

Bromine and bromide in rainfall, cloud, stream and groundwater in the Plynlimon area of mid-Wales

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Abstract

Bromine in rainfall, cloud water, stream water and groundwater were measured in the upper River Severn catchments at Plynlimon in mid-Wales using two analytical procedures for bromide determination: a colorimetric method and, later, ion chromatography. Discrepancies between the methods indicated that the colorimetric method was measuring more than just bromide so it was ‘dissolved labile bromine’ (DLBr) (Neal *et al.* 2007). This paper reports the variation in DLBr and bromide across the Plynlimon region and assesses the differences between these two measures. The average DLBr concentration in the streams ranges between 18.3 and 27.8 $\mu\text{g l}^{-1}$ compared with a rainfall average concentration of 15.6 $\mu\text{g l}^{-1}$. The corresponding bromide concentrations in the streams are 13.8–18.6 $\mu\text{g l}^{-1}$ and 13.2 $\mu\text{g l}^{-1}$ in rainfall. For cloud water, throughfall and stemflow, DLBr concentrations are an order of magnitude higher than in rainfall and the concentrations are strongly correlated with chloride. Average values of bromide in rainfall and cloud water are similar to those of DLBr and are strongly correlated with chloride: unfortunately, no bromide measurements were taken in throughfall and stemflow. These results indicate that marine aerosol inputs are high and that the DLBr in these inputs is dominated by bromide. For cloud water, DLBr was correlated with dissolved organic carbon (DOC) as well as with chloride; hence, there may well be an organic-associated component. Within the streams draining the forested areas, DLBr increases with time as DOC increases. DLBr concentrations in the streams are correlated with DOC in most cases and, to a lesser degree, with chloride. However, for bromide there is no correlation with DOC, but a weak correlation with chloride remains and the gradient is higher than for the DLBr case. Increasing concentrations of both DLBr and DOC may well reflect the wetting up of the catchments as transpiration diminishes as the trees age as well as through felling. In groundwater, only DLBr has been measured, and its concentration is similar to that for the streams. However, in the groundwater zone, DLBr is poorly correlated with DOC concentrations, in which DOC is largely converted to CO_2 . Atmospheric input–stream output flux estimates indicate a net uptake of bromide by the catchment of around 30%, matched by a corresponding release of DOC-associated bromine.

Keywords: bromide, cloud water, chloride, dissolved labile bromine, dissolved organic carbon, organobromine, Hafren, Hore, groundwater, mist, organobromine, Plynlimon, rainfall, stemflow, Tanllwyth, throughfall, river

Introduction

In nature, bromine, one of the key halogens, occurs mainly in the inorganic form of bromide (Greenwood and Ernschaw, 2005). Although bromine is the 46th most abundant element in the Earth’s crust (2.5 ppm), because of its high solubility, bromine is found predominantly, as bromide, in sea water, (65 000 $\mu\text{g l}^{-1}$) and in brines (Greenwood and Ernschaw, 2005). The level of bromide in groundwaters varies considerably and is usually linked with chloride concentration (Edmunds, 1996). For potable groundwaters of low salinity, bromide concentrations are typically less than 400 $\mu\text{g l}^{-1}$ (Edmunds, 1996; Davis *et al.*, 2004).

Although, in nature, bromide is usually considered as a relatively conservative ion, often used as a tracer for water movement, it can also sorb onto sediments and be involved in biogeochemical cycling (Davis *et al.*, 1998; Korom, 2000; Huggenberger *et al.*, 1998; Neal *et al.*, 1990). Bromine can occur in various oxidation states from -1 up to $+7$ (-1 , 0 , 1 , 3 , 4 , 5 , 7) but, of these higher oxidation states, dissolved inorganic bromine is of environmental concern as the ion bromate. Bromide is oxidised to bromate when water is disinfected using ozone or chlorine dioxide: bromate is a suspected carcinogen and, within the Drinking Water Directive, a statutory limit of 10 $\mu\text{g l}^{-1}$ has been proposed

(EA, 1997). Natural organic matter can influence the rate of such bromide oxidation to bromate and can lead to the formation of organobromine compounds as well (Rathburn, 1996; Nicolaou *et al.*, 2004; Westerhoff *et al.*, 1998). The organobromines formed during the chlorination (Rook, 1974) constitute three of the four main trihalomethanes (THMs) of critical concern: bromodichloromethane, chlorobromomethane and bromoform (the other trihalomethane being chloroform). In drinking water, the maximum contaminant level of THMs is being set at a total of $40 \mu\text{g l}^{-1}$ although there may well be issues over setting a level based on total concentration as the organobromines may be more hazardous than chloroform (Rathburn, 1996). Strategic work has been undertaken in examining the potential of surface and groundwaters for generating trihalomethanes (Rathburn, 1996; Stuart *et al.*, 2001) and there can be marked costs to the water industry (Batjer *et al.*, 1980). There is also a wide range of organobromines in the environment. For example, methyl bromide is an effective nematocide and general pesticide (herbicide, fungicide and insecticide). Correspondingly, ethylene dibromide and dibromochloropropane are used as pesticides and the former was used extensively as a gasoline additive for scavenging lead from the anti-knock PbEt_4 before lead additives were phased out of some 20 years ago. Organobromine compounds are also used extensively as fire retardants: in 1990, the primary usage of bromine was 29% as flame retardants, 16% as ethylene dibromide in agriculture, 16% as drilling fluids, 11% as bromides and 5.5% as water treatment chemicals (Greenwood and Ernschaw, 2005). Indeed, the use of organobromines as fire retardants has led to contamination of the ecosphere on a widespread scale (Santillo and Johnson, 2003). Certainly, there can be a wide range of organobromine contaminants in river, lake and estuarine/marine environments (Bedard *et al.*, 1998; Hashimoto *et al.*, 1998; Manninen and Hasanen, 1992; Weigel *et al.*, 2005). Nonetheless, a range of organobromines occurs naturally in the environment; for example, almost 4000 organohalogen compounds containing mainly chlorine or bromine (about 50% of each) are produced by living organisms or formed during natural abiotic processes. These organobromines can be transferred from the sea to the atmosphere and can be involved in global biogeochemical processes (Cloern, 1996; Gribble, 1989; 2000, 2003; Laturnus *et al.*, 2000; Quack and Wallace, 2003).

Over the past 20 years, detailed hydrobiogeochemical studies have been undertaken for the Plynlimon catchments in upland Wales (Reynolds *et al.*, 1986; Neal *et al.*, 1997a,b, 2001). Within these studies, a wide range of chemicals has been determined in rainfall, cloud water (mist), throughfall,

stemflow, stream water and groundwater. Included in the assessment has been what was originally thought of as bromide and the earlier findings have been presented by Neal *et al.* (1990). However, since that time, much more extensive data have been collected, including measurements in groundwater. Clear, long-term temporal variations are now much more marked with increasing concentrations consistent with increases in dissolved organic carbon (DOC) (Neal *et al.*, 1997a, 2005). Furthermore, and most critically, a change in methodology in the late 1990s has revealed that what was originally thought of as a measurement of bromide, is in fact a measure of dissolved labile bromine (DLBr) which may well comprise a sum of the bromide and bromine bearing labile organic carbon. The method was then changed in 1999 to measure bromide directly as the DLBr methodology had to be decommissioned due to age (Neal *et al.*, 2007).

Hughes *et al.* (1996, 1998) in the Plynlimon area showed, as did Vinogradov in 1959, that bromide is correlated strongly with organic matter in soils and is especially enriched in peat. Rewetting organic-rich soils can result in marked increases in bromide and dissolved organic carbon (DOC) in solution, an issue of importance for drinking water, especially in areas such as Plynlimon in the UK uplands because of their primary importance in relation to water resources. Also, a study in Chile, on the role of halogen retention and cycling in two peat bogs, found that up to 91% of bromine is bound in an organic form (Biester *et al.*, 2004). In the UK, Wilkins (1978) surveyed the distribution of bromide in topsoil of north-west Pembrokeshire and found a range of 10 to $515 \mu\text{g/g Br}$, with a mean of $54 \mu\text{g/g Br}$. Such high concentrations of Br in topsoil are to be expected since the west of Wales receives high inputs of sea salts in precipitation. Yuita *et al.* (1991) studied the effects of a range of physical and chemical variables on the dissolution rates of the halogens iodine, bromine and chlorine from a range of Japanese soils, which contain large amounts of bromine and iodine. They concluded that soil moisture content was the most important environmental factor affecting the dissolution of bromine and iodine, the values of which increased markedly under flooded conditions. This is consistent with the results of a study of bromide dissolution in peat following experimental rewetting of naturally drained gully mire at Plynlimon; in the peat-water the bromide concentrations increased substantially on flooding (Hughes *et al.*, 1996). Moreover, bromide release was highly seasonal, with the largest concentrations observed in early autumn (Hughes *et al.*, 1998).

In this paper, the findings for DLBr and bromide are described (a) to update and, in places, correct the earlier interpretations, (b) to examine the relationship between

DLBr and bromide and (c) to assess how important dissolved labile organobromine might be, based on a comparison of DLBr, bromide and DOC.

Study area and sampling programme

DLBr and bromide data have been amassed both from long-term (10 to 25 years) and more recent shorter term monitoring programmes (1 to 5 years); rainfall, cloud water (mist), throughfall, stemflow, stream water and groundwater were measured in the headwaters of the River Severn. Weekly monitoring began in May 1983 for the atmospheric inputs and most of the stream outputs. Rainfall was the accumulation of the catch in two rainfall collectors about 1 km apart, one near the top and the other near the bottom of the catchment. Cloud water was collected near the top of the catchment using a specialised collector (Wilkinson *et al.*, 1997), while throughfall and stemflow were collected using a network of collectors further down the catchment. There were five primary stream water monitoring points with catchment areas varying between 50 and 300 ha. One stream site represents the upper moorland area (upper Afon Hafren) while the other four sites, all afforested to different degrees, were the lower Afon Hafren, including the moorland drainage from the upper Hafren, the Nant Tanllwyth, the upper Afon Hore and the lower Afon Hore. More recently, additional sites examined the interaction between soil type and forest harvesting on water quality. They were smaller catchment areas (usually much less than 5 ha); four of them were paired with control and manipulated forested catchments (the south-east, SE, and Tanllwyth, Tan, sites): the fifth site is south2Hore. The sites represented two of the main soil types of concern, peaty podzols (South2Hore, SE1, SE3) and peaty gleys (TanN, TanS). The manipulated sites at Plynlimon are South2Hore, SE1, and TanS. The SE and Tan streams drain into the Afon Hafren while South2Hore drains into the Afon Hore. The site names for the paired catchments are given the suffix 'f' for felling and 'c' for control. For the paired sites, shallow groundwater was monitored for water quality and stream and groundwater was monitored fortnightly. Two additional borehole sites provided information on the influence of felling (HA4bf and quarry). Groundwater was collected by 'grab' using a down-borehole sampler, i.e. the borehole was not purged prior to sampling.

Details of the period of monitoring at each site and of the areas and timing of felling are in Neal and Kirchner (2000): from 2001, measurements have been restricted to rainfall, cloud water, the upper and lower Afon Hafren and Afon Hore, and the Nant Tanllwyth. The overall water quality of the area is described by Neal *et al.* (1997a,b, 2001).

Chemical analysis

The samples were filtered in the field (0.45 µm cellulose acetate membranes) and stored in the dark at 4°C in highly cleaned glass bottles prior to analysis to minimise sample contamination and deterioration. DLBr (formerly and incorrectly denoted as bromide) was determined using an automated procedure based on the catalytic effect of bromide on the oxidation of iodine to iodate by potassium permanganate in sulphuric acid solution (Moxon and Dixon, 1980; Neal *et al.*, 2007). The unreacted iodine was extracted into carbon tetrachloride and measured spectrophotometrically at 0.5°C, with correction for chloride which also catalysed the reaction. This analysis was undertaken from the start of the study in May 1983 up to January 1999. Thereafter, bromide was determined by ion chromatography (IC) using a Dionex system (Neal *et al.*, 2007). For the colorimetric and IC determinations, the samples were assayed in duplicate and singularly, and the detection limits were 2 and 10 µg l⁻¹, respectively. The DLBr measurement may contain colloidal material that passes through the filter papers and this may be similar for DOC.

Results

The results for DLBr and bromide are presented in Tables 1 and 2 and Figs. 1 to 4. In Table 1, a comparison is made between DLBr and bromide for those sites where measurements have been taken consecutively with monitoring for DLBr from May 1983 to January 1999 and for bromide thereafter). Table 2 contains information on DLBr which has been monitored at many more sites than bromide. In particular, additional information on DLBr is provided on throughfall, stemflow, groundwater and the paired catchments. The Tables include information on DOC and chloride concentrations which indicate linkages of DLBr and bromide with an organic and a sea-salt component, respectively. For both Tables, means and flow weighted values are provided — the latter are more appropriate when flux is considered (here annual flux is taken as the sum of the flow weighted average concentration and the annual average flow). Figures 1 to 4 provide time series for DLBr, bromide and DOC for the long-term monitoring stream sites. They show the temporal changes and the difference between the DLBr and bromide concentrations. DOC measurements show the relationship with DLBr and bromide and DOC concentrations have increased over time (Neal *et al.*, 2005). Chloride does not change uniformly over time (Neal *et al.*, 2001) and, hence, has not been plotted.

Table 1. Dissolved labile bromine, bromide, dissolved organic carbon and chloride in Plynlimon waters.

		<i>Br</i> <i>avg</i> $\mu\text{g l}^{-1}$	<i>Br</i> <i>fw avg</i> $\mu\text{g l}^{-1}$	<i>Br</i> <i>min</i> $\mu\text{g l}^{-1}$	<i>Br</i> <i>Max</i> $\mu\text{g l}^{-1}$	<i>DOC</i> <i>avg</i> mg l^{-1}	<i>Cl</i> <i>avg</i> mg l^{-1}	<i>Br/DOC</i> $\mu\text{g:mg}$	<i>Br/Cl</i> $\mu\text{g:mg}$
Rain Water	DLBr	15.6	17.2	1	128	0.72	4.09	21.7	3.8
	Bromide	13.2	15.0	0	110	0.56	3.74	23.8	3.5
Cloud Water	DLBr	162.5	138.0	6	2300	2.68	53.60	60.7	3.0
	Bromide	127.5	116.0	4	648	1.83	47.14	69.5	2.7
Upper Hafren	DLBr	18.3	19.1	13	34	1.30	5.74	14.1	3.2
	Bromide	13.8	11.8	0	34	1.60	5.89	8.6	2.3
Lower Hafren	DLBr	22.2	23.5	9	53	1.46	7.11	15.2	3.1
	Bromide	18.6	16.9	6	43	2.15	7.06	8.6	2.6
Upper Hore	DLBr	22.1	21.9	12	62	1.33	7.45	16.6	3.0
	Bromide	17.8	15.6	7	55	2.05	7.57	8.7	2.4
Lower Hore	DLBr	23.7	23.7	10	80	1.36	7.51	17.5	3.2
	Bromide	17.9	16.2	6	39	1.93	7.72	9.3	2.3
Tanllwyth	DLBr	27.8	31.9	18	60	2.76	8.04	10.1	3.5
Tanllwyth	Bromide	17.0	14.5	0	43	3.83	7.66	4.4	2.2

Table 2. Dissolved labile bromine, dissolved organic carbon and chloride in Plynlimon waters.

	<i>Br</i> <i>avg</i> $\mu\text{g l}^{-1}$	<i>Br</i> <i>fw avg</i> $\mu\text{g l}^{-1}$	<i>Br</i> <i>min</i> $\mu\text{g l}^{-1}$	<i>Br</i> <i>max</i> $\mu\text{g l}^{-1}$	<i>DOC</i> <i>Avg</i> mg l^{-1}	<i>Cl</i> <i>avg</i> mg l^{-1}	<i>Br/DOC</i> $\mu\text{g:mg}$	<i>Br/Cl</i> $\mu\text{g:mg}$
ATMOSPHERIC INPUTS								
Rainfall	15.6	17.2	1	128	0.72	4.09	21.7	3.8
Cloud	162.5	138.0	6	2300	2.68	53.6	60.7	3.0
Throughfall	110.7	77.4	22	600	11.4	28.5	9.7	3.9
Stemflow	148.2	143.6	24	475	19.2	30.9	7.7	4.8
STREAMS								
Upper Hafren	18.3	19.1	13	34	1.30	5.74	14.1	3.2
Upper Hore	22.2	23.5	9	53	1.46	7.11	15.2	3.1
Lower Hafren	22.1	21.9	12	62	1.33	7.45	16.6	3.0
Lower Hore	23.7	23.7	10	80	1.36	7.51	17.5	3.2
Tanllwyth	27.8	31.9	18	60	2.76	8.04	10.1	3.5
South2Hore	26.6	22.1	4	66	1.74	6.97	15.3	3.8
SE1f	40.8	42.0	16	70	1.16	8.36	35.2	4.9
SE3c	30.7	28.2	15	50	0.62	7.54	49.8	4.1
TanNc	68.0	55.2	9	148	15.24	8.06	4.5	8.4
TanSf	52.6	40.5	8	174	12.76	6.25	4.1	8.4
GROUNDWATER								
Ha4B	36.4	na	14	128	0.64	9.78	57.3	3.7
Quarry	32.1	na	16	70	0.42	12.1	76.0	2.7
SE1bf	34.9	na	17	60	0.59	8.86	58.7	3.9
SE3bc	37.7	na	20	80	0.42	11.1	89.7	3.4
TanNbc	16.6	na	12	30	0.50	10.2	33.3	1.6
TanSbf	46.1	na	14	103	1.48	9.27	31.1	5.0

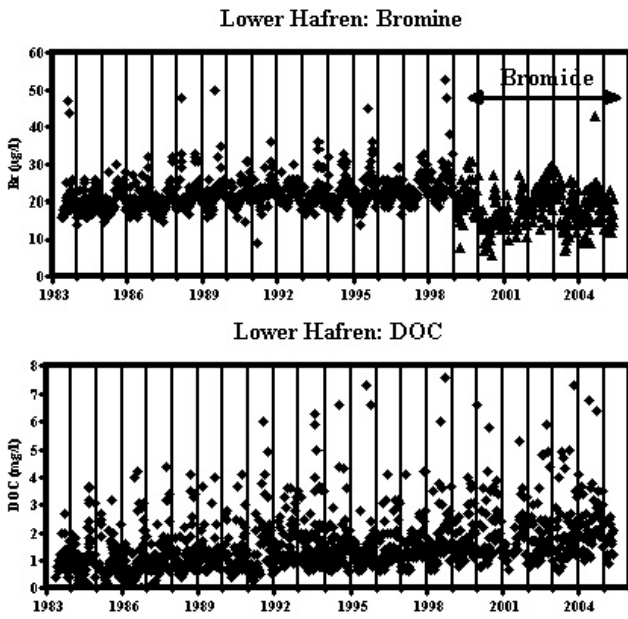


Fig. 1. Dissolved labile bromine, bromide and DOC concentration time series for the lower Afon Hafren.

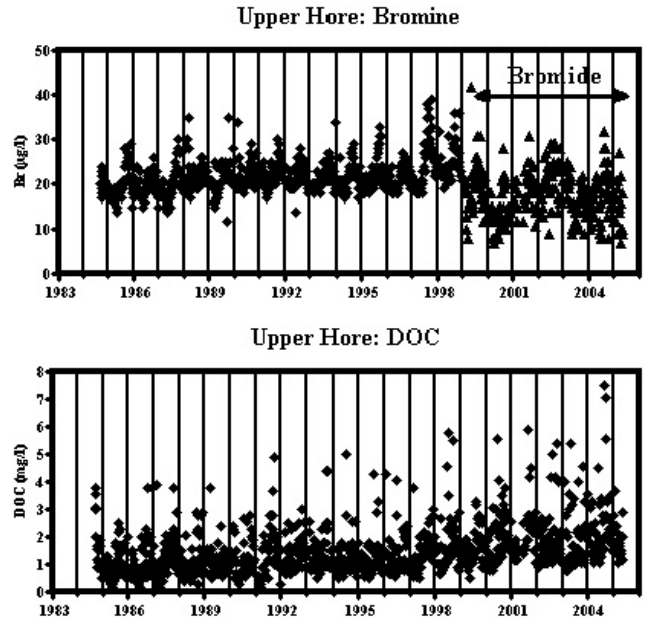


Fig. 2. Dissolved labile bromine, bromide and DOC concentration time series for the upper Afon Hore.

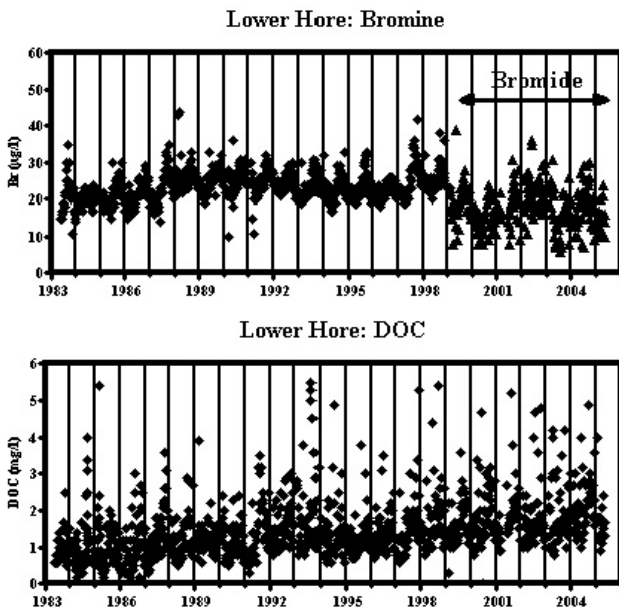


Fig. 3. Dissolved labile bromine, bromide and DOC concentration time series for the lower Afon Hore.

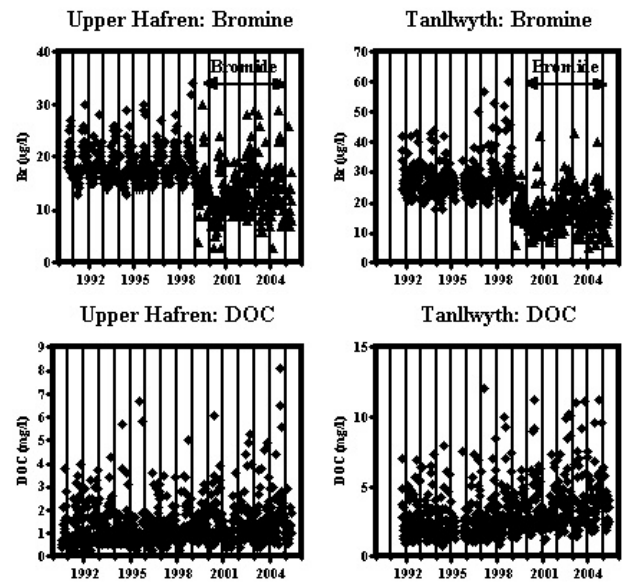


Fig. 4. Dissolved labile bromine, bromide and DOC concentration time series for the upper Afon Hafren and the Nant Tanllwyth.

ATMOSPHERIC INPUTS

Values of DLBr show a large range of concentrations in rainfall, cloud water, throughfall and stemflow. For example, the DLBr concentrations in rainfall varied between 1 and 128 $\mu\text{g l}^{-1}$ while the corresponding range for cloud water was 6 to 2300 $\mu\text{g l}^{-1}$. In all cases, the values were skewed towards lower concentrations. Compared with rainfall

(average 15.6 $\mu\text{g l}^{-1}$), average DLBr concentrations in cloud water, throughfall and stemflow were an order of magnitude higher (average 162.5, 110.7 and 148.2 $\mu\text{g l}^{-1}$, respectively). In the case of bromide, a similar pattern is observed for rainfall and cloud water although the average concentrations are about 20% lower than their DLBr counterparts.

For rainfall, cloud water, throughfall and stemflow, the

DLBr concentrations were highly linearly correlated with chloride concentration and similar results were found for bromide with rainfall and cloud water (Tables 3 and 4) — no bromide data were available for throughfall and stemflow. The regression gradients range from 2.78 to 3.37 $\mu\text{g}:\text{mg}$, a value slightly lower than that for bromide in sea water (3.42 $\mu\text{g}:\text{mg}$). Further, sodium shows a strong linear relationship with chloride in rainfall at Plynlimon and the gradient $\delta\text{Na}/\delta\text{Cl}$ is also slightly lower than that in sea water (Neal and Kirchner, 2000) — i.e. there is a moderate

enrichment of chloride in the atmospheric deposition. Thus, atmospheric inputs of DLBr and bromide originate in the sea and bromide is the dominant component of the DLBr. In the case of cloud water and stemflow, DLBr and DOC are also correlated.

The similarity in gradient for DLBr and bromide with respect to chloride in rainfall and cloud water indicates that the difference in their average concentrations reflects the difference in bromide concentrations between the two monitoring periods. Such variability is to be expected since

Table 3. Regression of dissolved organic carbon and chloride with dissolved labile bromine for Plynlimon waters. Concentration units are $\mu\text{g l}^{-1}$ for DLBr and mg l^{-1} for dissolved organic carbon and chloride.

	<i>GradDOC</i>	<i>2*std</i>	<i>GradCl</i>	<i>2*std</i>	<i>Const</i>	<i>2*std</i>	<i>r</i> ²	<i>N</i>
Rainfall	-0.61	0.74	2.78	0.10	5	11	0.836	625
Cloud	3.58	1.58	2.99	0.08	-7	100	0.937	380
Throughfall	0.33	0.25	3.11	0.19	18	60	0.884	142
Stemflow	1.99	0.29	2.88	0.21	21	62	0.889	132
Upper Hafren	2.38	0.29	0.58	0.30	12	5	0.385	435
Upper Hore	1.43	0.36	0.54	0.17	16	7	0.104	752
Lower Hafren	2.56	0.25	0.36	0.20	16	7	0.322	852
Lower Hore	1.81	0.40	0.58	0.19	17	8	0.101	859
Tanllwyth	2.86	0.24	0.49	0.27	16	8	0.634	349
South2Hore	-1.00	0.65	0.62	0.20	24	14	0.100	638
SE1f	1.58	1.69	0.27	0.67	37	18	0.023	174
SE3c	-0.21	1.85	1.37	0.58	21	8	0.161	124
TanNc	3.28	0.59	-0.13	0.97	19	34	0.619	106
TanSf	3.39	1.11	2.86	2.45	-9	63	0.230	152
Ha4B	-0.29	3.97	-2.13	0.81	57	20	0.133	190
Quarry	1.14	2.17	1.83	0.82	9	11	0.138	136
SE1bf	6.82	5.08	-5.90	1.93	83	18	0.324	102
SE3bc	-1.86	6.31	0.65	0.76	31	14	0.033	102
TanNbc	1.26	2.85	-1.88	1.98	62	35	0.029	136
TanSbf	0.20	1.70	-1.34	0.37	30	4	0.314	132

Table 4. Regression of dissolved organic carbon and chloride with bromide for Plynlimon waters. Concentration units are $\mu\text{g l}^{-1}$ for bromide and mg l^{-1} for dissolved organic carbon and chloride.

	<i>GradDOC</i>	<i>2*std</i>	<i>GradCl</i>	<i>2*std</i>	<i>Const</i>	<i>2*std</i>	<i>r</i> ²	<i>N</i>
Rainfall	-0.02	1.36	3.37	0.14	0.6	8.5	0.922	210
Cloud	-0.97	3.05	2.88	0.16	-7.2	69.1	0.910	140
Upper Hafren	-0.62	0.50	1.67	0.60	4.5	9.2	0.116	303
Upper Hore	-0.15	0.64	0.76	0.49	12.4	11.4	0.033	305
Lower Hafren	0.07	0.41	1.20	0.49	10.0	9.6	0.074	304
Lower Hore	0.35	0.69	0.87	0.49	10.5	10.8	0.042	302
Tanllwyth	-0.12	0.31	1.22	0.43	8.2	11.8	0.101	303

the marine signal (sodium and chloride) shows strong year to year variations that may be linked to the North Atlantic Oscillation in climate (Neal *et al.*, 2001).

RIVER WATER

The DLBr and bromide concentrations in the stream waters are moderately higher than those in rainfall and their variation in concentration is much smaller, with a maximum range of 0 to 80 $\mu\text{g l}^{-1}$. For all the main river sites where both DLBr and bromide have been measured (sequentially), average concentrations are between 18.3 and 27.8 $\mu\text{g l}^{-1}$ for DLBr and 13.8 and 18.6 $\mu\text{g l}^{-1}$ for bromide; bromide concentrations are 17 to 39% lower than DLBr.

The DLBr and bromide concentrations vary seasonally; both are higher in autumn when DOC concentrations are also at their highest (Fig. 5). For the lower Hafren and the upper and lower Hore, where there is a 15-year continuous weekly record of values of DLBr, there are small longer term (decadal) changes in concentration, while for the lower Hafren and upper Hore, DLBr concentrations increase over time. For example, in the case of the lower Hafren, average concentrations in 1983, 1990 and 1998 are 21.1, 22.2 and 26.0 $\mu\text{g l}^{-1}$, respectively. The equivalent values for the upper Hore in 1984, 1990 and 1998 are 20.4, 22.7 and 24.9 $\mu\text{g l}^{-1}$, respectively. For the lower Hore, concentrations of DLBr increase over time between 1983 and 1989, with a 'bulge' between 1987 and 1993: average concentrations in 1983, 1990 and 1998 are 20.9, 26.3 and 25.5 $\mu\text{g l}^{-1}$, respectively. For the lower Hore, the bulge in DLBr corresponds with the period just after major clear-fell.

In the case of DLBr, concentrations have also been measured for the paired catchments and the south2Hore

streams. For the paired catchments, DLBr concentrations were higher than for the main streams with averages ranging between 30.7 and 40.8 $\mu\text{g l}^{-1}$ for the podzol and 52.6 and 68.0 $\mu\text{g l}^{-1}$ for the gley sites: for south2Hore, the average DLBr concentration (26.6 $\mu\text{g l}^{-1}$) is within the range for the main streams. In the case of the gley sites, DOC concentrations were particularly high (around 12.5 mg l^{-1} ; Table 2). Further, for all the streams other than the paired sites on podzol, the average DOC and DLBr concentrations were correlated linearly with a gradient of around 3.3 $\mu\text{g}:\text{mg}$ and an intercept of DLBr for zero DOC was around 17 $\mu\text{g l}^{-1}$ (Fig. 6) — i.e. a value close to that for the average bromide concentrations in the streams. This feature, coupled with approximately the same gradient for the Tan sites with particularly high DOC concentrations, indicates that the bromine component associated with the DOC has a bromine to carbon content of around 3.3 $\mu\text{g}:\text{mg}$ that corresponds to a molar ratio of 0.5×10^{-3} .

DOC versus DLBr

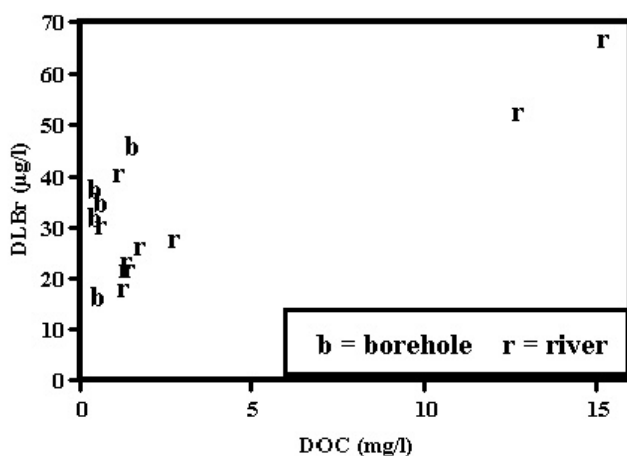
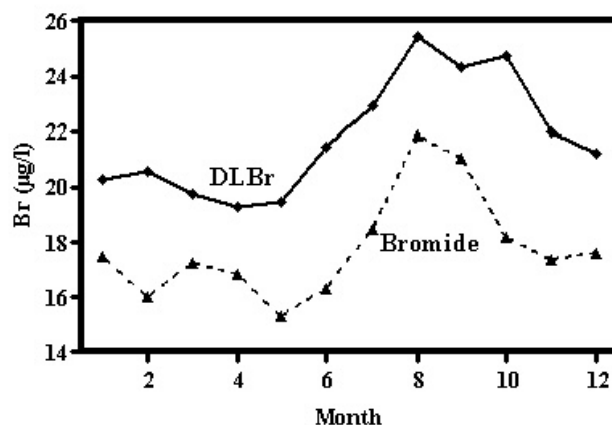


Fig. 5. The relationship between average concentrations of dissolved labile bromine and DOC in river water (r) and groundwater (g).

Lower Afon Hafren: Bromine



Lower Afon Hafren: DOC

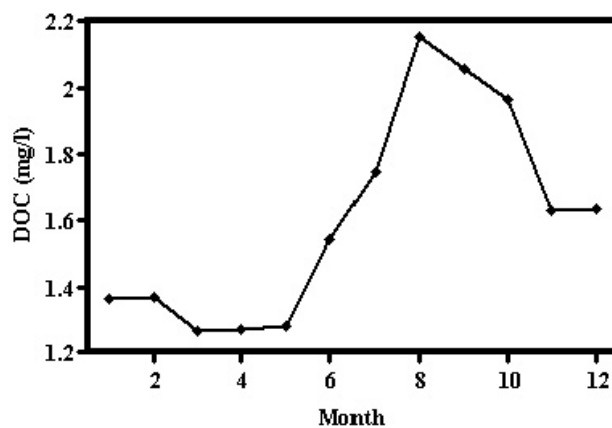


Fig. 6. The average monthly variation in dissolved labile bromine, bromide and DOC in the lower Afon Hafren.

While some statistically significant correlations occur ($p < 0.005$) between DLBr and bromide with DOC and chloride, the correlations are much weaker than those for the atmospheric inputs. For the upper and lower Hafren and the Tanllwyth, there were marked statistically significant relationships for DLBr with both DOC (gradients 2.38 ± 0.29 to $2.86 \pm 0.24 \mu\text{g}:\text{mg}$) and chloride (gradients 0.49 ± 0.27 to $0.58 \pm 0.30 \mu\text{g}:\text{mg}$). For the Tanllwyth paired catchment only the relationship with DOC was significant statistically (gradients 3.28 ± 0.59 and $3.39 \pm 1.11 \mu\text{g}:\text{mg}$). Correlations for DLBr with DOC and chloride are lower for the other streams monitored.

Bromide had no statistically significant relationship with DOC and a poor, although statistically significant relationship with chloride, the gradient of which varies between 0.8 ± 0.5 and $1.7 \pm 0.6 \mu\text{g}:\text{mg}$.

FELLING EFFECTS

The patterns of DLBr concentration change over time for the upper and lower Hore, probably because of felling. Neal *et al.* (1992) indicated that, for the felled area only, bromine concentrations may have increased by around a third (from 24 to $32 \mu\text{g l}^{-1}$) an increase which is also observed for DOC. The current study indicates that the major enrichment of DLBr with felling ceases after about six years. Thus, breakdown of organic debris (brush) produced when the trees were felled, coupled with increased wetting (Hughes *et al.*, 1996, 1998; Marc and Robinson, 2007), led to increased DOC and DOC-associated bromine until growth of the next generation of trees led to carbon/bromine retention by the soil. For the south2Hore and the paired

felling sites, there was no clear change in DLBr and hence the felling effects were not significant at these other sites.

TRENDS IN DLBR OVER TIME

To explore the trends in bromine over time, the DLBr concentrations have been examined using linear statistical analysis (Table 5) for the sites with the longest data runs for DLBr (rainfall, cloud water and the upper and lower Afon Hafren and Hore): bromide trends were not examined due to the more limited extent of the data. The regression took two forms. Firstly DLBr concentrations were regressed against time to obtain a general pattern of change. Secondly, DLBr was regressed against time and DOC concentration to factor out the effect of the increasing DOC concentrations over time for the lower Hafren and the upper and lower Hore.

Regression of DLBr with time

- No statistically significant relationship for rainfall, cloud water and the upper Hafren.
- Statistically significant relationships for the lower Hafren and the upper and lower Hore with a gradient of around $0.28 \mu\text{g l}^{-1} \text{yr}^{-1}$ (range 0.24 to $0.29 \mu\text{g l}^{-1} \text{yr}^{-1}$).

Regression of DLBr with time and DOC

- No statistically significant relationship for rainfall and cloud water.
- A statistically significant relationship for the upper Hafren determined by the correlation with DOC ($2.2 \pm 0.3 \mu\text{g l}^{-1}:\text{mg l}^{-1}$); there was no statistically significant relationship with time.

Table 5. Regression of DLBr ($\mu\text{g l}^{-1}$) against time (year) and DOC (mg l^{-1}).

	Year		DOC		Constant		r^2	N
	grad	2*std	grad	2*std	2*std			
DLBr = a*year + c								
Upper Hafren	0.01	0.13			4	7	0.000	435
Upper Hore	0.28	0.06			-542	7	0.104	751
Lower Hafren	0.29	0.06			-547	8	0.090	855
Lower Hore	0.24	0.06			-460	9	0.063	859
Tanllwyth	0.46	0.30			-890	12	0.027	349
DLBr = a*year + b*DOC + c								
Upper Hafren	-0.03	0.10	2.23	0.28	78	5	0.364	435
Upper Hore	0.25	0.06	1.00	0.33	-475	7	0.146	751
Lower Hafren	0.16	0.06	2.30	0.26	-292	7	0.338	855
Lower Hore	0.19	0.07	1.15	0.40	-354	8	0.098	859
Tanllwyth	0.18	0.19	2.68	0.23	-346	8	0.625	349

- A statistically significant relationship for the lower Hafren and the upper and lower Hore that is determined by the correlation with both time ($0.2 \mu\text{g l}^{-1} \text{yr}^{-1}$ (range 0.16 to $0.25 \mu\text{g l}^{-1} \text{yr}^{-1}$) and DOC ($1.5 \mu\text{g l}^{-1}$: mg l^{-1} , range 1.0 to $2.3 \mu\text{g l}^{-1}$: mg l^{-1}).

Thus, temporal trends in DLBr occur not in the atmospheric inputs but only in the rivers, wherein DLBr is correlated with DOC and temporal changes occur only for those sites where the concentration of DOC increases over time (i.e. the streams draining the forested areas).

INPUT-OUTPUT MASS BALANCES

Although there are some differences in the concentrations of DLBr and bromide between rainfall and stream water, to compare the values for the atmospheric inputs and stream outputs, there is a need to compare input-output fluxes. There are two reasons for this. Firstly, cloud water input flux might be significant: although the cloud water volume is small compared with the rainfall, the concentration of DLBr and bromide in cloud water is an order of magnitude higher than that in rainfall. Wilkinson *et al.* (1997) estimated that, of the total flux of bromine at Plynlimon, cloud water accounts for around 12% and 34% for the moorland and forested catchments respectively. Secondly, evaporation and transpiration of the rainfall input is also important (Neal *et al.*, 1997a). Here, the input-output fluxes have been compared using hydrological and hydrochemical approaches. In the hydrological approach, flow weighted concentrations for DLBr and bromide are combined with the rainfall, cloud water and stream water fluxes. Annual average rainfall is around 2518 mm while the average annual volumetric input from cloud water is 33 mm for moorland and 140 mm for forest. The evaporation and transpiration from moorland is 496 mm and from forest 627 mm (Neal

and Kirchner, 2000). In the hydrochemical approach, chloride is used as a conservative tracer and the ratios of DLBr and bromide to chloride in atmospheric deposition are compared with the ratios in the streams. The atmospheric ratio was calculated using the rainfall and cloud water fluxes, while, for the calculations, flow weighted DLBr, bromide and chloride concentrations were used.

The percentage retention of DLBr and bromide by the catchments, estimated using water and chloride balances (Table 6) indicate:

- that results using the hydrological and hydrochemical approaches were similar, with in some cases moderately higher estimates of uptake using a chloride balance.
- the uptake of DLBr by the catchments was small (average 5 to 12% with a range -10 to +20); the lowest uptake occurred for the highest forest cover (lower Hore and Nant Tanllwyth).
- a significant uptake of bromide across the catchments (average 30 to 35% with a range of 14 to 42%).

GROUNDWATER

The average DLBr concentration in groundwater ranges between 16.6 and $46.1 \mu\text{g l}^{-1}$ across the monitoring sites (the range of individual data points rather than averages is 12 to $103 \mu\text{g l}^{-1}$). These ranges are similar to those found for the streams.

DOC concentrations in groundwaters were low compared with those in the stream waters and DLBr in the groundwater is poorly correlated with DOC and chloride: only with SE1B is there a slightly significant positive relationship with DOC. While DOC concentrations are low in the groundwater, dissolved carbon dioxide levels can be very high (Neal *et al.*, 1997b). Within the groundwater zone, DOC supplied from the soil zone decomposes to generate CO_2 so that the

Table 6. Percentage retention of DLBr and bromide by the catchment as estimated using water and chloride balances.

	DLBr % Retention		Bromide % Retention	
	Water balance	Chloride balance	Water balance	Chloride balance
Upper Hafren	18	19	42	42
Lower Hafren	-4	17	14	30
Upper Hore	15	20	30	36
Lower Hore	3	3	24	31
Tanllwyth	-10	1	42	38
avg	5	12	30	35
min	-10	1	14	30
max	18	20	42	42

link between DLBr and DOC in the soils and streams is broken within the groundwater zone.

For chloride, there can be weak positive or negative relationships with DLBr. Further, even for the average concentrations there is a very weak relationship between DLBr, DOC and chloride.

Discussion

The study shows that, while bromide might represent the main form of bromine in rainfall and the atmospheric inputs as well as in the streams and groundwaters, bromine associated with DOC can be significant within the streams. Felling can lead to small increases in bromine associated with DOC in the streams but not always. Also, there can be longer term changes in DOC-associated bromine in the streams but only in streams draining forests as opposed to moorlands. Hughes *et al.* (1996, 1998) noted that organic soils, on rewetting, release both DOC and bromide and one of the effects of tree harvesting (and, indeed of tree ageing: Marc and Robinson, 2007) is lower water usage. As such, the increase in both DLBr and DOC — observed only in the forested catchments — may well be related to this wetting-up process (Marc and Robinson, 2007). This increase may be associated with both organic associated bromine and with bromide, as indicated in the main streams (upper and lower Hafren and Hore) by the lower DLBr to DOC gradient (average of 1.87 $\mu\text{g}:\text{mg}$ with range 1.00 to 2.30 $\mu\text{g}:\text{mg}$) when time is factored out compared with

- (a) The main streams where time is not factored out (average of 2.05 $\mu\text{g}:\text{mg}$ and range of 1.43 to 2.56 $\mu\text{g}:\text{mg}$).
- (b) The high DOC and DLBr values in the Tanllwyth streams: 3.28 to 3.39 $\mu\text{g}:\text{mg}$ for the small streams and an average of 2.86 $\mu\text{g}:\text{mg}$ for the main stem of the Tanllwyth.

The same feature is also observed in the main stem of the Tanllwyth where factoring out of time reduced the gradient to 2.68 versus 2.86 $\mu\text{g}:\text{mg}$.

In the streams, the variation in DLBr and bromide concentration is less than in rainfall and cloud water, because the catchments damp the rainfall signal, not just for DLBr and bromide but also for many other components of low chemical reactivity and high atmospheric input (Neal and Kirchner, 2000). It reflects the highly heterogeneous nature of water and chemical flux through catchments with a wide range in water residence times (Kirchner *et al.*, 2000, 2001; Feng *et al.*, 2004).

While the major component of the DLBr in the

atmospheric input is bromide, in the streams there is probably a bromine component associated with DOC for the organic-rich soils of the area. Indeed, hill-top peats cover 52% of the Afon Hafren and 33% of the Afon Hore catchments (Reynolds *et al.*, 1989). The linkage may be as organo-bromine or colloidal material; within the catchment, the loss of bromide from the atmosphere is approximately balanced by a gain in bromine associated with DOC.

The difference in bromide and bromine associated with DOC for the atmospheric inputs and the streams will not be connected with a straight conversion between inorganic and organic forms in the dissolved phase. There are four reasons for this conjecture. Firstly, the transport of DLBr and bromide and their interaction with the soil matrix will be complex and highly heterogeneous. Secondly, DLBr is weakly correlated with chloride. If there was just conversion in the water, the strong correlation observed in the atmospheric inputs would be maintained. Thirdly, seasonal changes in DLBr and bromide concentration are linked to the seasonal changes for DOC but not for chloride; this implies biogeochemical cycling. Fourthly, there are longer term variations in DLBr and DOC that probably reflect changes in biogeochemical functioning.

Within the groundwater zone, some DOC is broken down to produce CO_2 . In the stream, the water chemistry will depend on the relative proportions of soil and groundwater inputs (Neal *et al.*, 1997d). Generally, under baseflow conditions, the stream waters are derived from groundwater areas while, under stormflow conditions, the waters are mainly from the soil zone. However, there is no simple correlation between DLBr and flow just as there is no simple relationship between DOC and flow. Thus, at intermediate flows, there can be a high input of DLBr, bromide and DOC (Fig. 7). Further, the proportion of soil and groundwater inputs can vary considerably from site to site (Hill and Neal, 1997; Neal *et al.*, 1997c). Indeed, in the case of the south-east sites (SE1f and SE3c) on podzol, the streams are perennial when they might be expected to be ephemeral; even at high flows, there is a large component of groundwater. This explains why the DLBr-DOC relationship for these sites differs from that for the other streams (Fig. 6). In contrast, for the Tan sites on gley, the low permeability of the soils means that the runoff comes essentially from the organic-rich soil zone. This explains why DLBr and DOC concentrations are particularly high and why there is the strong relationship between DLBr and DOC.

The present study cannot gauge the total input-output balance for bromine, because there is no certainty that the more refractory components for bromine are associated with DOC. Indeed, the evidence of a bromine association with DOC in the waters is only secondary as it is based on the

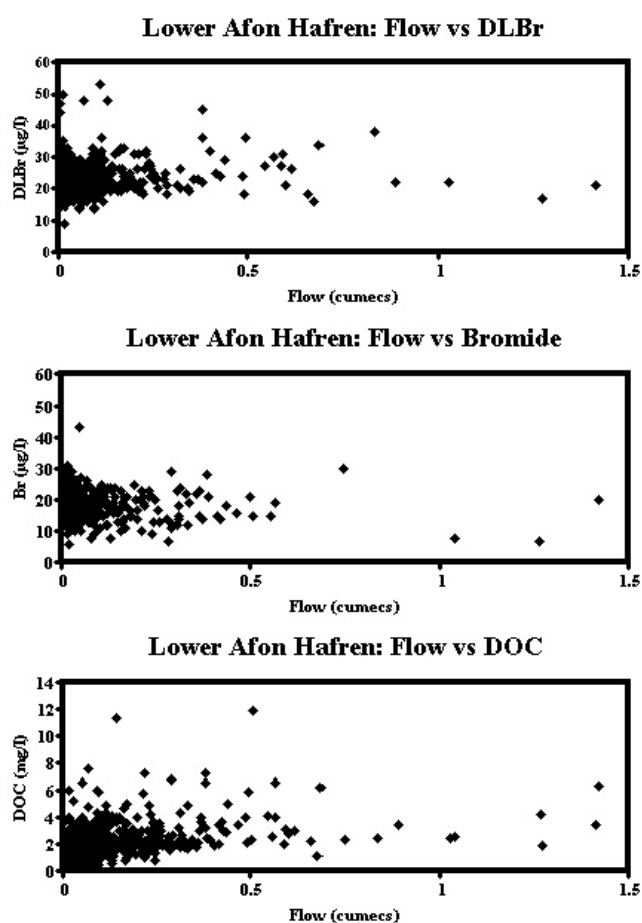


Fig. 7. The relationship of flow with DLBr, bromide and DOC concentration for the lower Afon Hafren.

relationships between DLBr and DOC using an analytical procedure for DLBr that is only defined operationally. Despite this limitation, the study flags the need to monitor bromine speciation in upland waters, to examine the hydrogeochemical functioning and to determine what natural and anthropogenic forms of humic/fulvic acid-bromine and organobromines are present. This is necessary in assessing the pollution climate for the uplands with respect to organobromine contaminants as well as the role of natural humic and fulvic acids in determining bromine speciation and the applied issues of the formation and levels of trihalomethanes in drinking waters. The work is particularly relevant because, in many areas of the UK, there are organic-rich soils in which DOC is increasing over time (Neal *et al.*, 2005).

With regard to bromine in the streams and groundwaters, comparison can be made with data from other parts of the UK and further afield. For the main Plynlimon streams, the average DLBr and bromide concentrations are 46 and 35 $\mu\text{g l}^{-1}$, respectively, which compares with an average for bromide in eastern UK rivers of less than 50 $\mu\text{g l}^{-1}$ for

relatively clean systems to up to 1716 $\mu\text{g l}^{-1}$ for industrial/urban contaminated systems. Indeed, for the latter point source pollution under baseflow conditions, concentrations can reach up to 9500 $\mu\text{g l}^{-1}$ (Neal and Robson, 2000). In this context, the bromide levels at Plynlimon must be classed as low and perhaps typical of UK upland areas. For the groundwaters at Plynlimon, the average bromide concentration is 34 $\mu\text{g l}^{-1}$ which compares favourably with the range of 60 to 340 $\mu\text{g l}^{-1}$ for potable groundwaters in the UK (Edmunds, 1996).

References

- Batjer, K., Gabel, B., Koschorrek, M., Lahl, U., Lierse, W.K., Stachel, B. and Thiemann, W., 1980. Drinking water in Bremen – trihalomethanes and social costs – a case study of bromoform formation during chlorination of river water highly contaminated with bromide ions. *Sci. Total Environ.*, **14**, 287–291.
- Bedard, D.L., Van Dort, H. and Deweerdt, K.A., 1998. Brominated biphenyls prime extensive microbial reductive dehalogenation of Aroclor 1260 in Housatonic River sediment. *Appl. Environ. Microbiol.*, **64**, 1786–1795.
- Biestler, H., Keppler, F., Putschew, F., Martinez-Cortizas, A. and Petri, M., 2004. Halogen retention, organohalogens, and the role of organic matter decomposition on halogen enrichment in two Chilean peat bogs. *Environ. Sci. Technol.*, **38**, 1984–1991.
- Cloern, J.E., 1996. Phytoplankton bloom dynamics in coastal ecosystems: a review with some general lessons from sustained investigation of San Francisco Bay, California. *Rev. Geophys.*, **34**, 127–168.
- Davis, S.N., 2004. Variations of bromide in potable groundwater in the United States. *Ground Water*, **42**, 902–909.
- Davis, S.N., Whittenmore, D.O. and Fabryka-Martin, J., 1998. The use of chloride/bromide ratios in studies of potable water. *Ground Water*, **36**, 338–350.
- EA, 1997. *The determination of bromate, chlorate and chlorite in waters by ion chromatography*. Environment Agency, Rio House, Waterside Drive, Aztec West, Aldmondsbury, Bristol, BS32 4UD, UK. 18pp.
- Edmunds, W.M., 1996. Bromide in British Groundwater. *Min. Mag.*, **60**, 275–284.
- Feng, X., Kirchner, J.W. and Neal, C., 2004. Spectral analysis of chemical time series from long-term catchment monitoring studies: Hydrochemical insights and data requirements. *Water Air Soil Pollut., Focus*, **4**, 221–235.
- Gibble, G.J., 1999. The diversity of naturally occurring organobromine compounds. *Chem. Soc. Rev.*, **28**, 335–346.
- Gibble, G.J., 2000. The natural production of organobromine compounds. *Environ. Sci. Pollut. Res.*, **7**, 37–49.
- Gibble, G.J., 2003. The diversity of naturally produced organohalogens. *Chemosphere*, **52**, 289–297.
- Greenwood, N.N. and Ernschaw, A., 2005. *Chemistry of the elements*. Elsevier, Amsterdam, The Netherlands. 1342pp.
- Hashimoto, S., Azuma, T. and Otsuki, A., 1998. Distribution, sources, and stability of haloacetic acids in Tokyo Bay, Japan. *Environ. Toxic. Chem.*, **17**, 798–805.
- Hill, T. and Neal, C., 1997. Spatial and temporal variation in pH, alkalinity and conductivity in surface runoff and groundwater for the Upper River Severn catchment. *Hydrol. Earth Syst. Sci.*, **1**, 697–716.
- Huggenberger, P., Hoehn, E., Beschta, R. and Woessner, W., 1998. Abiotic aspects of channels and flood plains in riparian ecology. *Freshwater Biol.*, **40**, 407–425.

- Hughes, S., Reynolds, B. and Hudson, J., 1996. Release of bromide following rewetting of a naturally drained acid gully mire. *Soil Use Manage.*, **12**, 62–66.
- Hughes, S., Reynolds, B., Brittain, S.A., Hudson, J.A. and Freeman, C., 1998. Temporal trends in bromide release following rewetting of a naturally drained gully mire. *Soil Use Manage.*, **14**, 248–250.
- Kirchner, J.W., Feng, X. and Neal, C., 2000. Fractal stream chemistry and its implications for contaminant transport in catchments. *Nature*, **403**, 524–527.
- Kirchner, J.W., Feng, X. and Neal, C., 2001. Catchment-scale advection and dispersion as a mechanism for fractal scaling in stream tracer concentrations. *J. Hydrol.*, **254**, 81–100.
- Korom, S.F., 2000. An adsorption isotherm for bromide. *Water Resour. Res.*, **36**, 1969–1974.
- Laternus, F., Giese, B., Wiencke, C. and Adams, F.C., 2000. Low-molecular-weight organoiodine and organobromine compounds released by polar macroalgae – the influence of abiotic factors. *Fresenius J. Anal. Chem.*, **368**, 297–302.
- Manninen, P.K.G. and Hasanen, E., 1992. Total organochlorine and organobromine in Finnish water courses. *Hydrobiologia*, **234**, 475–479.
- Marc, V. and Robinson, M., 2007. Assessing the long-term water balance of upland grassland and forestry. *Hydrol. Earth Syst. Sci.*, **11**, 44–60.
- Moxon, R.E.D. and Dixon, E.J., 1980. An automatic method for the determination of bromide in water. *J. Automat. Chem.*, **2**, 139–142.
- Neal, C. and Kirchner, J.W., 2000. Sodium and chloride levels in rainfall, mist, streamwater and groundwater at the Plynlimon catchments, mid-Wales: inferences on hydrological and chemical controls. *Hydrol. Earth Syst. Sci.*, **4**, 295–310.
- Neal, C., and Robson, A.J., 2000. A summary of river water quality data collected within the Land Ocean Interaction Study: core data for Eastern UK rivers draining to the North Sea. *Sci. Total Envir.*, **251/252**, 587–668.
- Neal, C., Smith, C.J., Walls, J., Billingham, P., Hill, S. and Neal, M., 1990. Comments on the hydrochemical regulation of the halogen elements in rainfall, stemflow, throughfall and stream waters at an acidic forested area in Mid-Wales. *Sci. Total Envir.*, **91**, 1–11.
- Neal, C., Fisher, R., Smith, C.J., Hill, S., Neal, M., Conway, T., Ryland, G.P. and Jeffery, H.A., 1992. The effects of tree harvesting on stream water quality at an acidic and acid sensitive spruce forested area: Plynlimon, Mid-Wales. *J. Hydrol.*, **135**, 305–319.
- Neal, C., Wilkinson, R.J., Neal, M., Harrow, M.L., Wickham, H., Hill, L. and Morfitt, C., 1997a. The hydrochemistry of the headwaters of the River Severn, Plynlimon, Wales. *Hydrol. Earth Syst. Sci.*, **1**, 583–618.
- Neal, C., Robson, A.J., Shand, P., Edmunds, W.M., Dixon, A.J., Buckley, D.K., Hill, S., Harrow, M.L., Neal, M. and Reynolds, B., 1997b. The occurrence of groundwater in the Lower Palaeozoic rocks of upland Central Wales. *Hydrol. Earth Syst. Sci.*, **1**, 3–18.
- Neal, C., Hill, T., Hill, S. and Reynolds, B., 1997c. Acid neutralization capacity measurements in surface and ground waters in the Upper River Severn, Plynlimon: from hydrograph splitting to water flow pathways. *Hydrol. Earth Syst. Sci.*, **1**, 687–696.
- Neal, C., Robson, A.J. and Christophersen, N., 1997d. Towards coupling hydrological, soil and weathering processes within a modelling perspective. In: *Geochemical Processes, Weathering and Groundwater Recharge in Catchments*, O.M. Saether and P. de Caritat (Eds.), Balkema, Rotterdam. 329–380.
- Neal, C., Reynolds, B., Neal, M., Pugh, B. and Wickham, H., 2001. Long term changes in the water quality of rainfall, cloud-water and stream water for moorland, forested and clear-felled catchments at Plynlimon. *Hydrol. Earth Syst. Sci.*, **5**, 459–476.
- Neal, C., Robson, A.J., Neal, M., and Reynolds, B., 2005. Dissolved organic carbon for upland acidic and acid sensitive catchments in mid-Wales. *J. Hydrol.*, **304**, 203–220.
- Neal, M., Neal, C., Wickham, H. and Harman, S., 2007. Determination of bromide, chloride, fluoride, nitrate and sulphate by ion chromatography: comparisons of methodologies for rainfall, cloud water and river waters at the Plynlimon catchments of mid-Wales. *Hydrol. Earth Syst. Sci.*, **11**, 294–300.
- Nikolaou, A.D., Golfinopoulos, S.K., Arhonditsis, G.B., Kolovoyiannis, V. and Lekkas, T.D., 2004. Modelling the formation of chlorination by-products in river waters with different quality. *Chemosphere*, **55**, 409–420.
- Quack, B. and Wallace, D.W.R., 2003. Air-sea flux of bromoform: controls, rates, and implications. *Global Biogeochem. Cycle.*, **17**, 1023.
- Rathburn, R.E., 1996. Bromine incorporation factors for trihalomethane formation for the Mississippi, Missouri and Ohio Rivers. *Sci. Total Envir.*, **192**, 111–118.
- Reynolds, B., Neal, C., Hornung, M. and Stevens, P.A., 1986. Baseflow buffering of streamwater acidity in five mid-Wales catchments. *J. Hydrol.*, **87**, 167–185.
- Reynolds, B., Hornung, M. and Hughes, S., 1989. Chemistry of streams draining grassland and forest catchments at Plynlimon, mid-Wales. *Hydrolog. Sci. J.*, **34**, 667–686.
- Rook, J.J., 1974. Formation of haloforms during chlorination of natural waters. *Water Treatment Exam.*, **23**, 234–243.
- Santillo, D. and Johnson, P., 2003. Playing with fire: the global threat presented by brominated flame retardants justifies urgent substitution. *Environ. Int.*, **29**, 725–734.
- Stuart, M.E., Goody, D.C., Kinniburgh, D.G. and Klinck, B.A., 2001. Trihalomethane formation potential: a tool for detecting non-specific organic groundwater contamination. *Urban Water*, **3**, 173–184.
- Vinogradov, A.P., 1959. *The geochemistry of rare and dispersed chemical elements in soils*, 2nd edn. Consultants Bureau, New York, USA.
- Weigel, S., Bester, K. and Huhnerfuss, H., 2005. Identification and quantification of pesticides, industrial chemicals and organobromine compounds of medium to high polarity in the North Sea. *Mar. Pollut. Bull.*, **50**, 252–263.
- Westerhoff, P., Song, R.G., Amy, G. and Minear, R., 1998. NOM's role in bromine and bromate formation during ozonation. *J. Amer. Water Works Ass.*, **19**, 82–94.
- Wilkins, C., 1978. The distribution of Br in the soils and herbage of north-west Pembrokeshire. *J. Agr. Sci.*, **90**, 109–114.
- Wilkinson, R.J., Reynolds, B., Neal, C., Hill, S., Neal, M. and Harrow, M.L., 1997. Major, minor and trace element composition of cloud water and rain water at Plynlimon, Mid-Wales. *Hydrol. Earth Syst. Sci.*, **1**, 557–570.
- Yuita, K., Tanaka, T., Abe, C. and Aso, S., 1991. Dynamics of iodine, bromine and chlorine in soil. I. Effect of moisture, temperature, and pH on the dissolution of the triad from soil. *Soil Sci. Plant Nutr.*, **37**, 61–63.