

STUDIES OF SNOW CHEMISTRY IN THE SCOTTISH HIGHLANDS.

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ABSTRACT.

An outline of recent work on snowfall, snowcover and snowmelt chemistry in the Scottish Highlands is presented. Snowfalls associated with polluted airmasses have very different major and trace ion chemistries when compared to snowfalls associated with relatively unpolluted or maritime airmasses.

Wind action gives rise to snowcover whose chemical content is spatially and temporally variable. Sublimation of ice crystals during wind transport may be one variable contributing to the variability. Meltwaters derived from the snowcover are proportionally enriched in some ions, especially sulphate and nitrate. These meltwaters have a large impact on streamwater chemistry during the Spring thaw, because the contribution of pre-event or groundwater is smaller than in many other European or North American catchments.

Introduction.

Studies of snow chemistry in the Scottish Highlands have mainly been undertaken in the 1980'es. They have focused on three main questions:

- a) what is the chemical composition of acidic deposition and how does it differ from event to event?
- b) what processes operate on the snowcover to modify its chemical composition? and
- c) what impact does snowmelt have on streamwater chemistry?

It is the purpose of this paper to summarise our findings of the last five years with these questions in mind.

Fieldwork area.

The semi-permanent snowpack is located within a small, remote, high-altitude catchment in the Cairngorm Mountains, Scotland.

The catchment, Ciste Mhearad (57°To^T 06'N 03°To^T 38' W), is located to the NE of the Cairn Gorm peak, has an area of 0.4km^2 and an elevation of 1010-1160 m. The bedrock is granite, overlain by thin soils, classified as Alpine (humus ranker) and Alpine podzols. The vegetation is Alpine tundra (Abrahams et al, 1988). A single stream drains the catchment. The catchment experiences strong winds, which may approach 160 km/hr on occasions, and there is much local redistribution of surface snows. There are no woodland influences on the catchment (cf. Jones, 1985; Jones and Souchanska, 1985).

The main characteristics of snowcover in this region are; a) surface layers of wind-blown snow forming hard or soft slab, and b) basal layers of coarse, granular snow with grain diameters usually > 2 mm. Intercalated are ice layers, some of which are multiple-bedded and up to 5 cm thick (Ward, 1980; Ward et al, 1985). Equi-temperature and melt metamorphism dominate the evolution of the snowcover for much of the season. Ice layers are formed by repeated melting and refreezing of surface snow, possibly as a consequence of diurnal cycles, or when surface meltwaters penetrate the pack and refreeze at a temperature inversion a few cm below the surface. Slush layers may form during spring (Ward et al, 1985). Snow typically resides in the catchment throughout the year for seven in every ten years.

#### The chemical composition of fresh snowfall.

Fresh snowcover in Ciste Mhearad is chemically heterogeneous. Coefficients of variation (Cof) for individual major ions range from 5-113%, assuming a normal distribution, or 1-144% assuming a lognormal distribution. In general, the distribution of the concentration of major ions in snowcover is better described by the lognormal distribution (Tranter et al, 1987a). Such heterogeneity has important implications for snowpack sampling. To obtain statistically significant values for the mean concentration of an event requires the collection of a large number of samples. This is usually not logistically or financially feasible, especially in remote regions. Hence in our studies we recognise the shortcomings of only collecting one sample from each event, but adopt the pragmatic view that variability between events is greater than variability within events. We therefore place more emphasis on the collection of one sample from many events, rather than many samples from a few events.

The chemistry of relatively unpolluted snow is shown in Table 1. The mean and coefficient of variation (hereafter CV) of the concentration of 13 elements in the dissolved phase is presented. Results of both regional (or inter-site) and intra-site surveys are presented. The regional survey extended some 360 km<sup>2</sup>. The solute appears to be derived largely from marine aerosol. This is consistent with trajectory analysis, which shows a large maritime component (Landsberger et al, 1989).

Table 1. The solute content of Scottish snowfall.

RELATIVELY UNPOLLUTED SNOW

Element	Inter-site survey.		Intra-site survey.	
	Concentration (ug/l)	CV (%)	Concentration (ug/l)	CV (%)
Al	19.2	78	52.2	70
Br	30.6	31	33.2	3
Ca	419	47	310	29
Cl	9,110	35	10,600	4
Cu	4.36	18	5.38	57
Fe	10.8	55	6.13	21
I	3.98	25	4.75	32
Mg	641	31	673	4
Mn	3.63	79	1.46	78
Na	5,210	35	6,000	4
Pb	4.49	64	2.79	66
SO <sub>4</sub>	1,260	31	1,430	3
V	0.18	25	0.47	49

n = 8 (or 7 for Mn and Cu)

n = 6 (5 for Mn and 3 for V)

RELATIVELY POLLUTED OR BLACK SNOW (March 14, 1986).

Element	Concentration (ug/l)
Al	84 ± 3
Br	65 ± 2
Ca	630 ± 50
Cl	3,200 ± 110
Cu	12 ± 3
Fe	199 ± 10
I	9.7 ± 0.5
Mg	254 ± 3
Mn	27 ± 2
Na	827 ± 28
Pb	122 ± 5
SO <sub>4</sub>	33,100 ± 201
V	15 ± 1
Cd	<3
Cr	<4
Ni	<10

Table 2.

Median concentrations of metals in wet deposition (from Galloway et al, 1982).

	Urban	Rural	Remote
Cu	41	5.4	0.06
Mn	23	5.7	0.19
Pb	44	12	0.09
V	42	9.0	0.16

Units are ug/l.

The recommended upper limits for metal concentrations in water (from Galloway et al, 1982).

	Potable water	Aquatic organism toxicity
Cu	1000	20.0
Mn	50	1000
Pb	50	10
V	No standard	500

Units are ug/l.

Table 3. The elemental composition and enrichment factors of particulate matter found within Scottish snow.

Inter-site survey.

	Concentration (ppm)	CV (%)	EF	CV (%)
Al	20,600	72	1	0
Ba	237	44	3	64
Br	14	21	30	61
Ca	2,400	52	0.3	31
Cl	199	96	7	79
Co	7.13	20	2	71
Cu	118	20	10	79
Dy	2.25	74	3	52
I	5.75	24	200	72
Mn	135	66	0.6	26
Na	2,940	59	0.6	36
Ti	1,350	79	1	19
U	2	0	2	34
V	29	87	1	12

n = 8 (for U, n = 3)

Intra-site survey.

	Concentration (ppm)	CV (%)	EF	CV (%)	n
Al	21,100	68	1	0	6
Ba	215	54	2	23	4
Br	17.3	16	30	61	5
Ca	2,160	32	0.2	33	5
Cl	142	43	8	110	6
Co	4.40	20	0.9	55	4
Cu	*	*	*	*	
Dy	4.50	67	2	7	3
I	5.33	36	200	59	4
Mn	135	76	0.5	11	5
Na	2,850	70	0.5	9	5
Ti	1,575	75	1	10	5
U	1.8	36	2	51	3
V	24	64	1	5	5

Table 4 (cont).

Black snowfall, March 14, 1986.

	Concentration (ppm)	EF
Al	52,300	1
Ba	430	1
Br	110	70
Ca	3,530	0.1
Cl	2,060	20
Co	30	2
Cu	170	5
Dy	9.6	2
I	131	1000
Mn	600	0.9
Na	3,370	0.2
Ti	3,260	1
U	2.8	2
V	142	2
As	47	40
Ce	79	2
Cr	240	4
Eu	1.3	2
Fe	34,600	1
In	1.6	40
La	38	2
Lu	0.3	0.8
Ni	200	4
Rb	44	0.8
Sc	10.5	0.8
Se	14	400
Sm	5.0	1
Ta	1.5	1
Th	7.3	1
Yb	0.5	0.2
Zn	1038	20

The Cl, Na, Mg, SO<sub>4</sub>, and Br ions are within 1-6% of their sea-salt proportions, using Na as the reference element (see discussion in Keene et al, 1986). The intra-site samples have averaged Cl : Na : Mg : SO<sub>4</sub> : Br ratios of 1.02 : 1 : 0.95 : 1.01 : 0.99 : 0.94 (1.00 = standard seawater concentrations; Wilson, 1975). Similarly, the inter-site samples have ratios of 0.97 : 1 : 1.03 : 0.96 : 0.94. This suggests that there is little fractionation of Na, Mg, Cl, SO<sub>4</sub>, and Br during the formation, deposition and dissolution of the aerosol. Br is depleted by 6%, possibly indicating some loss of Br from the original marine aerosol (Raemdonck et al, 1986). In contrast, all other ions are in excess, including Ca (by a factor of 2) and I (by a factor of 60), and are probably derived from the dissolution of terrigenous or anthropogenic aerosol. Cu is enriched in marine aerosol (eg Buat-Menard, 1979), and hence a proportion of the excess Cu could be derived from the dissolution of marine aerosol. The concentrations of Cu, Pb,

Mn and V in the marine snow at each site fall between the median values for rural and remote sites (cf Tables 2 and 3). The range in concentration of particulate material was 1.1 - 2.7 mg/l for the intra-site survey and 1.2 - 3.0 mg/l for the inter-site survey (although one sample contained 14 mg/l). These concentrations are an order of magnitude greater than those found in the Greenland Ice sheet (Davidson et al, 1985). The mean chemical composition and the enrichment factor (hereafter, EF) of 14 elements can be found in Table 4. Some of the variability in concentration may arise from weighing errors and dilution with an Si-rich or a C-rich component. Enrichment factors are derived from the following expression;

$$EF_{i,rm} = (C_{i,p}/C_{rs,p}) / (C_{i,rm}/C_{rs,rm}) \dots\dots(1)$$

where C denotes concentration and the subscripts have the following definitions; i = species of interest, rm = reference material (eg shale or seawater), rs = reference species (eg Al or Na), and p denotes the particulate material. It should be noted that the EFs reported below are for bulk particulate material which are > 0.45 um in diameter.

High EFs (> 10) are found for I, Br and Cu. Cl is also enriched to some extent. Low EFs (< 1) are found for Ca, and perhaps Mn and Na. The lower EF elements co-vary more with Al than with the halogens, and provides support for the hypothesis that at least two types of aerosol are scavenged by the marine snow, local terrestrial aerosol and regional marine aerosol.

Perhaps the most interesting feature of snowfall in the Scottish Highlands is the occurrence of coloured or black snowfall (Davies et al, 1984). This snowfall is acidic, with pH as low as 3, and has a high trace metal content. Such snowfalls occur several times each year, and have a large impact on the chemistry of the snowcover.

In comparison to the relatively unpolluted snows described above, the polluted black snow contains elevated concentrations of all ions, apart from the major seawater ions, Na, Mg and Cl (see Table 1). Normalising to Na, non-seasalt or excess SO<sub>4</sub>, Cl and Br is present, which is diagnostic of anthropogenic emissions (Likens and Bormann, 1974; Kallend et al, 1983; Sturges and Harrison, 1986). The concentrations of Mn and Pb are greater than median values for "urban" sites, while those of Cu and V lie between median values for "rural" and "urban" sites (cf Tables 2 and 3).

The concentration of particulate material was 16 mg/l. Compared to the relatively unpolluted aerosol described above, the EFs for Ba, Ca, Co, Cu, Dy, Na, Ti and U are slightly lower, while only the halogens, Br, Cl and I, and perhaps Mn show any slight increase (see Table 4). At most, the EF values for the same species in marine and polluted snows differ by a factor of approximately 5. Apart from Co and Cu, these elements are predominantly lithophilic in nature (Mason and Moore, 1982). Large variations in EF would not be anticipated, since the

lithophiles are relatively unreactive elements, residing largely in silicate, aluminosilicate or refractory oxide lattices (Goldschmidt, 1954). An anthropogenic or terrestrial origin for the halogens, which are lithophiles, is required to explain their high EF.

The EF of 17 elements not determined in the intra- and inter-site surveys are also shown in Table 4. High EF values are observed for As, In, Se and Zn. All four are chalcophiles (Mason and Moore, 1982), which are elements preferentially incorporated into sulphide phases (Goldschmidt, 1954). Chalcophiles are likely to be concentrated onto particulate material derived from the combustion of fossil fuels or the smelting of sulphides (Raask and Goettz, 1981). Elements with EF near 1 are predominantly lithophiles. Co, Ni, Sc and U may also be enriched in coal ash relative to crustal material (Mason and Moore, 1982). Particulates in the black snow give rise to EF values (normalised to crustal material) of greater than 1 for Co, Ni and U.

#### Variability in the composition of fresh snowfall with altitude.

There is some evidence that snowfall becomes less concentrated with altitude, especially for ions such as sulphate and nitrate (Davies et al, 1987a).

#### Variability in the composition of snowcover.

In addition to any variability in the composition of fresh snowfall, local redistribution of snowcover by wind action must lead to a certain amount of mixing of different snow strata, and give rise to further variability in the composition of snowcover. Imagine mixing sand and cement together. Not all areas of the mixture will contain similar proportions of the constituents. Localised diurnal melting and freezing may also redistribute solute throughout the snowcover in a non-uniform manner. Other processes such as photooxidation and microbial activity may also have local influence on the chemical composition of snowcover.

Wind action may also have a large influence on the composition of the snow cover, by processes other than simple mixing. Sublimation may occur during wind transport which tends to concentrate snow aloft, hence snow in localised deposition sites may be more concentrated than snow at contemporaneous erosional sites (Pomeroy et al, in prep).

#### The chemical composition of snowmelt.

Four distinct types of snowmelt experiments have been performed in order to determine changes in the proportional anionic composition of snow and meltwater during snowmelt; i) controlled laboratory experiments which involved totally melting a snow sample (Brimblecombe et al, 1987; Abrahams et al, 1988), ii) a series of partial melt experiments (Brimblecombe et al, 1986, 1987), iii) controlled melting of artificial ices (Brimblecombe et al, 1987, 1988) and iv) field experiments, where meltwater is collected during periods of thaw (Tranter et al, 1986, 1987b). All types of laboratory experiments demonstrate that different anions fractionate into meltwater to different degrees. The



results of these experiments have been compared with changes in the proportional anionic composition of meltwaters collected from different depths within a snowpack. There is consistency between field and laboratory experiments. Sulphate is always preferentially eluted with respect to chloride, except when chloride concentrations are very high (see below), and the position of nitrate is variable. The general elution sequence is  $SO_4 > NO_3 > Cl$ . Hence, chloride is proportionally enriched in residual, leached snows, while sulphate and nitrate are proportionally enriched in the initial meltwaters (Davies et al, 1987b).

Artificial ices of known composition were melted under laboratory conditions to monitor significant shifts relative ionic composition of meltwaters. Chloride, bromide and iodide tended to be lost from the melting ice more readily than fluoride, which is probably incorporated in the ice grain interior. The presence of ammonium ions causes the fluoride ion to be less readily lost during melting. Hydrogen ions cause fluoride to be lost as readily as the other halides. Sulphate is lost more rapidly than chloride at environmental concentrations ( $< 100 \mu\text{mol/l}$ ), but, at higher concentrations, ( $0.01 \text{ mol/l}$ ) chloride can be lost just as readily as sulphate. The composition of melt water may be described in terms of the mixing of two types of solutions: i) intergranular surficial brines with a high solute concentration, which occupy the ice grain boundaries and ii) relative dilute meltwater derived from the ice grain interiors. Deviations from simple two component behaviour suggest slightly different distributions for the chloride and the sulphate ions in the interfacial region between the brine and the intragranular ice. The melting of such systems has been examined using a simple mathematical model (Brimblecombe et al, 1988).

The chemical composition of meltwaters collected within Ciste Mhearad was modeled by the mixing of two components. The first component is concentrated and may originate from the solute-rich waters held at the crystal surfaces, whereas the second is dilute and possibly originates from the melting of the solute-poor interiors of snow and ice crystals. The proportional ionic composition of the components differ. In general, meltwaters become more dilute as ablation proceeds, and solute near to the surface of the snowpack is rapidly leached. Meltwaters do not necessarily become more concentrated as they percolate through the snowpack. Snowpack hydrology is likely to be a major control on the depth-concentration relationship. The composition of meltwaters from deeper within the snowpack provides some evidence for the preferential elution of acidic solute (H,  $SO_4$  and  $NO_3$ ) with respect to sea salt (Na and Cl). However, changes in the ionic composition of these meltwaters, which are already proportionally enriched in sea salt, brought about by preferential elution are small in comparison to changes in concentration as a result of two component mixing or dilution (Tranter et al, 1988).

#### Changes in streamwater chemistry during snowmelt.

During snowmelt, ions fractionate into the first meltwaters (Johanessen and Henriksen, 1978), giving rise to concentrated,

often acidic, solutions. This may cause transient acidification of streamwaters, the so-called "acid-flush", in poorly-buffered upland catchments, and can give rise to fish kill (Leivstad and Muniz, 1976) or, more commonly, recruitment failure (Gunn and Keller, 1984). The chemistry of snow and meltwater can affect the magnitude and duration of the so-called "acid flush", particularly when stream discharge is not dominated by pre-event water. Such conditions are found in the Scottish Highlands (Morris and Thomas, 1987). In March 1987, two acid flush events with minimum recorded pH of 4.25 and 4.10 respectively were monitored. An acidic black snow (pH 3.4) fell in the 8 day period between the events. The meltwater composition during the first event was influenced by the composition of the existing snowcover, whereas the second event showed the effect of the fall of polluted snow. These observations demonstrate that a single black snowfall can strongly influence the composition of meltwaters and highlights how chance associations of episodic events (coloured snowfall and snowmelt) may amplify acidification of streamwaters (Tranter et al, 1988).

#### Conclusions.

The chemistry of snowfall is unusual, in that periodic falls of highly polluted or black snow occurs. The chemistry of the consequent snowcover is spatially and temporally variable, in part due to the wind action. Meltwaters are proportionally enriched in some ions, particularly sulphate and nitrate with respect to chloride. Since snowmelt may be a dominant contributor to streamwaters during the Spring thaw, streamwater chemistry is influenced by the composition of the snowpack.

#### References.

Abrahams PW, Tranter M, Davies TD, Blackwood I, and Landsberger S. 1988. Trace-element studies in a remote Scottish upland catchment I. Chemical composition of snow and meltwater. *Water, Air and Soil Pollution*, 37, 255-271.

Abrahams PW, Tranter M, Davies TD and Blackwood I 1989. Trace element studies in a remote Scottish upland catchment. 2. Chemical composition of streamwaters. *Water, Air and Soil Pollution*, 43, 231-248.

Brimblecombe P, Tranter M, Tsiouris S, Davies TD and Vincent CE 1986. The chemical evolution of snow and meltwater. In: *Modelling snowmelt-induced processes*, IAHS Publ. 155, 283- 295.

Brimblecombe P, Clegg S, Davies TD, Shooter DS and Tranter, M 1987. Laboratory observations of the preferential loss of major ions from melting snow. *Water Research*, 21, 1279-1286.

Brimblecombe P, Clegg S, Davies TD, Shooter D and Tranter M 1988. The differential loss of halide and sulphate ions from melting ice. *Water Research*, 22, 693-700.

Buat-Menard P 1983. Particle geochemistry in the atmosphere and oceans. In: *Air-Sea Exchange of Gases and Particles* (eds PS Liss and WGN Slinn), NATO ASI Series (D. Reidel, Hingham, Mass.),

455-532.

Davidson CI, Suthanam S, Fortmann RC and Olson MP 1985. Atmospheric transport and deposition of trace elements into the Greenland Ice Sheet. *Atmospheric Environment*, 19, 2065-2081.

Davies TD, Abrahams PW, Tranter M, Blackwood I, Brimblecombe P and Vincent CE 1984. Black acid snow in the remote Scottish Highlands. *Nature*, 312, 58-61.

Davies TD, Brimblecombe P, Tranter M, Abrahams Pw and Blackwood IL 1987a. Chemical composition of snow in the remote Scottish Highlands. In: *Acid deposition processes at high elevation sites*, NATO ARW.

Davies TD, Brimblecombe P, Tranter M, Tsiouris S, Vincent CE, Abrahams PW and Blackwood IL 1987b. The removal of soluble ions from melting snowpacks. In: *The chemical dynamics of seasonal snowcover*, NATO ASI.

Galloway JN, Thornton JD, Norton SA, Volchok HL and McLean RAN 1982. Trace metals in atmospheric deposition: a review and assessment. *Atmospheric Environment*, 16, 1677-1700.

Goldschmidt, VM 1954. *Geochemistry*, 730pp, Claredon Press, Oxford.

Gunn JM and Keller W 1984. Spawning site water chemistry and lake trout (*Salvelinus namaycush*) sac fry survival during spring snowmelt. *Canadian Journal of Fisheries and Aquatic Sciences*, 41, 319-329.

Johannessen M and Henriksen A 1978. Chemistry of snow meltwater. Changes in concentration during melting. *Wat. Resour. Res.*, 14, 615-619.

Jones HG 1985. The chemistry of snow and meltwaters within the mesostructure of a boreal forest snowcover. *Annals of Glaciology*, 7, 161-166.

Jones HG and Sochanska W 1985. The chemical characteristics of snowcover in a northern boreal forest during the spring runoff period. *Annals of Glaciology*, 7, 167-174.

Kallend AS, Clark PA, Cocks AT, Fisher BEA, Glover GM, Marsh ARW, Moore DJ, Sloan SA and Webb AH 1983. The fate of atmospheric emissions along plume trajectories over the North Sea - summary report. EPRI EA-3217, RP1311-1.

Keene WC, Pszenny AAP, Galloway JN and Hawley ME 1986. Sea-salt corrections and interpretation of constituent ratios in marine precipitation. *Journal of Geophysical Research*, 91, D6, 6647-6658.

Landsberger S, Davies TD, Tranter M, Abrahams PW and Drake JJ 1989. The solute and particulate chemistry of background snowfall on the Cairngorm Mountains, Scotland: a comparison with a black acid snowfall. *Atmospheric Environment*, 23, 395-401.

Leivestad H and Muniz IP 1976. Fish kill at low pH in a Norwegian river. *Nature*, 259, 391-392.

Likens GE and Bormann FH 1974. Acid rain: a serious regional environmental problem. *Science*, 184, 1176-1179.

Mason B and Moore CB 1982. *Principles of Geochemistry*, 4th edition, Wiley.

Morris EM and Thomas AG 1985. Preferential discharge of pollutants during snowmelt in Scotland. *J. Glaciology*, 31, 190-193.

Pomeroy JW, Davies TD, Tranter M, Zeman Z, Jones HG, Jones A, Pomeroy DJ and Varley M in prep. Blowing snow measurement techniques: application to the study of snow chemistry in extreme environments. Submitted to *Arctic*.

Raask E and Goetz L 1981. Characteristics of captured ash, chimney solids and trace elements. *Journal of the Institute of Energy*, 54, 163-173.

Raemdonck H, Maenhaut W and Andreae MO 1986. Chemistry of marine aerosol over the tropical and equatorial Pacific. *Journal of Geophysical Research*, 91, D8, 8623-8636.

Sturges WT and Harrison RM 1986. The use of Br/Pb ratios in atmospheric particles to discriminate between vehicular and industrial lead sources in the vicinity of a lead works - I. Thorpe, West Yorkshire. *Atmospheric Environment*, 20, 833-843.

Tranter M, Brimblecombe P, Davies TD, Vincent CE, Abrahams PW and Blackwood I 1986. The composition of snowfall, snowpack and meltwater in the Scottish Highlands - evidence for preferential elution. *Atmospheric Environment*, 20, 517- 525.

Tranter M, Davies TD, Abrahams PW, Blackwood I, Brimblecombe P, and Vincent, CE 1987a. Spatial variability in the chemical composition of snowcover in a small, remote Scottish catchment. *Atmospheric Environment*, 21, 853-862.

Tranter, M, Davies TD, Brimblecombe P, and Vincent, CE 1987b. The composition of acidic meltwater during snowmelt in the Scottish Highlands. *Water, Air and Soil Pollution*, 36, 75-90.

Tranter M, Abrahams PW, Blackwood IL, Brimblecombe P and Davies TD 1988. The impact of a single, black snowfall on streamwater chemistry in the Scottish Highlands. *Nature*, 332, 826-829.

Ward RDW 1980. Avalanche hazard in the Cairngorms Mountains, Scotland. *J. Glaciology*, 26, 31-41.

Ward RGW, Langmuir EDG and Beattie B 1985. Snow profiles and avalanche activity in the Cairngorm Mountains, Scotland. *J. Glaciology*, 31, 18-27.

Wilson TRS 1975. Salinity and the major elements of sea water.

In: Chemical Oceanography, 1 (eds JP Riley and G Skirrow,  
Academic Press, Orlando, Fla.), 365-413.

