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Major, minor and trace element composition of cloudwater and rainwater at Plynlimon

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Abstract

The composition of cloudwater samples collected at Plynlimon, Mid Wales by the Institute of Hydrology is described based on one of the most comprehensive chemical records for deposition in the UK. Comparison with bulk rainwater samples for the same area demonstrates a tenfold enrichment of most elements in cloudwater. Large variations in cloudwater composition occur due to variations in marine and terrestrial/anthropogenic sources, general weather patterns, atmospheric circulation and seasonal effects. All trace metal concentrations are associated with anthropogenic contamination. The lanthanides La, Ce and Pr, and Y are highly correlated in ratios associated with lithogenic sources and fossil fuel combustion. Outliers suggest the influence of catalysts used in the petro-chemical cracking process. Plantation forestry significantly enhances the annual deposition of solutes from cloudwater; between 15 and 40% of most constituents to upland forested catchments and around 50% for NO₃, B and Cd come from cloud deposition. In upland moorland areas, only 10% of the annual deposited load of inorganic constituents comes from cloudwater.

Introduction and Background

Atmospheric pollution and its resultant impacts remain an area of great concern to the scientific community (Grennfelt *et al.*, 1996; De Vries and Bakker, 1996). Long-term data to describe the changes in concentrations of a wide range of atmospheric contaminants in deposition is essential to an understanding of catchment hydrochemistry. While data on the deposition of the major constituents in rainfall in the UK have been published (Robson and Neal, 1996; Campbell *et al.*, 1994; Davison and Hewitt, 1992; Donald and Stoner 1989; Fowler *et al.*, 1988; Reynolds *et al.*, 1984), relatively few data on cloud water chemistry are available (see, Reynolds *et al.*, 1996), and data for trace elements (in rainfall or cloud water) are even more scarce (Neal *et al.* 1996). Land in western Britain at altitudes of over 400m and above is typically in cloud for between 500 and 2000 hours per year (Fowler *et al.* 1991) and vegetation captures wind driven cloud droplets very efficiently (Dollard *et al.* 1983). As solute concentrations in cloud are large compared to those in rain, cloud deposition is a potentially important pathway for the input of pollutants to upland ecosystems. Indeed, cloud water deposition may increase water inputs by up to 12% and solute deposition by c.40% (Fowler *et al.* 1989).

This paper examines the deposition of major, minor and trace elements in rain and cloud water at Plynlimon in

Mid-Wales for the period 22 December 1992 to 27 December 1995. Element inter-relationships are examined to establish sources of cloudwater constituents. Estimates are made of the relative extent of atmospheric deposition from cloud and rainwater sources to upland moorland and afforested catchments for a wide range of contaminants. The work comprises the first detailed examination of this comprehensive dataset held at the Institute of Hydrology.

Study Area and Analysis

The Plynlimon study area is located in Mid-Wales and forms the headwater area of the Upper Wye (Gwy) and Severn catchments. Bulk rainfall samples are collected at weekly intervals from two continuously open collectors. The first is located in the Afon Gwy catchment at NGR 2823 2855, 390 m elevation. The second rainfall collector and the cloudwater collector are located at the Carreg Wen meteorological station operated by the Institute of Hydrology at NGR 2828 2886, 570 m elevation. Originally rainwater samples were analysed separately, but since the concentrations were found to be very similar, the samples are now bulked and a single analysis is made. The cloudwater collector is of the passive, lidded 'harp type' described by Milne *et al.* (1988) and Reynolds (1991). In brief, the collector consists of a low density polyethylene-coated metal frame over which an inverted cone of nylon

filaments is stretched. Beneath the collector, a 30 cm diameter glass funnel directs the moisture droplets into a polypropylene bottle. The whole assembly is capped with a 1.2 m diameter lid mounted on a tubular steel framework to exclude droplets of greater than 5 mm diameter at wind-speeds of up to 5 m.s⁻¹. Some rainwater contamination can occur under windy conditions, but the collectors provide good qualitative estimates of cloudwater chemistry (Crossley *et al.*, 1992).

Two sub-samples of the rainfall and cloud waters were taken for analysis in the Institute of Hydrology laboratories. One sub-sample was filtered with 0.45 µm membranes and acidified with high purity concentrated nitric acid to 1% v/v within 2 hours of sampling. This sub-sample was then stored in the dark at 4°C in 10% acid-washed polyethylene bottles prior to analysis. The acidification minimized the loss of metals through adsorption to the bottles and precipitation reactions. Analysis of the acidified sub-sample was as follows; inductively-coupled-plasma optical emission spectrometry (ICPOES) for Ca, Mg, Na, SO₄, Mn and Fe. Atomic absorption spectrophotometry (AA) for K, and inductively-coupled-plasma mass spectrometry (ICPMS) for the trace metals, transition elements (see Table 1 for a full listing of these elements), lanthanides (La, Ce and Pr) and actinides (Th and U). The second sub-sample was filtered with 2 µm glass fibre filters into chromic acid-washed glass bottles and stored with the other sub-samples prior to analysis. These sub-samples were analysed colorimetrically for F, Cl, Br, I, NO₃, NH₄, PO₄ and Si. Dissolved organic carbon (DOC) was analysed using a TOCSin II aqueous carbon analyser. Electrical Conductivity (EC), and pH were determined by electrometric techniques and Alkalinity (Alk) by Gran titration on unfiltered samples at field temperature.

Results and Discussion

INITIAL OBSERVATIONS

Table 1 lists the mean values of the 42 elements determined in the rain and cloudwater analysis; the elements are ranked in descending order of concentration in cloudwater. The ranks for rainwater demonstrate the effect of differing enrichments (E, the ratio of cloud to rainwater average concentrations) of the elements. Elements with a high enrichment factor are more concentrated in cloudwater than in rainwater. Pb, for example, is the 20th most concentrated element in cloudwater, but in rainwater it is the 12th most concentrated. Unlike the majority of other constituents, it is in fact more concentrated in rainwater than in cloud water, with an enrichment factor of 0.4. Thus Pb appears to be a special case and is examined in more detail later. Table 1 also includes maximum and minimum values to demonstrate how concentrated (or dilute) the samples can be. Nc and Nr indicate the numbers of samples contributing to the calculated means. These mean values are displayed graphically in Fig. 1; the

major constituents have been converted from milligrams to micrograms per litre and all values were log₁₀ transformed to normalise the plots. The figure shows the constituents by order of concentration and highlights the differences in enrichment across the range of elements.

The data span a wide range of concentrations; Na and Cl have the highest concentrations and U the lowest in both rain and cloudwaters. There were high concentrations of acidifying pollutants SO₄, NO₃ and NH₄ present in cloudwater; over 80% of the sulphate was of non-marine origin in both cloud and rain waters. Of the remaining major ions, Mg was the next most concentrated in cloudwater, followed by Ca, DOC, K, Si, F, PO₄ and the trace elements.

Constituents with concentrations of less than 0.1 micrograms per litre are below the detection limit; nonetheless, these are greater than the values found for de-ionised water and are included for interest and to give as full a picture as possible of sample composition.

Maximum values indicate very high concentrations of sea-salts (> 1 g Na/l), acidic anions (0.5 g SO₄/l) and metals (7 mg Zn/l) occurring in the cloudwater collector: load calculations presented later in this paper demonstrate the large contribution made by cloud deposition to the overall input of contaminants to forested catchments. Peak concentrations of the trace elements were between 50 and 1000 times greater than their mean values. For the major constituents, the difference between mean and maximum values were in the order of 10 to 40 times. The very high concentrations of trace elements were associated with low sample volumes, high acid anion concentrations and acid pH (pH < 4). Fig. 2 is a plot of mean and maximum elemental concentrations in cloudwater plotted against rank (x axis) and demonstrates the greater difference between the mean and maximum values for the trace elements compared to the major constituents. This difference may result from the relative increase in solubility of particle-associated trace elements at low pH compared to the major constituents (Faust and Aly, 1981).

ENRICHMENT OF CLOUDWATER WITH RESPECT TO RAINWATER

Concentrations of major solutes in cloud water and enrichment factors (cloud/rain ratios) were very similar to those observed further south in Wales at Llyn Brianne (Reynolds *et al.* 1996). The values were also consistent with long-term monitoring data from a rural site at Dunslair Heights in the Southern Uplands of Scotland (Fowler *et al.* 1995). Cloudwater was enriched in all major ions compared to rainwater (Figure 1). The enrichment factor for the major constituents was in the order of 11 (Si and DOC are an exception due to contamination of the rainwater samples from the breakdown of the plastic funnel at the collector). Of the trace elements, the degree of enrichment between cloud and rainwaters varied widely;

Table 1. Volume weighted mean cloud and rainwater chemistry at Plynlimon in Mid-Wales for the period 22 December 1992 to 27 December 1995. The solutes are ranked in order of mean concentration. E is the enrichment factor; the ratio of the cloud to rainwater means. The units of concentration for Cl to K are mg/l, Br to U are in $\mu\text{g/l}$. Alkalinity (Alk) is in eq/l and EC (electrical conductivity) in $\mu\text{Siemens}$.

Det.	Cloudwater data					Rainwater data					E
	Rank	Nc	mean	min	max	Rank	Nr	mean	min	max	
Cl	1	137	42.989	1.2000	460.0	1	123	3.941	0.2000	18.0	10.9
Na	2	144	25.284	0.6300	1034.2	2	136	2.133	0.0450	12.4	11.9
SO ₄	3	144	14.060	0.4650	510.4	3	136	1.512	0.2150	30.0	9.3
SO ₄ *	4	137	11.922	0.0601	101.1	4	123	1.289	0.2034	15.6	9.2
NO ₃	5	137	11.669	0.0508	205.0	5	123	0.741	0.0169	11.8	15.7
NH ₄	6	137	3.497	0.0551	54.0	7	123	0.276	0.0109	4.4	12.7
Mg	7	144	3.000	0.0600	130.5	9	136	0.241	0.0050	1.7	12.4
Ca	8	144	1.895	0.1400	107.1	8	136	0.253	0.0050	11.8	7.5
DOC	9	137	1.734	0.1500	16.4	6	123	0.616	0.1000	4.2	2.8
K	10	144	1.063	0.0400	44.0	10	133	0.096	0.0250	2.0	11.1
Br	11	137	138.274	4.5000	1550.0	13	123	15.258	0.5000	66.0	9.1
Si	12	137	102.000	0.0500	900.0	11	123	66.000	0.0750	1300.0	1.5
B	13	144	71.251	0.5001	1595.8	19	136	2.552	0.0835	99.4	27.9
Zn	14	144	58.396	1.0983	7155.5	16	136	7.603	0.3295	169.6	7.7
F	15	137	46.000	0.0100	600.0	14	123	11.000	0.0100	100.0	4.2
PO ₄	16	136	44.000	0.0033	2000.0	15	123	11.000	0.0033	400.0	4.0
Al	17	144	42.591	0.9302	5891.6	17	136	4.797	0.1330	319.8	8.9
Fe	18	144	40.652	0.0500	2332.0	18	136	4.411	0.0500	374.1	9.2
Sr	19	144	20.396	0.5137	2506.3	20	136	1.837	0.1250	23.7	11.1
Pb	20	144	12.811	0.1571	3384.1	12	136	33.773	0.1916	2935.5	0.4
Mn	21	144	10.052	0.0500	1130.0	25	136	0.791	0.0500	58.3	12.7
I	22	137	8.276	0.4000	40.0	24	123	1.118	0.2000	5.2	7.4
Ba	23	144	5.467	0.2818	298.9	23	136	1.237	0.0781	194.1	4.4
Cu	24	144	5.098	0.0820	427.4	21	136	1.667	0.0377	47.7	3.1
Ni	25	144	2.116	0.0686	234.7	26	136	0.371	0.0050	18.0	5.7
Cd	26	144	1.429	0.0193	63.2	30	136	0.080	0.0007	7.3	17.9
Sb	27	144	0.726	0.0108	46.4	28	136	0.185	0.0037	1.7	3.9
Rb	28	144	0.652	0.0470	114.2	31	136	0.062	0.0003	1.8	10.5
Li	29	144	0.570	0.0030	64.8	32	136	0.053	0.0004	0.9	10.8
Zr	30	36	0.429	0.0015	2.2	27	32	0.188	0.0011	1.1	2.3
Cr	31	144	0.412	0.0043	86.2	22	136	1.253	0.0043	121.6	0.3
Mo	32	144	0.340	0.0081	7.5	29	136	0.083	0.0008	3.9	4.1
Co	33	144	0.158	0.0050	15.7	37	136	0.017	0.0012	0.7	9.3
Ce	34	144	0.080	0.0001	60.1	34	136	0.021	0.0001	2.3	3.8
Sc	35	144	0.058	0.0002	6.9	35	136	0.020	0.0003	2.3	2.9
La	36	144	0.056	0.0017	60.8	40	136	0.006	0.0002	0.5	9.3
Th	37	144	0.054	0.0001	3.6	33	136	0.032	0.0002	0.5	1.7
Y	38	144	0.052	0.0023	19.3	38	136	0.008	0.0001	0.3	6.5
Be	39	144	0.039	0.0005	1.5	36	136	0.017	0.0001	0.2	2.3
Cs	40	144	0.038	0.0001	7.6	39	136	0.008	0.0001	0.1	4.8
Pr	41	144	0.012	0.0003	12.0	41	136	0.002	0.0001	0.1	6.0
U	42	144	0.011	0.0001	1.1	42	136	0.001	0.0001	0.0	11.0
pH		144	5.058	2.92	6.9		136	4.996	3.49	6.9	
Alk		142	-43.708	-1202.26	115.1		136	-16.01	-323.59	25.5	
EC		144	209.787	42.00	78000.0		136	25.174	8	240	

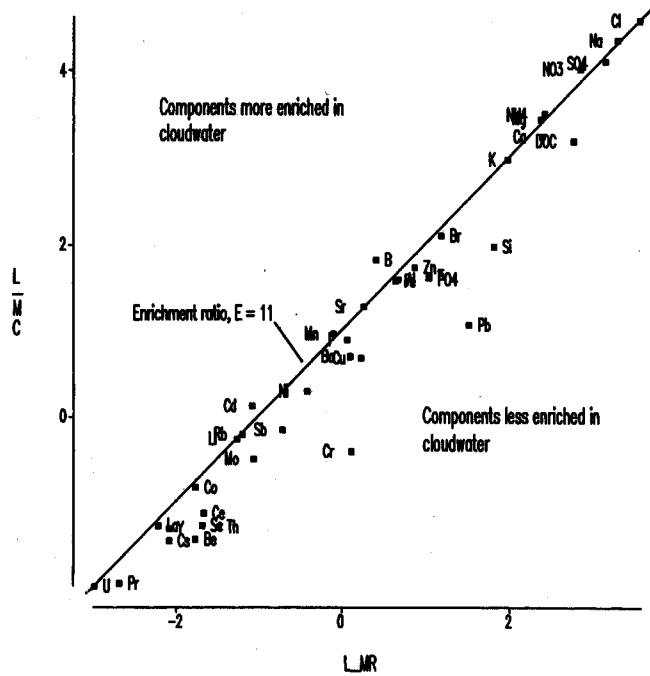


Fig. 1. Plot to demonstrate the relationship between mean concentrations of solutes in cloudwater and rainwater. L_{MR} is the log of the mean rainwater concentration, L_{MC} is the log of the mean cloudwater concentration. From bottom left to top right; U is the least abundant component, Cl is the most concentrated. Cloudwater samples had concentrations which were approximately 11 times higher than those in rainwater.

0.3 (Cr) to 27.9 (B); both Cd and B, were highly enriched in cloudwater. The enrichment value for B resulted from a period of high concentration in cloudwater between 1992 and 1993; no concurrent period was observed for rainwater samples. The mean enrichment factor for data before and after the period of enhancement was 6.12, within the range of values for the other elements (Table 1). Lead and chromium, were the only elements that had lower mean concentrations in cloudwater than in rainwater for the period of study. This was due to unusually high Pb and Cr (and Ca) concentrations in rainfall compared to the preceding (Pb only) and subsequent period of record (Cr exhibited enhanced concentrations from 1986 to 1990, see Neal *et al.*, 1996). These high concentrations were not reflected in the cloud water samples and the cause of the elevated concentrations is the subject of on-going investigation. For data falling outside the period of enhanced concentration, the mean enrichment for Pb and Cr was very similar at about 1.4.

The large enrichment in cloud water with respect to rain occurs mainly because cloud water samples are collected quite close to the cloud base. Hill clouds are typically up to 1000m deep, and solute concentrations decrease rapidly with height above cloud base due to the adiabatic increase in liquid water content of the cloud with altitude. Thus, the average concentration of cloud water solutes through-

out the cloud depth is smaller than that obtained by ground level sampling. Additional factors contributing to the large ratios are artefacts related to the collectors. The high windspeeds encountered at Carreg Wen will lead to aerodynamic sorting of the raindrop size spectrum with smaller drops being carried around or over the collector. As chemical concentration is related to drop size, with smaller drops having larger concentrations, this will result in an underestimate of ion concentrations in the bulk precipitation samples. The cloud collectors are also subject to dry and particulate deposition both between and during cloud and rain events. This material will be washed into the collector funnel and be included in the cloudwater sample. Dry and particle deposition will affect the rain collectors as well, but the nature of the cloud gauge means that it will be a more efficient collector than a rain funnel. Evaporation of cloud drops from the collector strings may also occur leading to enhanced solute concentrations, although such effects are relatively small (Milne *et al.* 1988). Despite the lid, cloud collectors are also subject to contamination by rain at windspeeds in excess of 5 ms^{-1} and this will dilute the cloud samples. The extent of this effect is not known for this study.

ION INTERRELATIONSHIPS AND SOURCES OF CONSTITUENTS

Deposition chemistry at Plynlimon is heavily influenced by the maritime climate experienced in the UK and is

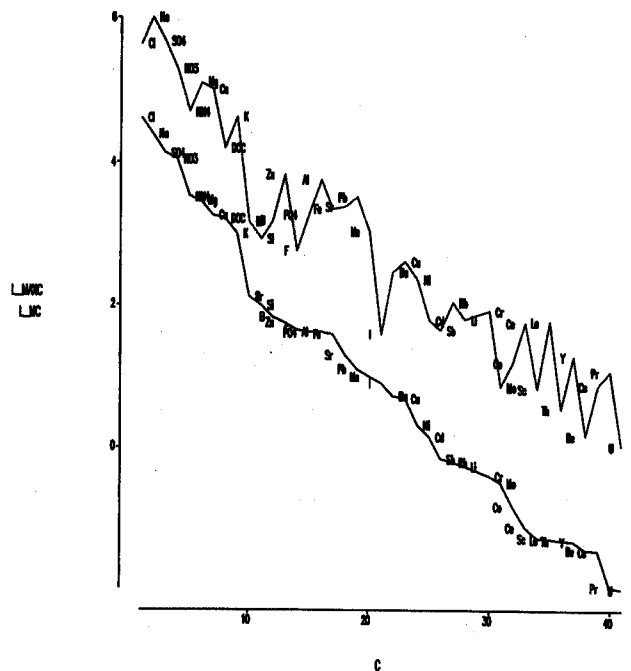


Fig. 2. The relationship between mean (L_{MC}) and maximum (L_{MAX}) concentrations of solutes in cloudwater, C is the rank order of L_{MC} . Note the increasing difference between the mean and maximum values for the minor and trace elements.

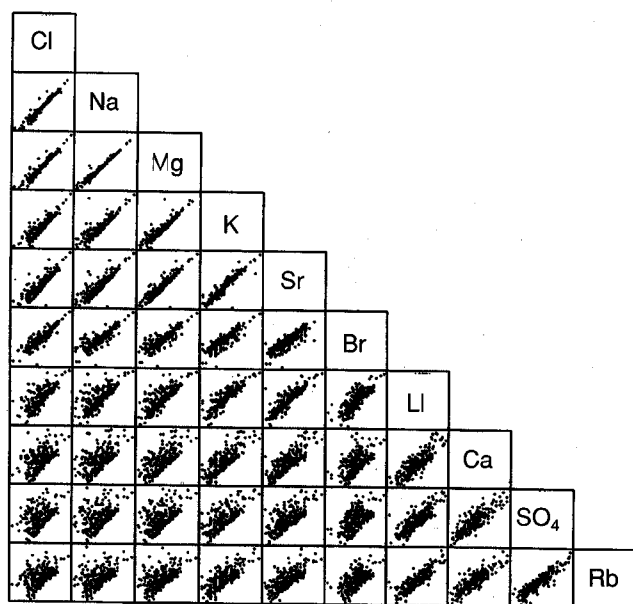


Fig. 3. The marine constituents of cloudwater composition at Plynlimon. From Cl, which is almost entirely of marine origin the constituents are increasingly affected by non-marine sources. The data are log transformed to normalise and assist in visualising the relationships.

characterised by two broad groups of constituents; those of marine origin and those of terrestrial/anthropogenic origin. Figure 3 shows scatter plots of cloudwater constituents influenced by the marine source; the data were normalised by log transformation to improve presentation. The constituents are plotted in order of decreasing marine dominance starting with Cl on the top left moving down to Rb in the bottom right. Cl, Na and Mg are dominated by marine aerosol in ratios within 4% of those for mean sea water (see, Riley and Skirrow, 1975). For the elements with decreasing marine influence, there are greater numbers of samples with concentrations in excess of mean sea-water composition (K, Sr, Br, Li, Ca, SO₄ and Rb) indicating significant alternative sources of these components. The main source of non-marine sulphur is the combustion of fossil fuels; the sources of K and Ca are thought to be terrestrial dust (Reynolds, 1984).

All other elements and determinands show no (or barely discernable) marine influence. These include the acidifying ions NO₃, NH₄, the trace elements and DOC. There is a strong correlation between all of these components including SO₄ in both rain and cloudwater samples (Figure 4). Cl is included in this plot to demonstrate the absence of a relationship with marine aerosol. These constituents are inversely related to pH; the most acid samples having the highest concentrations of acid anions and trace metals. The lowest windspeeds and easterly winds coincide with the most contaminated samples; those of marine composition are associated with higher winds from

southerly and south-westerly directions brought by low pressure weather systems progressing eastward over the Atlantic Ocean. The light easterly winds result from the presence of high pressure systems which tend to hold polluted air in the lower atmosphere and limit dispersion due to low turbulence. This pollutant-laden air then drifts across Wales depositing high concentrations of acidic anions and contaminants on the Plynlimon catchments. These ion interrelationships highlight the importance of the weather and atmospheric circulation in determining deposition quality at Plynlimon.

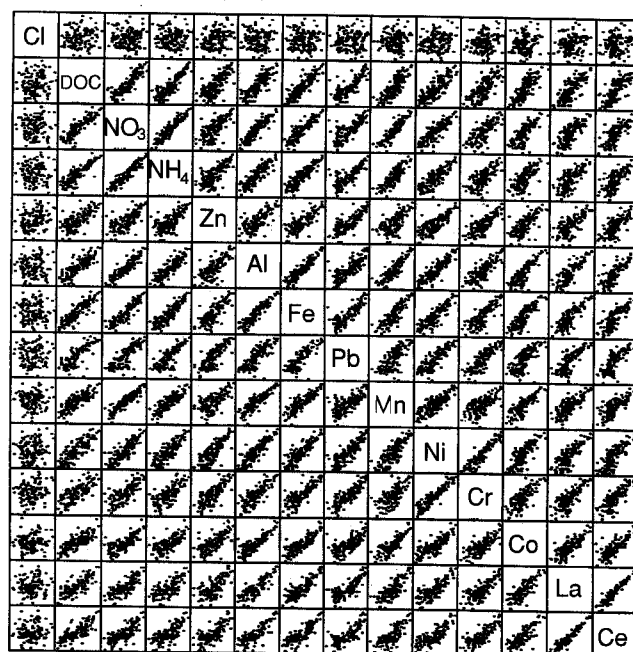


Fig. 4. A sample of constituents of predominantly anthropogenic and/or terrestrial origin. The data are log transformed to normalise and assist in visualising the relationships. Cl is added to show the lack of influence of the marine source. Note the strong correlation of La and Ce.

Within the broad groupings of marine or anthropogenic components there are distinct sub-groups of highly correlated variables; NO₃ and NH₄ are strongly correlated $r^2=0.87$ ($p<0.001$), and with these components in order of decreasing significance are DOC, Zn, Al, Fe, Pb, Mn, Ni, Co and Cr. The DOC component probably derives from uncombusted or partially combusted fuel from motor vehicles and the metals Zn, Al, Fe, Mn, Ni, Co and Cr from a variety of sources including incinerators, metals processing and oil and coal combustion by the power generators and other heavy industry. Pb most likely derives from fuels (see Gordon, 1988).

TRACE METALS AND RARE EARTH ELEMENTS

Table 1 demonstrates the presence of Zn, Al, Fe, Sr, Pb and Mn in much higher concentrations than the other trace elements in cloudwater, indeed, their maximum values indicate that they can reach concentrations of many milligrams per litre (during dry periods). With the exception of Pb their concentrations in rainwater are much lower. These high concentrations, however, indicate the potential for metals deposited with mist or as dry deposition on a rough forest canopy to form a major source of these contaminants to upland ecosystems. Load estimates are given in Table 4 and discussed later. The interrelationships and potential sources for the contaminants are discussed below in the light of existing studies which have attempted to use elemental ratios as source indicators for different sources of atmospheric contamination.

Metals are resident in the atmosphere only for a period of days or weeks (Hidy, 1973) but are capable of being transported great distances in these short periods (Salomons and Förstner, 1984). Their sources range from forest fires, wind blown dust, volcanic eruptions, vegetation and sea-spray, but by far the largest source is industrial emissions which account for some 70–80% of Cd, Cu, Pb and Zn (Salomons and Förstner, 1984). This would appear to be the case in the current study given the correlation of trace metals to acidic anion concentrations. The purpose, therefore, of examining trace element ratios might be to establish whether samples such as those collected in this study are suitable to distinguish between different pollutant sources within the general cocktail of emissions reaching the point of sampling.

Zn TO Sb RATIO

Ratios of Zn to Sb for aerosols collected at sites in Bermuda and Barbados were found to depend on the trajectory of the contributing air mass; samples from North America had ratios less than 36 (Table 2), whereas easterly air masses, that had crossed the Atlantic Ocean had Zn to Sb ratio of 120 (Arimoto *et al.* 1995). Similarly for Plynlimon cloudwater, the mean Zn to Sb ratio was 120 (5%ile = 14, 95%ile = 330) and Zn:Sb was significantly correlated to Cl ($p < 0.001$); high ratio (Zn:Sb > 80) samples were also associated with strong south-westerly winds (windspeed > 5 m/sec). Suggesting that, the greater the marine component, the greater the Zn content and hence the higher the value of Zn:Sb (assuming that the south westerly wind direction precludes emissions from the Irish Republic). Low Zn:Sb samples were associated with light south-easterly winds and these samples had the highest metals and sulphur concentrations indicating the impact of terrestrial pollution sources. This is in contrast with the data of Nriagu (1989) which indicate ratios of Zn to Sb in natural sources of less than 36. Arimoto *et al.* (1995) suggested that the high ratios resulted from metals industry emissions from Europe and North Africa. It seems more likely, given the results for Plynlimon, that the Zn:Sb composition of the air is subtly altered as it crosses the ocean. Otherwise, air of North American origin might be expected to have a similar Zn:Sb at both Bermuda and Plynlimon, which is not the case. Further, air which is clearly affected by industrial emissions has low Zn:Sb, i.e. the air from N.America at Bermuda (Arimoto *et al.*, 1995) and from central England at Plynlimon. This suggests that

Table 2. Ratios of Zn to Sb in cloudwater samples (this study) and other atmospheric and environmental samples studies.

Sample type	Zn:Sb	Reference
<i>Plynlimon cloudwater</i>		Current study
Westerly air	> 80	
Easterly air	< 80	
Rime ice	89	
Roadside dust	1940	
<i>Bermuda aerosol</i>		Arimoto <i>et al.</i> (1995)
N.American origin	36	
Easterly air	120	
<i>Ambient air</i>		Cawse (1981)
Wraymires, Lake District, U.K.	24	
Jungfrau, Alps, Central Europe	50.6	
Average of 20 U.K. sites	35.6	
Swansea, S.Wales	77.5	
<i>Seawater</i>		
Crustal average	20	Goldberg <i>et al.</i> (1965)
	350	Taylor (1964)

Zn:Sb may not be conservative and as such a poor indicator of different contaminant sources; the proximity to the pollution source or the fact that the air has crossed a large stretch of ocean is more significant than the nature of the actual source.

The oceans are not thought to be a significant source of Sb or Zn (Nriagu, 1989), according to Nriagu and Pacyna (1988) 42% of the global atmospheric flux of Sb comes from natural sources, with soil, volcanoes and sea-salt contributing some 10% each. Of anthropogenic sources a further 25% comes from non-ferrous metal processes, coal produces 22% and incinerators 11%. Enrichment of the sea-surface microlayer with Zn (Lion and Leckie, 1981) and the effect of metal scavenging by rising bubbles (Piotrowicz *et al.*, 1979) may contribute significantly higher concentrations of Zn than would be expected from bulk seawater. Given the dispersion of contaminant Zn and Sb with passage over the Atlantic ocean, the likely proportion of marine Zn in those samples may be sufficient to result in the higher Zn:Sb of samples influenced by long range transport mechanisms. A further consideration is the possibility for the preferential settlement of the heavier Sb component. Gravitational settling is not believed to contribute significantly to the composition of sea-surface aerosol (Salomons and Förstner, 1984) and it remains uncertain whether settling significantly effects Zn:Sb of long distances. Alternatively, in the case of Plynlimon cloudwater, the low Zn:Sb values in samples from easterly air may have been due to the leaching of Sb from particles, increasing the Sb content of the solution relative to the already very mobile Zn. Easterly samples tended to have low pH (around 3), a small sample volume and high concentrations of acidic anions. Clearly, this is a very complex issue and beyond the scope of the current study. It is hoped that a more detailed analysis will provide further clarification.

LA TO CE RATIO

One of the first observations to become apparent on initial visual examination of the data for cloud-water from the Plynlimon collector was the very close correlation of Ce, La, Pr and Y (Figure 4). The rare earth elements (REEs, which include the lanthanides; Ce, La and Pr) are chemically very similar to each other and other lithophile elements and are unlikely to be affected by combustion or other environmental processes. This makes them a very useful tracer for sources of atmospheric contamination (Olmez and Gordon, 1985, Sholkovitz *et al.*, 1993). The main mineral sources of La and Ce are bastnasite and monazite (Kilbourn, 1984). Y has similar properties to the lanthanides and the phosphate, zirconite, is its main mineral source which also contains the heavier lanthanides (Kilbourn, 1984). Possible anthropogenic sources of these elements to the atmosphere include cracking of oil during refining and oil and coal combustion, and motor vehicle

emissions (Olmez and Gordon, 1985; Kitto *et al.*, 1992; Mizohata, 1986). Petroleum cracking catalysts (FCCs) are highly enriched in La and Ce (Sholkovitz *et al.*, 1993) and the ratio of La to Ce can be used as a signature for different sources (Olmez and Gordon, 1985).

The data for La and Ce in cloudwater at Plynlimon were dominated by two occurrences of very high concentrations; far in excess of the main distribution of the data (Table 3). There was also a large number of very low concentration samples, with values below the minimum quotable ($0.1 \mu\text{g l}^{-1}$) for the analytical method (ICP-MS). Despite this, the correlation between these elements was maintained at very low concentrations, although with increased scatter. Examination of blank data used for quality assurance over a period of seven years gave maximum blank concentrations; Ce = $0.0632 \mu\text{g l}^{-1}$, La = $0.0248 \mu\text{g l}^{-1}$, Y = $0.0271 \mu\text{g l}^{-1}$, and Pr = $0.0111 \mu\text{g l}^{-1}$. These were above the minimum values for cloudwater samples but the blank data for La, Ce, Pr and Y showed no correlation. In previous studies (e.g., Tuncel *et al.*, 1985), values greater than blanks have been used; in this study an arbitrary minimum value of twice the maximum blank concentration was used.

Table 3. The distribution of La and Ce data for cloudwater samples collected at Plynlimon. The highest values are approximately 80 and 40 times greater than the 95%ile values.

	La	Ce
Median	0.048	0.072
95%ile	0.78	1.44
Highest value	60.80	60.1
2nd. highest value	13.55	11.27

To examine possible sources of La, Ce, Pr and Y in Plynlimon cloudwater, regression of La on Ce was carried-out. Pr and Y were not used in these analyses due to the paucity of data available in the literature for comparative purposes. The very high values were treated as outliers; they were discontinuous with the general distribution of the data and had much higher La:Ce value (Table 4, Figure 5). The regression slope of the remaining distribution of values gave a coefficient of 0.578, $r^2 = 0.9074$ ($p = 0.0001$) (Table 4). Table 4 provides a summary of data on La:Ce from a wide range of studies and geochemical texts for a variety of environmental samples and geochemical standards. These values help to set the Plynlimon samples into some kind of geochemical context and give an indication of possible influences.

The La:Ce ratio for bastnasite is around 0.7, although its value in the different FCCs varies widely according to the degree of enrichment of Ce or La in the ore; the final ratio is usually higher than that for bastnasite ore (Table 4). Of motor vehicle emissions, Kitto *et al.* (1992) indicated that catalytic converters may be a considerable

Table 4. Ratios of La to Ce in cloudwater samples (this study) and other atmospheric samples from around the world.

Source	Ratio La:Ce	Reference
<i>Earths crust</i>	0.50 +/-0.04	Olmez and Gordon (1985)
<i>Marine Shale</i>	0.49 (0.39-0.52)	Sholkovitz (1990)
<i>Soil & road dust (Japan)</i>	0.45 (0.25-0.68)	Mizohata (1986)
<i>U.S Coals:</i>		
Western	0.63 +/-0.02	"
Eastern	0.54 +/-0.05	"
<i>Minerals:</i>		
Bastnasite	0.67, 0.65, 0.703	", Kilbourn (1984), Kitto <i>et al.</i> (1992)
Monazite	0.51, 0.49, 0.61	", Kilbourn (1984), Taylor and MacLennan (1975)
<i>Power plants:</i>		
Coal-fired (US)	0.51 +/-0.04	"
Coal-fired (Japan)	0.55 +/-0.27	Mizohata (1986)
Oil-fired (US)	1.8 +/-0.2	Olmez and Gordon (1985)
Oil-fired (Japan)	0.24 (0.068-0.64)	Mizohata (1986)
<i>Fluidised catalytic cracker (FCC)</i>		
In fine airborne particles	1.24	Dzubay <i>et al.</i> (1988)
Cracking catalyst DA-200	1.034	Kitto <i>et al.</i> (1992)
Cracking catalyst GXO-25	1.065	"
<i>FCC reclaiming tower</i>	1.6	Mizohata (1986)
<i>Atmospheric particles</i>		
Fine fraction < 2.5 µm (Shennandoah)	0.311	Tuncel (1985)
Coarse particles > 1.5 µm	0.49 (0.44-0.59)	Mizohata (1986)
Fine fraction < 1.5 µm (Osaka, Japan)	0.84 or 1.067	Mizohata (1986)
Bermuda aerosol	0.454	Sholkovitz (1990)
Fine particles (Camden, NJ)	1.839	Dzubay <i>et al.</i> , (1988)
3 sites in New Jersey	1.23 +/-0.81 1.62 +/-1.16 1.54 +/-1.03	Kitto <i>et al.</i> , (1992)
<i>Wet deposition</i>	0.489 (0.34-0.57)	Sholkovitz <i>et al.</i> , (1990)
<i>Cloudwater</i>		
Regression slope	0.567	
Peak concentrations	1.017, 1.202	
<i>Roadside dust (Plynlimon)</i>	0.335	
<i>Rime ice (Tarenig Forest, N.Wales)</i>	0.779	

source of REEs and that US car manufacturers used mainly Ce oxides; thus Ce may be the major REE from vehicles, whereas La was the major REE from FCCs. The regression slope of the bulk of the La and Ce data for the Plynlimon samples falls well below the high values indicated for FCC associated sources. The low value falls within the range associated with lithogenic sources and coal combustion and possibly vehicle emissions. The La to Ce ratio of the two high concentration samples are very close to those for FCCs and FCC process related emissions. These data do not fall within the general distribution of values for cloudwater, not only in their La and Ce values but also in major ion chemistry, with the highest Na, Mg, Ca, SO₄, as well as Pb and Fe. They were dry weather winter samples with low pH, although the high

marine base cation concentrations appear to have increased the pH of these samples. Their pH was greater than would be expected at such high SO₄ concentrations. Due to the small sample volume, analysis for F, Cl, Br, I, NO₃, NH₄, PO₄, Si and DOC was not possible. Samples with high pollutant concentrations would normally be associated with stagnant air masses associated with high pressure; these trap land surface emissions and have low sea-salt concentrations. These samples had Na and Mg concentrations indicative of significant marine input. A dust source was ruled-out; a sample of Plynlimon roadside dust was acid-leached under pH conditions similar to those expected in cloudwater samples, giving base cation and metal concentrations quite different to cloudwater samples. Further comparison with contaminant source data

was hampered by the lack of data available on process emission and FCC composition and use in the UK. Data of FCC composition appear to be readily available in the US (see, Kitto *et al.*, 1992), as well as information regarding the major suppliers and their proportion of the market. This kind of information is clearly vital if an adequate assessment of contaminant sources is to be made. Unfortunately such information is not available in the UK.

SOLUTE DEPOSITION FROM CLOUD WATER

After examination of the nature and composition of cloud water at Plynlimon it is appropriate to assess its contribution to the overall solute deposition on the two main types of land cover in the area; moorland and plantation forestry. On the basis of data from Brienne and elsewhere in the UK (Reynolds *et al.*, 1996), a cloud exposure period of 1000 hours per year and an average windspeed of 5ms^{-1} have been assumed for the Plynlimon site. From the wind profile equation (Beswick *et al.*, 1991) and assuming reference heights of 2m and 15m for the grassland and forest, cloud droplet deposition velocities to 0.25m high grassland and 10m high forest have been calculated as 46mms^{-1} and 194mms^{-1} respectively (cf Reynolds *et al.*, 1996). The liquid water content of hill cloud typically varies between 0.1 and 0.4gm^{-3} . Assuming a value of 0.2gm^{-3} , which is comparable with measurements at the Brienne site and at similar altitudes at Great Dun Fell (Fowler *et al.*, 1991), this gives annual cloud water inputs to moorland and forest vegetation of 33mm and 140 mm respectively. The annual solute deposition can then be estimated from the mean cloud water chemistry and the hydrological inputs.

Table 5 shows the annual solute inputs from bulk precipitation on the basis of the 1976–85 annual average rainfall for the Severn of 2459 mm (Kirby *et al.*, 1991) along with estimated deposition to moorland and forest vegetation resulting from cloud water. For the moorland vegetation, cloudwater accounts for between 10 and 20% of the total wet deposition input, although for some trace elements, notably Cd and B, cloudwater contributes a much larger fraction reflecting the large enrichments of these solutes in cloudwater. Cloudwater is a much more significant deposition pathway for forest vegetation compared to the moorland, with cloud inputs contributing up to 50% of the total wet inputs to the trees. This is because trees are aerodynamically rougher than the shorter grassland which is reflected in the much higher deposition velocity for the forest. Significantly, the additional water inputs from cloud are relatively small compared to the annual rainfall at Plynlimon; it is the large concentrations which determine the importance of cloudwater to the annual solute deposition flux. The large cloudwater solute concentrations are also important in relation to direct phytotoxic effects on foliage. These effects may be enhanced if cloudwater is evaporated from the vegetation following deposition events (Unsworth 1984).

A comparison between data from the current study and earlier data (Cawse 1980) on major and trace element concentrations in bulk deposition at Plynlimon has been made. Cawse (1980) employed a continuously open collector for bulk deposition in a manner analogous to the current study. The figures in Table 6 are back calculated from these published deposition and rainfall amount data, omitting elements for which deposition was recorded as a 'less than' figure.

Whilst data for Na and Cl in Table 6 show reasonable agreement with ratios of Na to Cl close to the theoretical value for seawater (0.553), there are some large discrepancies between the two data sets for the other major ions, with consistently larger values reported by Cawse (1980). Assuming all the Na in the rain is derived from seasalts, then values for Mg and K, which are almost exclusively of seasalt origin at Plynlimon, are two and four times too large respectively. The trace element data also show a mixture of reasonably similar and very different results. There are large disparities between the data sets for Pb, Zn, Fe and Al, with the latter three being much larger in the Cawse (1980) data. From Table 5, there is nearly a kilogramme per hectare of Pb being deposited (mainly through rain water) to both moorland and forest sites at Plynlimon; this is about three times the amount ($0.28\text{kg ha}^{-1}\text{yr}^{-1}$) reported for a selection of rural and isolated sites by Lindberg *et al.* (1989). Comparison of concentrations with 'global' figures (Lindberg *et al.*, 1989) suggests that Plynlimon rainwater concentrations are large for a rural area, where concentrations are typically below $10\mu\text{g l}^{-1}$.

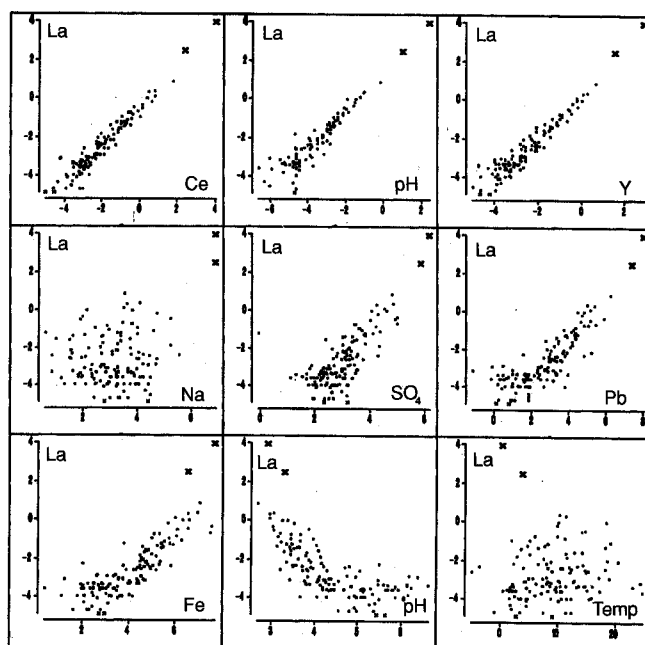


Fig. 5. La against Ce, Pr, Y, Na, SO_4 , Pb, Fe, in logarithmic form pH and temperature in $^{\circ}\text{C}$. The two samples marked with a cross are treated as outliers in the analysis.

Table 5. Wet deposition of major and trace solutes to moorland and forest vegetation at Plynlimon. The units for Cl to K are kg ha⁻¹ yr⁻¹ from Cl to K and Br to U g ha⁻¹ yr⁻¹.

	Moorland			%age of total as cloud	Cloud deposition	Forest	
	Wet deposition	Cloud deposition	Total deposition			Total deposition	%age of total as cloud
Cl	96.88	14.19	111.07	13	60.20	157.08	38
Na	52.38	8.35	60.73	14	35.42	87.80	40
SO ₄	37.13	4.65	41.78	11	19.74	56.87	35
SO ₄ *	31.72	3.93	35.65	11	16.66	48.38	34
NO ₃	18.20	3.86	22.06	18	16.38	34.58	47
NH ₄	6.89	1.16	8.04	14	4.90	11.79	42
Mg	5.90	0.99	6.89	14	4.20	10.10	42
Ca	6.15	0.62	6.77	9	2.65	8.79	30
DOC	15.25	0.57	15.82	4	2.42	17.67	14
K	2.46	0.35	2.81	12	1.48	3.94	38
Br	376.23	45.54	421.77	11	193.20	569.43	34
Si	1622.94	33.66	1656.60	2	142.80	1765.74	8
B	62.70	23.43	86.13	27	99.40	162.10	61
Zn	186.88	19.14	206.02	9	81.20	268.08	30
F	270.49	15.18	285.67	5	64.40	334.89	19
PO ₄	270.49	14.52	285.01	5	61.60	332.09	19
Al	118.03	13.86	131.89	11	58.80	176.83	33
Fe	108.44	13.53	121.97	11	57.40	165.84	35
Sr	45.25	6.60	51.85	13	28.00	73.25	38
Pb	828.68	4.29	832.97	1	18.20	846.88	2
Mn	19.43	3.30	22.73	15	14.00	33.43	42
I	27.54	2.64	30.18	9	11.20	38.74	29
Ba	30.49	1.82	32.31	6	7.70	38.19	20
Cu	41.07	1.68	42.75	4	7.14	48.21	15
Ni	9.10	0.69	9.79	7	2.94	12.04	24
Cd	1.97	0.46	2.43	19	1.96	3.93	50
Sb	4.43	0.24	4.67	5	1.02	5.45	19
Rb	1.48	0.21	1.69	13	0.91	2.39	38
Li	1.23	0.19	1.42	13	0.80	2.03	39
Zr	4.67	0.14	4.81	3	0.60	5.27	11
Cr	30.74	0.14	30.87	<1	0.57	31.31	2
Mo	1.97	0.11	2.08	5	0.48	2.44	19
Co	0.49	0.05	0.54	10	0.22	0.72	31
Ce	0.49	0.03	0.52	5	0.11	0.60	19
Sc	0.49	0.02	0.51	4	0.08	0.58	15
La	0.15	0.02	0.17	12	0.08	0.23	36
Th	0.74	0.02	0.75	2	0.07	0.81	9
Y	0.20	0.02	0.21	8	0.07	0.27	26
Be	0.49	0.01	0.51	3	0.06	0.55	10
Cs	0.20	0.01	0.21	6	0.06	0.25	22
Pr	0.05	<0.01	0.05	6	0.01	0.06	22
U	0.02	<0.01	0.03	12	0.01	0.04	36

Table 6. Comparison of solute concentrations in bulk deposition collected at Plynlimon during this study and by Cawse (1980) for the period 1972–75. Units are mg l^{-1} from Cl to K and $\mu\text{g l}^{-1}$ from Br to Sc.

Solute	This study	Cawse (1980)
Cl mg l^{-1}	3.94	4.13
Na	2.13	2.42
SO ₄	1.51	2.58
NO ₃	0.74	1.47
Mg	0.24	0.58
Ca	0.25	0.54
K	0.10	0.40
Br g l^{-1}	15.3	19.83
B	2.55	6.35
Zn	7.60	20.23
F	11.00	14.68
Al	4.80	103.13
Fe	4.41	75.37
Pb	33.77	9.12
Mn	0.79	2.90
Cu	1.67	8.33
Ni	0.37	3.97
Sb	0.18	0.22
Cr	1.25	1.59
Co	0.02	0.11
Sc	0.02	0.02

This combination of relatively large concentrations and high rainfall results in the large deposition figures. This high deposition value for Pb is associated with a period of very high lead concentrations in rainwater between 1992 and 1995. This period was not reflected in the cloudwater data, and may have been caused by the entry of road dust into one of the rainfall collectors. Rallying activities at Plynlimon during dry weather produce clouds of fine dust above the area (Hill, pers. comm.). Extraction of the soluble fraction from 0.5 g of road dust, added to 19.5 g of 1% nitric acid, produced high concentrations of Pb (4.05 mg/l), Zn, Cu, Ca and SO₄, as well as other metals, in ratios consistent with the spikes of high concentration observed in rainwater. The collector has now been resited. Cawse (1980) estimated total atmospheric deposition (wet + dry) of Pb at Plynlimon to be $0.23 \text{ kg ha}^{-1} \text{ yr}^{-1}$, equivalent to a concentration of $9.1 \mu\text{g l}^{-1}$ in bulk precipitation, which is consistent with measurements from before the period of enhanced Pb concentrations. Concentrations of Cd measured at Plynlimon (Table 1) are about one third of the mean of the rural data ($0.27 \mu\text{g l}^{-1}$) quoted by Lindberg *et al.* (1989), giving deposition values that are comparable with other rural sites even allowing for the additional cloudwater inputs to the forest and the high rainfall. Manganese and zinc concentrations at Plynlimon are also low compared with typical rural values ($3.2 \mu\text{g l}^{-1}$

for Mn and $21.3 \mu\text{g l}^{-1}$ for Zn; Lindberg *et al.* 1989), resulting in very low deposition figures in comparison with other rural sites.

Summary and Conclusions

Comparison of data for a total of 42 major, minor and trace elements in cloudwater and bulk rainwater samples collected at Plynlimon, Mid Wales shows that cloudwater is much more concentrated in most elements than rainwater. Cloudwater composition was also very variable. There were very dilute samples and samples with extremely high concentrations. These wide variations were associated with the sources of constituents and the atmospheric conditions during the period of sample collection. The highest concentrations coincided with low windspeeds and small sample volumes. High concentrations of anthropogenically derived NO₃, and metals came from easterly air movement from the inner industrial and urban areas of England. High sea-salt concentrations were associated with south-westerly air. Low concentration samples were associated with high windspeeds and larger sample volumes. The ratio of Zn to Sb was examined as a source indicator in cloudwater samples; high values (>80) were associated with a marine influence; ratios below 80 implied that samples were of terrestrial origin. The data exhibited a strong positive relationship between the lanthanides La, Ce and Pr, and Y in ratios associated with lithogenic sources and fossil fuel combustion. Outliers, which had much higher concentrations, indicated the influence of catalysts used in the petro-chemical cracking process. The lack of data for process emissions in the UK limited the scope of the investigation.

The importance of cloudwater deposition as a major pathway for the transport of major, minor and trace elements was demonstrated. Estimates of annual deposition from cloudwater and rainfall for moorland and plantation forestry, showed that cloudwater contributes between 15 and 40% of most constituents to upland forested catchments and around 50% for NO₃, B and Cd. Upland moorland areas receive only around 10% of their input of inorganic constituents from cloudwater.

This unique set of chemical data is one of the most comprehensive on cloudwater in the UK and this study is by no means a complete analysis. There remains much scope for further study especially where catchment solute budgets are concerned. Clearly, any study of acid deposition in an upland afforested system would be incomplete without estimates of cloudwater deposition.

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