analysis of throughflow (and soil porewaters from sites close to the Cairn Burn) showed that waters flowing through the near surface soil often had a lower ^{206}Pb/^{207}Pb ratio, sometimes statistically significantly lower than current rain water, but that waters flowing through deeper horizons generally had higher ratio values, which were closer to "old" anthropogenic and/or geogenic sources of Pb than to current rain water. Pb isotopes may therefore be useful in deconvoluting pathways of Pb transport particularly under high flow conditions. It is also clear from the Pb concentration and Pb isotopic results for throughflow that mobilisation of a small amount of previously deposited Pb is occurring. This is important because calculation of the amount of the current Pb input being retained by the catchment would be underestimated if stream water output was simply subtracted from the atmospheric input.

More widely, given that much of the Northern Hemisphere land surface at higher latitudes is covered by organic-rich, peaty soils, the findings here of only limited Pb release to, and removal by, receiving fresh waters at present are reassuring. Nevertheless, as demonstrated by some of the Pb isotopic data in this study, for example for soil throughflow, some previously deposited anthropogenic lead is being mobilised, albeit to a limited extent. This could, however, increase in the future if forecasts of global-warming-induced climatic and weather extremes (*e.g.* prolonged dry and wet periods)[51] are correct, factors which will be considered further in the discussion of storm events by Graham *et al.*[36]

Acknowledgements

References

1   J. G. Farmer, *Environ. Geochem. Health*, 1991, **13**, 76.
2   G. P. Hekstra, in *The Global Environment: Science, Technology and Management*, ed. D. Brune, D. V. Chapman, M. D. Gwynne and J. M. Pacyna, VCH, Weinheim, 1997, **vol. 1**, pp. 159–164.
3   W. M. Stigliani, *Environ. Monit. Assess.*, 1998, **10**, 245.
4   E. K. Miller and A. J. Friedland, *Environ. Sci. Technol.*, 1994, **28**, 662.
5   E. X. Wang, F. H. Bormann and G. Benoit, *Environ. Sci. Technol.*, 1995, **29**, 735.
6   E. X. Wang and G. Benoit, *Environ. Sci. Technol.*, 1996, **30**, 2211.
7   C. E. Johnson, T. G. Siccama, C. T. Driscoll, G. E. Likens and R. E. Muller, *Ecol. Appl.*, 1995, **5**, 813.
8   E. X. Wang and G. Benoit, *Water, Air, Soil Pollut.*, 1997, **95**, 381.
9   R. M. Sherrell and J. M. Ross, *Geochim. Cosmochim. Acta*, 1999, **63**, 3321.
10 Y. Erel and C. C. Patterson, *Geochim. Cosmochim. Acta*, 1994, **15**, 3289.
11 Y. Erel, A. Veron and L. Halicz, *Geochim. Cosmochim. Acta*, 1997, **61**, 4495.
12 R. Bindler, M.-L. Brannvall, I. Renberg, O. Emteryd and H. Grip, *Environ. Sci. Technol.*, 1999, **33**, 3362.
13 M. L. Brannvall, R. Bindler, O. Emteryd and I. Renberg, *Water, Air, Soil Pollut.*, 2001, **1**, 357.
14 S. Emmanuel and Y. Erel, *Geochim. Cosmochim. Acta*, 2002, **66**, 2517.
15 J. M. Kaste, A. J. Friedland and S. Stürup, *Environ. Sci. Technol.*, 2003, **37**, 3560.
16 R. M. Semlali, F. Van Oort, L. Denaix and M. Loubet, *Environ. Sci. Technol.*, 2001, **35**, 4180.
17 R. M. Semlali, J. B. Dessogne, F. Monna, J. Bolte, S. Azimi, N. Navarro, L. Denaix, L. M. Loubet, C. Chateau and F. Van Oort, *Environ. Sci. Technol.*, 2004, **38**, 1513.
18 S. A. Watmough and T. C. Hutchinson, *Environ. Pollut.*, 2004, **128**, 419.
19 J. R. Bacon, M. L. Berrow and C. A. Shand, *Int. J. Environ. Anal. Chem.*, 1992, **46**, 71.
20 J. R. Bacon, M. L. Berrow and C. A. Shand, *Int. J. Environ. Anal. Chem.*, 1995, **59**, 253.
21 J. R. Bacon, K. C. Jones, S. P. McGrath and A. E. Johnston, *Environ. Sci. Technol.*, 1996, **30**, 2511.
22 C. L. Sugden, J. G. Farmer and A. B. MacKenzie, *Environ. Geochem. Health*, 1993, **15**, 59.
23 J. R. Bacon and D. C. Bain, *Environ. Geochem. Health*, 1995, **17**, 39.
24 J. G. Farmer, L. J. Eades, A. B. MacKenzie, A. Kirika and A. E. Bailey-Watts, *Environ. Sci. Technol.*, 1996, **30**, 3080.
25 J. G. Farmer, A. B. MacKenzie and C. L. Sugden, *Water, Air, Soil Pollut.*, 1997, **100**, 253.
26 J. G. Farmer, L. J. Eades and M. C. Graham, *Environ. Geochem. Health*, 1999, **21**, 257.
27 J. G. Farmer, L. J. Eades, M. C. Graham and J. R. Bacon, *J. Environ. Monit.*, 2000, **2**, 49.
28 J. G. Farmer, L. J. Eades, H. Atkins and D. F. Chamberlain, *Environ. Sci. Technol.*, 2002, **36**, 152.
29 A. B. MacKenzie, J. G. Farmer and C. L. Sugden, *Sci. Total Environ.*, 1997, **203**, 115.
30 L. J. Eades, J. G. Farmer, A. B. MacKenzie, A. Kirika and A. E. Bailey-Watts, *Sci. Total Environ.*, 2002, **292**, 55.
31 F. Monna, J. Lancelot, I. W. Croudace, A. B. Cundy and J. T. Lewis, *Environ. Sci. Technol.*, 1997, **31**, 2277.
32 A. Veron, P. Flament, M. L. Bertho, L. Alleman, R. Fliegel and B. Hamelin, *Atmos. Environ.*, 1999, **33**, 3377.
33 J. R. Bacon, *J. Environ. Monit.*, 2002, **4**, 291.
34 J. G. Farmer, M. C. Graham, J. R. Bacon, S. M. Dunn, S. I. Vinogradoff and A. B. Mackenzie, *Sci. Total Environ.*, 2005, in press.
35 J. R. Bacon, J. G. Farmer, S. M. Dunn, M. C. Graham and S. I. Vinogradoff, *Environ. Pollut.*, submitted.
36 M. C. Graham, S. I. Vinogradoff, A. J. Chipchase, S. M. Dunn, J. R. Bacon and J. G. Farmer, in preparation.
37 S. M. Dunn, S. I. Vinogradoff, G. J. P. Thornton, J. R. Bacon, M. C. Graham and J. G. Farmer, *Hydrol. Proc.*, submitted.
38 J. D. Miller and J. D. Hirst, *Sci. Total Environ.*, 1998, **216**, 77.
39 B. W. Avery, *Soil classification for England and Wales, Soil Survey Technical Monograph No. 14*, Harpenden, 1980.
40 J. D. Miller, J. K. Adamson and D. Hirst, *Sci. Total Environ.*, 2001, **265**, 27.
41 J. D. Miller, A. Kelly and F. W. Milne, *Sci. Total Environ.*, 2000, **262**, 137.
42 J. D. Miller, A. W. Stuart and G. J. Gaskin, *J. Environ. Sci. Health A*, 1995, **30**, 1843.
43 I. M. Sykes and A. M. J. Lane, *The United Kingdom Environmental Change Network: Protocols for standard measurements at terrestrial sites*, HMSO, London, 1996.
44 J. G. Farmer, 1993–2000, unpublished data.
45 *OSPAR Commission, Monitoring and Assessment Series*, publication number 66, 1997.
46 H. Yang, N. L. Rose, R. W. Batterbee and J. F. Boyle, *Environ. Sci. Technol.*, 2002, **36**, 1383.
47 *Digest of Environmental Statistics*, Department for Environment, Food and Rural Affairs (DEFRA), 2002, www.defra.gov.uk/environment/statistics/des/index.htm.
48 W. M. Landing, J. J. Perry, J. L. Guentzel, G. A. Gill and C. D. Pollman, *Water, Air, Soil Pollut.*, 1995, **80**, 343.
49 N. M. Lawson and R. P. Mason, *Water Res.*, 2001, **35**, 4039.
50 S. M. Dunn, 2001–2003, unpublished data.
51 *Impacts of Europe's Changing Climate: An Indicator-Based Assessment*, European Environment Agency (EEA), http://reports.eea.eu.int/climate_report_2_2004/en.