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Highlights

Highlights (Cape et al. Long-term trends in rain and cloud chemistry in a region of complex topography)

Cloud and rain water analysis from low and high elevation sites in Pennines, UK

Orographic (seeder-feeder) enhancement of cloud ion concentrations estimated

Long-term (1994-2008) downward trends in non-sea sulfate and nitrate

No trends in cloud:rain scavenging ratios, implying consistent mechanism

Uncertainties in extrapolation to upland UK are quantified

1 Long-term trends in rain and cloud chemistry in a region of complex topography.

2

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9 **Abstract**

10 Rain and cloud water from a high-elevation site and an adjacent lower-level site in the
11 northern Pennines of England were sampled and analysed between 1994 and 2008. The
12 comparison of wet deposition and rainfall depth at the high and low-level sites has been used
13 to estimate the additional deposition of pollutants arising from ‘seeder-feeder’ enhancement
14 by washout of the orographic cap cloud that forms over the high-level site. The derived
15 ‘orographic scavenging ratio’ for different ions is used to map the orographic enhancement of
16 wet deposition across the U.K.. The ratio of ion concentrations in cloud and in rain at the
17 high-level site is also important for estimating the input of pollutants through the direct
18 capture of cloud water droplets at high elevation sites.

19 Long-term trends in ion concentrations in cloud and rain showed significant downward trends
20 in non-sea sulphate, and a weaker downward trend in nitrate, but no trend in other ions. There
21 was also no trend in the orographic scavenging ratios, implying that the methods used to
22 estimate orographic enhancement across the U.K. are robust over time.

23

24

25 **Keywords**

26 Orographic scavenging; seeder-feeder enhancement; cloud deposition; rainfall concentrations

27

28 **1. Introduction**

29 Routine measurements of cloud composition and rainfall composition at high elevation in the
30 U.K. were started in 1993, following a series of intensive field campaigns at Great Dun Fell
31 in the northern Pennines, which showed that not only rainfall amount but also the
32 concentrations of ions in rain increased with altitude, leading to much greater wet deposition
33 of pollutants on western hills than had been expected (Choularton et al., 1988; Fowler et al.,
34 1988). The intensive field campaign measurements of individual rain events also
35 demonstrated the mechanism for these increases, in terms of the ‘seeder-feeder’ effect
36 (Supplement Figure S1). As rain from high-level clouds falls through the atmosphere to low
37 elevation sites, it does not efficiently scavenge the fine (sub-micron) aerosols in the
38 atmosphere, so that rain composition measured at low levels reflects the composition of the
39 high level precipitating cloud. However, as surface air is lifted over a range of hills or
40 mountains, it is cooled, permitting activation of the aerosol particles, which quickly grow to
41 sizes of a hundred micrometres or more in diameter. The hill cap cloud formed in this way
42 has a different chemical composition from the precipitating high-level cloud, which may have
43 formed over the ocean; the cap cloud composition reflects the composition of the inflowing
44 surface air, which may contain a range of pollutants in both gas and particulate form. As the
45 falling rain from the upper cloud passes through the hill cap cloud, the cloud droplets (now

46 much larger than the original aerosol particles) are efficiently scavenged, leading to increased
47 amounts of water deposited, as well as deposition of the material present in the inflowing air.

48 Subsequent field campaigns elsewhere in the U.K. (Snowdon, N W Scotland, central
49 Scotland) (Fowler et al., 1995; Inglis et al., 1995) showed that such ‘seeder-feeder’
50 enhancement occurred wherever an orographic cap cloud formed, and the process was
51 successfully modelled by researchers at UMIST (now University of Manchester) (Dore and
52 Choularton, 1992).

53 The challenge was to use this information to estimate the deposition of acidifying and
54 eutrophying pollutants in all upland areas of the U.K., in order to quantify deposition for
55 comparison with Critical Loads, and in order to calculate a pollutant deposition budget for the
56 U.K. The field campaigns using daily data showed that the average concentration of many
57 ions in the scavenged cloud was approximately twice that in the low-level rain measured
58 nearby – this factor of 2 as an ‘orographic scavenging factor’ has been used routinely in the
59 U.K. for modelling wet deposition to upland areas (Smith and Fowler, 2001). Moreover, the
60 measurements of cloud composition on hill tops showed that concentrations were very much
61 greater than in rain, depending on the proximity of the sampling site to cloud base, where
62 droplets were smallest and concentrations largest. It was recognised that direct capture (by
63 turbulent deposition) of cloud droplets by upland vegetation would therefore comprise an
64 important contribution to total deposition; the cloud:rain concentration factor for modelling
65 direct cloud water deposition (in the absence of rain) was empirically established as a factor
66 of 5.

67 The long-term measurements at Holme Moss in the southern Pennines (north-west England)
68 were established to provide a check on the continuing validity of these parameterisations over
69 time, given that trends in emissions of sulphur and nitrogen-containing pollutants were likely

70 to lead to significant changes in air composition. However, daily measurements were
71 impracticable, and integrated weekly samples were taken. This necessarily reduces the
72 amount of event-based information available for attributing any changes over time to changes
73 in weather patterns (including wind direction), and for assessing directly the impact of
74 ‘seeder-feeder’ scavenging on the composition of high elevation rainfall events. However, the
75 data should provide evidence of any temporal trends in the ‘orographic scavenging factor’.
76 The assumption used to assess the scavenging of pollutants by hill cloud is that the rainfall
77 composition at the nearby lower elevation (and usually upwind) site is characteristic of the
78 rain falling through the hill cap cloud, and that the rain is predominantly from frontal weather
79 systems, with negligible contributions of local convective storms to the small-scale variability
80 of rainfall amount and composition.

81 The measurements at Holme Moss up to 2001 have already been described (Beswick et al.,
82 2003); they showed decreasing sulphate concentrations and deposition, and increasing
83 amounts of cloud water over 8 years. This review takes the period up to the end of 2008, and
84 examines temporal trends in composition and deposition at both the hill and adjacent lower
85 sites (Holme Moss and Wardlow Hay Cop), trends in cloud composition, and in orographic
86 scavenging factors derived from the seeder-feeder analysis. On the basis of the trends in U.K.
87 emissions since 1994, we might expect to see a large decrease in concentration and
88 deposition of sulphate, a smaller decrease in nitrate, a much smaller decrease in ammonium,
89 following the trends in U.K. emissions, and no significant change in sea salts (sodium,
90 chloride, magnesium). For direct cloud water deposition to upland vegetation, we also need to
91 establish whether there has been any trend in the relative concentration of cloud and rain
92 water, and whether a factor of 5 is still appropriate for modelling deposition in cloud water.

93 **2. Methods**

94 2.1. Sites and measurement methods

95 The data described here refer to the site established at Holme Moss, 25 km ENE of the
96 Manchester conurbation (lat. 53.532° N, long. -1.857° E, elevation 525 m), for which the
97 linked low-level site in the UKEAP network (UK Eutrophying and Acidifying Pollutants –
98 see <http://uk-air.defra.gov.uk/networks/network-info?view=ukeap>) is at Wardlow Hay Cop
99 (lat. 53.260° N, long. -1.735° E, elevation 330 m). Holme Moss is 30 km north of Wardlow
100 Hay Cop (Figure 1). The assumption is that the site at Wardlow Hay Cop is outside the
101 influence of the orographic cloud formed at Home Moss, and experiences only ‘seeder’ rain
102 (Supplement Figure S1). At Holme Moss, rain was sampled using a 20 cm diameter high-
103 density polyethylene funnel mounted at a height of 1.5m above ground, feeding into a 20 litre
104 black polypropylene bottle at ground level. The co-located cloud collector was identical, but
105 with the addition of a conical array of PTFE strings mounted above, which collect cloud
106 droplets by interception, with the droplets running down the strings into the collecting funnel
107 (Dollard et al., 1983; Fowler et al., 1988). All items were rinsed with deionised water after
108 each sample was taken. For each weekly sample, the total volume was measured, and a sub-
109 sample of 150 ml taken for ion analysis. The cloud collector samples rain with around 90–
110 95% of the efficiency of the rain collector, based on a comparison of identical collectors
111 logged to an automatic weather station on site, and using the ‘present weather’ sensor to
112 determine cloud-free periods. The ‘cloud’ sample is therefore contaminated by rainwater of a
113 different composition. If the concentration and amount of the rain sample are known, then the
114 concentrations of ions in the ‘cloud’ sample can be used to estimate the actual concentrations
115 in cloud; data presented here refer to the derived ‘cloud-only’ concentration. Additional
116 meteorological instruments provided information on wind speed and direction, rain and cloud
117 water amount (by tipping bucket rain gauge). At Wardlow Hay Cop, rain samples were taken
118 using the U.K. standard bulk rain sampler (UKEAP, 2010); this lower elevation site is seldom

119 in cloud, so no cloud samples were taken. Rain and cloud samples were taken every week at
120 Holme Moss, and until November 2001 at Wardlow Hay Cop, when the regular sampling
121 period for the UKEAP network changed to 2 weeks.

122 **2.2 Chemical analysis**

123 Cloud and rain samples from Holme Moss were analysed at the University of Manchester
124 using ion chromatography for the major cations and anions, conductivity, and pH
125 measurements with appropriate calibration for low ionic strength samples. pH was not
126 measured routinely through the whole period. When analysis of all ions was available, the ion
127 balance of the samples was within 10%. All samples were analysed in duplicate, with
128 agreement on individual samples better than 10%. Non-sea-salt concentrations (e.g. for
129 sulphate) were calculated by assuming that all sodium in the samples originated from sea
130 water. Rain samples from Wardlow Hay Cop were analysed using the protocols and methods
131 of the UKEAP network (ion chromatography, ICP-OES, conductivity, pH) with documented
132 procedures for quality assurance (UKEAP, 2010).

133 **2.3 Quality control for contamination**

134 To compare the chemical composition of rain and cloud water at the two sites, rigorous
135 quality control measures were needed to avoid the inclusion of samples which had been
136 contaminated. Data from the UKEAP site at Wardlow Hay Cop were retrieved from the
137 archive (<http://uk-air.defra.gov.uk>) and checked for consistency, especially with respect to
138 potential contamination as evidenced by concentrations of potassium, which is associated
139 with bird droppings. Samples with very small volumes (< 100 mL) were also discounted.
140 Similar procedures were applied to the rain and cloud composition data measured at the
141 University of Manchester, including comparison of ion balances and measured vs. theoretical
142 conductivity. Periods where the amount of sample from the cloud collector was less than that

143 in the rain collector were also excluded. These quality control measures led to reduced data
144 coverage, but reduced the risk of contaminated samples causing bias in the subsequent data
145 analysis. Because of the requirement to compare like with like, periods for which data were
146 not available (or excluded) at either of the sites were removed from the datasets prior to
147 statistical analysis and calculation of relative concentrations and deposition. The effects of
148 the quality control measures are seen in Table 1, which shows for each year the % of the
149 measured rain or cloud volume sampled that was included in the subsequent analysis. With
150 the exception of 1995, removal of contaminated samples made only a small difference to the
151 annual volume of precipitation or cloud water used in the analysis below.

152 **3. Results**

153 **3.1 Rain and cloud water amounts**

154 The amount of rain and cloud collected has consequences for the concentrations of ions in the
155 samples averaged over long periods. In general, the greater the rainfall amount, the more
156 dilute the samples are likely to be to be; raindrops will on average have passed through a
157 greater thickness of cloud, thereby enhancing their volume, but scavenging larger and more
158 dilute cloud droplets. Rainfall amounts used for deposition calculations are derived from the
159 tipping-bucket collector at ground level.

160 The data in Figure 2 show that the difference in recorded precipitation amount between
161 Wardlow Hay Cop and Holme Moss varies greatly from year to year, and is not directly
162 related to the amount of cloud water sampled at Holme Moss. The difference in precipitation
163 amount reflects the average depth and water content of the cap cloud scavenged by falling
164 rain, whereas the cloud volume collected reflects the water content and amount (frequency)
165 of cloud at the sampling site. For example, in 2004 although the amount of additional
166 precipitation recorded at Holme Moss was relatively small, the amount of cloud water

167 collected was large, implying greater frequency and water content of cloud at Holme Moss in
168 2004 despite the lack of rainfall. In 2003, the ratio of rainfall amount at Holme Moss relative
169 to Wardlow Hay Cop was small, implying very few ‘seeder-feeder’ cloud events in that very
170 dry year.

171 Over the entire period there was no obvious trend in rain or cloud amount at either site. The
172 apparent trend from 1994 to 2001 (Beswick et al., 2003) was not sustained in subsequent
173 years. The ‘orographic enhancement factor’, i.e. the ratio of rain amount at Holme Moss
174 relative to Wardlow Hay Cop, also showed no overall trend, with an average over the 15
175 years of 2.9 (± 0.9).

176 **3.2 Trends in wind direction, climate etc.**

177 The concentration of ions in individual samples depends on the source of the air flowing over
178 Holme Moss, with some directions expected to be associated with higher levels of pollutants
179 as a result of the geographical location of major pollutant sources such as heavy industry and
180 power generation. Over longer periods, the volume-averaged concentrations will be heavily
181 influenced by the prevailing wind direction.

182 At Holme Moss, the prevailing wind direction is from the south-west. Between the periods
183 1996-9 and 2006-9 there was a shift towards a greater proportion of the air arriving at Holme
184 Moss having come from the south-west, increasing from 55 to 65% of all 1 hour data (Figure
185 1). There was also a narrowing and shifting of the north-eastern lobe of the wind direction
186 frequency distribution. There were clear maxima in the distribution of wind speed as a
187 function of wind direction (Supplement Figure S2), with a major peak in the S to W sector,
188 and a secondary peak in the NNE to E sector. These peaks became noticeably better defined
189 over the measurement period, with mean wind speeds across all sectors increasing
190 significantly, from 6 to 8 m s⁻¹ (Supplement Figure S3). These measurements suggest that

191 there were changes in the prevailing weather conditions at the site over the period, with
192 unspecified effects on the ion concentrations observed.

193 **3.3 Trends in rainfall composition (high level and low level)**

194 The trends in concentration in rain at Wardlow Hay Cop and Holme Moss are shown as the
195 annual rainfall-weighted concentrations for each of the major ions in Figure 3. These data are
196 derived from the quality-controlled data set and are matched between the two sites to avoid
197 any bias caused by omitting a sampling period from one site and not the other. The weekly
198 sampling periods do not match exactly, but the best estimate of temporal matching has been
199 used in creating the quality-controlled datasets.

200 The trends show a small decline in concentrations of nitrate at both sites, with no systematic
201 difference between the sites. By contrast, there is a marked decrease in non-marine sulphate
202 over the period, by a factor of 4, and with concentrations on average slightly higher at Holme
203 Moss. There is very little trend in ammonium concentrations; there is a particularly high
204 value at Holme Moss in 2003, which was a very dry year. Concentrations at Wardlow Hay
205 Cop are less variable from year to year and show a small downward trend. Concentrations of
206 sodium show no strong trend, although concentrations at Holme Moss from 1996 to 2007
207 were higher than the years immediately before and after. At Wardlow Hay Cop
208 concentrations were more stable. The non-marine calcium concentrations are fairly stable at
209 Holme Moss, but show a large step change at Wardlow Hay Cop in 2000. This large change
210 has been seen at other sites in the U.K. network, and was caused by a change in analytical
211 method for cations in the laboratory analysing the samples (Hayman et al., 2001).

212 **3.4 Trends in cloud composition**

213 The annual volume-weighted concentrations in cloud water sampled at Holme Moss are
214 compared with the concentrations in rain in Figure 4. No significant trends in cloud water

215 concentrations are obvious, with the exception of non-marine sulphate, which decreases
216 through the period. The pattern of a decrease in concentrations of other ions before 2003-4
217 followed by an increase is most easily explained by changes in the volume of cloud water
218 sampled, which showed the opposite pattern (Figure 2).

219 **3.5 Trends in cloud:rain concentration ratios**

220 The current modelling approach for estimating the direct deposition of ions in cloud water to
221 the surface assumes that the ratio of concentrations in cloud to concentrations in rain is a
222 uniform factor of 5, based on earlier studies. Figure 5 shows that this is a reasonable
223 approximation for all ions, although for some ions such as nitrate the measured ratio is
224 somewhat greater (average 7.6) and for non-marine calcium it is somewhat lower (average
225 3.6). There is some variation in this ratio between years, but no clear trend over the period for
226 any of the ions measured.

227 **3.6 Trends in rainfall deposition**

228 Long-term trends in concentration in rainfall (Figure 3) may be masked by variations in
229 rainfall amount from year to year. The annual deposition in rain (the product of average
230 concentration and rainfall amount) at Holme Moss and Wardlow Hay Cop is shown in Figure
231 6. The very dry year of 2003 (see Figure 2) is particularly obvious at Holme Moss; the data
232 for 1995 have been omitted because of the poor data capture that year (see Table 1). The
233 downward trends in non-marine sulphate are apparent at both sites ($-5.8\% \text{ yr}^{-1}$ at Holme
234 Moss, $-7.0\% \text{ yr}^{-1}$ at Wardlow Hay Cop), but there are no significant trends in any of the other
235 components except for a downward trend in nitrate at Wardlow Hay Cop, of $-2.3\% \text{ yr}^{-1}$. For
236 all ions, deposition is greater at Holme Moss than at Wardlow Hay Cop (with the exception
237 of calcium before 2000, which is related to analytical problems – see above). The difference
238 between deposition at Holme Moss and Wardlow Hay Cop represents the additional material
239 scavenged by falling rain from the cap cloud – the ‘seeder-feeder’ enhancement. The average

240 concentration of the scavenged cloud water (Figure 7) is calculated from the difference in
241 deposition and the difference in the amount of rain between the two sites. The ratio of this
242 concentration to the concentration in rain at the low-level site (Wardlow Hay Cop) is used in
243 modelling orographic enhancement, and is referred to as the orographic scavenging factor.
244 Note that the concentrations of ions scavenged from cloud represent the average throughout
245 the total depth of the cloud, as opposed to the measured concentrations at ground level, which
246 are made much closer to cloud base, with smaller droplets, and therefore have larger values.

247 **3.7 Trends in orographic scavenging factors**

248 The orographic scavenging factor used in mapping deposition across the U.K.(2 for all ions)
249 was based on the earlier event-based measurements of orographic enhancement at several
250 sites in the U.K.. At Holme Moss, this value is not supported by the weekly integrated
251 measurements (Figure 8); for nitrate, non-marine sulphate and calcium the value is closer to
252 1, as is also the case for ammonium if the anomalous value for 2003 is omitted. For sea salts
253 the orographic scavenging factor is larger, with an average of 3.6 for sodium. There have
254 been no trends in the ratios throughout the period, but large variation from year to year.

255 **4. Discussion**

256 **4.1 Trends in weather patterns**

257 The wind direction data reported here suggest no clear temporal trend in weather patterns
258 throughout the period, even though some characteristics appear to be significantly different
259 between the early and late part of the study period. There is much greater year-to-year
260 variability in rainfall amount at Holme Moss compared with Wardlow Hay Cop, which is
261 directly related to the frequency, depth and water content of the hill cap cloud. Even here, no
262 clear relationships emerge; the driest year in terms of rainfall (2003) gave higher-than-
263 average capture of hill cloud at Holme Moss, implying greater frequency of occurrence,

264 greater water content, higher wind speeds, or some combination of these three factors. That
265 year also showed anomalous behaviour in orographic scavenging factors, particularly for
266 ammonium and nitrate ions, with very low concentrations of nitrate, and high concentrations
267 of ammonium, in the scavenged cloud (Figure 7).

268 **4.2 Individual ions - nitrate**

269 There was a weak downward trend in nitrate concentrations in rain at both sites, but not in
270 cloud concentration. There was a weak downward trend in wet deposition only at Wardlow
271 Hay Cop. This observation contrasts with the ca. 40% decrease in oxidised N emissions in the
272 U.K. over the same period, but reflects the general pattern across the country of only small
273 changes in nitrate concentrations in rainfall from 1994 to 2008 (RoTAP, 2012).

274 Perhaps more surprising is the rather small and highly variable values obtained for the
275 orographic scavenging factor, with values as small as zero in 2003. This observation suggests
276 that some of the assumptions made in using an orographic scavenging factor are not valid. In
277 order for the simple seeder-feeder model to work, it has to be assumed that all the
278 contributory ions are in the particle phase, and therefore are not scavenged efficiently by
279 falling rain drops. However, for nitrate (and to a lesser extent for other ions) a significant
280 proportion of the soluble nitrate may be in the gas phase, as nitric acid. Under such
281 conditions, because of nitric acid's high solubility in water, rain falling upwind of the hill cap
282 cloud would be expected to scavenge efficiently the gas-phase nitric acid, which would be
283 deposited as nitrate at the 'low-level' site. The air mass would therefore be depleted of nitric
284 acid before entering cloud and activation of the aerosol. Moreover, higher concentrations of
285 gas-phase nitric acid at the lower elevation site would lead to enhanced dry deposition to the
286 bulk collector used to sample rainfall, providing a positive bias in the amount of nitrate
287 sampled (Gonzalez-Benitez et al., 2009).

288 The orographic scavenging factor (as applied strictly to aerosol particles) would therefore be
289 underestimated, because the low-level rain composition would have been enhanced by the
290 solution of nitric acid, and the scavenged cloud deposition would have been depleted by
291 removal of the nitric acid. Expressing this algebraically:

$$\begin{aligned} 292 \text{ Orographic scavenging factor} &= \frac{(\text{deposition at hill top} - \text{deposition upwind})}{(293 \text{ rain volume at hill top} - \text{rain volume upwind})} \end{aligned}$$

294

295 Deposition at the hill top

$$296 = (\text{volume rain} * \text{rain concentration} + \text{volume scavenged cloud} * \text{cloud concentration})$$

$$297 = (\text{volume rain} * \text{rain concentration} + \text{amount of aerosol scavenged})$$

298 Deposition upwind

$$299 = (\text{volume rain} * \text{rain concentration} + \text{amount of gas scavenged})$$

300

301 If the amount of gas scavenged upwind is equal to the amount of aerosol scavenged in the cap
302 cloud, then the orographic scavenging factor is zero.

303

304 In this case, an orographic scavenging factor of zero implies that there was approximately the
305 same quantity of nitric acid in the gas phase upwind of the cloud as there was of nitrate
306 aerosol entering the cap cloud. At normal U.K. temperatures, the balance between gas and
307 aerosol phase is strongly in favour of the aerosol phase, with 'nitrate' existing mostly as
308 ammonium nitrate. Under conditions of high temperature, the equilibrium is pushed towards
309 the gas phase – possibly accounting for the rather low orographic scavenging factor observed
310 in 2003, despite the high orographic scavenging factors for ammonium observed that year,
311 which implies that most of the ammonium was present as particles rather than as ammonia
312 gas. Looking at the relative amounts of ammonium and other ions, in all years except 2003,

313 and for both Holme Moss and Wardlow Hay Cop, the ratio of ammonium to the sum of
314 nitrate and non-marine sulphate (as ion equivalents) was much less than unity, with the ion
315 balance largely made up by non-marine calcium. However in 2003 and in 2008 there was an
316 excess of ammonium measured in rain at Holme Moss – presumably the ion balance was
317 maintained by organic anions and/or bicarbonate. This also suggests that there may have been
318 additional (local) sources of ammonia gas in these years at Holme Moss that did not influence
319 rainfall composition at Wardlow Hay Cop.

320

321 **4.3 Non-marine sulphate**

322 There was a significant decrease in non-marine sulphate in all the sampled rain and cloud at
323 both sites, responding to the 90% reduction in U.K. emissions of sulphur dioxide over the
324 period. The orographic scavenging factor occasionally falls below unity, implying a
325 contribution from gas-phase sulphur dioxide, as for nitric acid in the case of nitrate. However,
326 SO₂ is much less water-soluble than nitric acid, and so is less likely to be scavenged
327 efficiently by falling rain, and less likely to affect the orographic scavenging factor.

328 **4.4 Ammonium**

329 There were no significant trends in ammonium concentration or deposition throughout the
330 period, reflecting the relatively small change in U.K. emissions. The orographic scavenging
331 factor was around unity with the exception of 2003, as noted above, again suggesting gas-
332 phase scavenging of ammonia by falling rain. Because of the widespread agricultural sources
333 of ammonia and its rapid removal from the atmosphere by wet and dry deposition, there is the
334 potential for a contribution from ammonia gas at one site from sources that do not contribute
335 to concentrations and deposition at the other, thereby invalidating the assumptions of the
336 seeder-feeder modelling approach.

337 **4.5 Sea salts**

338 These ions, represented in the figures by sodium, have no gas-phase contribution and
339 therefore act as ‘ideal’ tests of the seeder-feeder model. The orographic scavenging factor
340 (Figure 8) is much higher than for the other ions, at an average of 3.6. No temporal trends
341 were observed, although there was large year-to-year variation.

342 **4.6 Non-marine calcium**

343 The source of non-marine calcium is presumably re-suspended dust from agricultural or
344 mining activity, and is likely therefore to be in the larger (super-micron) particle sizes, and
345 consequently more local in character. Also, as for ammonia, there may be localised sources
346 that contribute differently to deposition at the two sites, making it difficult to match the
347 assumptions necessary for operation of the seeder-feeder model. The average value of the
348 orographic scavenging factor is much smaller than that for sodium, and given that there are
349 no gaseous sources of calcium it would appear that different local sources are contributing to
350 the two sites, in contrast to the sodium ions, which come from long-range transport of sea-salt
351 particles. From 2000 onwards, after the initial analytical problems with calcium
352 concentrations at Wardlow Hay Cop, concentrations and deposition were fairly stable at
353 Wardlow Hay Cop, but varied greatly at Holme Moss, implying varying amounts of input to
354 the cap cloud between years, either from changes in wind direction and wind speed, or
355 changes in activities leading to resuspension of calcium-containing particles.

356

357 **4.7 Mapping of seeder-feeder enhancement**

358 The method for mapping the seeder-feeder enhancement of wet deposition across the U.K.
359 (the CBED model, Smith & Fowler, 2001) is illustrated in Figure 9. From the UKEAP
360 monitoring network, the average annual concentration of ions is established (by kriging or
361 interpolation) across the country, using the data from the low-level monitoring sites. The

362 amounts of rainfall are similarly established for low elevations at the west and east coast,
363 using modelled data at 5 km resolution from the U.K. Meteorological Office. For an upland
364 area in the centre of the U.K. the expected ‘low-level’ rainfall quantity and concentration are
365 calculated based on the interpolated/modelled data. The additional rainfall amount predicted
366 for the high elevation from the 5 km estimates is then taken to represent the volume of cloud
367 water scavenged at the high elevation, and the concentration of this scavenged cloud water is
368 set as twice the expected concentration for low-level rain at the site (i.e. the orographic
369 scavenging factor is taken as a factor of 2). The total additional wet deposition at the high
370 elevation is then calculated as the product of the additional scavenged cloud water and its
371 concentration, added to the predicted low-level deposition at that geographical location.

372 This method of calculation is used for all the maps of wet deposition used in the U.K. for
373 Critical Load assessments (<http://cldm.defra.gov.uk/>), and drives the exceedance of Critical
374 Loads in many upland areas of the U.K., but has little influence on wet deposition in lower-
375 lying areas, and has a small impact on the overall U.K. deposition budget.

376 **4.8 Relationship to previous long-term studies of cloud composition**

377 This study is unique in providing data on precipitation and cloud chemical composition
378 throughout the whole year, and over a period of many years during which the methods did
379 not change. Earlier studies in the U.K., in mid-Wales, showed overall decreases in cloud
380 water concentrations of major ions between 1990 and 2000, particularly at the end of the
381 period (Neal et al., 2001), but rainfall composition measurements were not co-located, so
382 direct comparison of cloud and rain composition is not possible. In the United States there
383 have been several long-term studies of cloud and rain composition at high elevation sites.
384 However, all of these are restricted to the warm season (normally June to September) and the
385 cloud composition data refer only to non-precipitating cloud, i.e. omitting periods during

386 rainfall (Aleksic et al., 2009; Anderson et al., 2006), so cannot be used to quantify
387 relationships between cloud and rain composition. One long-term study, although restricted
388 to the growing season, does provide direct comparison of cloud and rain composition over
389 several years (Murray et al., 2013) at Mount Washington, NH. The data show small temporal
390 trends, with the most significant observation an increase in ammonium:sulphate ratios
391 between 1996 and 2010. However, rainfall composition at this high elevation site appears not
392 to be strongly influenced by orographic enhancement, because the rainfall composition is
393 very similar to that at Hubbard Brook, a low elevation site some 47 km distant.

394

395 **5. Uncertainty analysis**

396 The assumptions of the seeder-feeder model in estimating deposition of ions at high altitudes
397 lead to uncertainty in the use of simple ratios for estimating direct deposition of cloud water,
398 and the orographic enhancement of wet deposition. In order to put these uncertainties into
399 context, the wet and dry deposition of different ions across the U.K. have been calculated for
400 the years 2000 to 2008 inclusive, using a range of different values for the parameters used in
401 estimating direct cloud deposition and orographic enhancement.

402 The simplest analysis is for sodium, which (as it is always in the particulate phase) conforms
403 most closely to the seeder-feeder assumptions. The average orographic scavenging factor at
404 Holme Moss (Figure 8) is 3.6, somewhat greater than the default value of 2 used in the
405 CBED model (Smith and Fowler, 2001) for all ions. Although we have no data on the spatial
406 variation of this ratio for sodium across the U.K., this difference in orographic scavenging
407 factor would make a 30% difference to annual wet-deposited sodium if it applied at all sites.
408 For other ions, as seen in Figure 8, the measured orographic scavenging factors at Holme
409 Moss are smaller than those for sodium, reflecting deficiencies in the simple seeder-feeder
410 model that ignore gas-phase constituents (section 4.2 above), so that a value for the

411 orographic scavenging factor for these ions which is smaller than that for sodium is likely to
412 be more appropriate (i.e. 2 rather than 3.6).

413 At Holme Moss the average orographic scavenging factor for sulphate is close to 1,
414 suggesting that if that value is appropriate elsewhere, overall U.K. deposition of S may be
415 overestimated by around 15% by the default parameter, which is well within the year-to-year
416 variation in S deposition (Supplement Figure S4). This is likely to be a ‘worst-case’ estimate,
417 however, because the upland areas of the U.K. where orographic enhancement is important
418 are remote from sources of gaseous pollutants (NH_3 , SO_2 , HNO_3), and air concentrations
419 contributing to the composition of orographic cloud are dominated by secondary aerosols
420 (NH_4^+ , SO_4^{2-} , NO_3^-), with a much smaller relative contribution from gases than at Holme
421 Moss, which is surrounded by urban areas. Under these conditions, the assumptions of the
422 ‘seeder-feeder’ mechanism are more closely met.

423 Similarly, for total N deposition, the use of an overall orographic scavenging factor of 2 (the
424 default) rather than 1 (as observed at Holme Moss) may lead to an overestimate of annual N
425 deposition to the U.K. of up to 12%, also within the year-to-year uncertainty.

426 By contrast, the effect on the direct capture of cloud water of changing the ratio of cloud
427 concentration to rainfall (default 5), is minimal (<0.3% for a change from a factor of 5 to a
428 factor of 1) both for U.K. deposition and for Critical Load exceedance, because the absolute
429 deposition from this pathway is small.

430 **6. Conclusions**

431 Long-term monitoring of rain and cloud at Holme Moss from 1994 to 2008 has shown strong
432 downward trends only in non-marine sulphate concentrations. Trends in nitrate concentration
433 are weakly downward, despite the large decrease in NO_x emissions in the U.K. over the

434 period. This behaviour is similar to that seen in the U.K. rainfall network. There was no trend
435 in sea-salt concentrations over the period, but there was large year-to-year variability,
436 emphasising the need to collect data over many years before drawing conclusions about
437 temporal trends.

438 Rainfall and cloud amounts showed no overall trend, although amounts were largest in the
439 period 1998-2002. There was some evidence of a shift in wind direction at the site, with
440 increasing wind speeds from the south-west; this shift in direction may have affected patterns
441 of concentration and deposition, because of the varied sources of pollutant emissions close to
442 Holme Moss and further afield. This makes the interpretation of temporal trends in
443 concentration and deposition more difficult, especially with the use of time-integrated (two-
444 weekly) sampling, which combines rainfall events from different types of weather system and
445 wind directions.

446 The main purpose of the long-term monitoring of rain and cloud was to confirm the lack of
447 any long-term trend in the parameters used to estimate direct cloud deposition and orographic
448 enhancement of wet deposition over the U.K.. Although year-to-year variation is substantial,
449 the data from Holme Moss show no evidence of either a temporal trend, or a need to change
450 the default factors in the deposition model, despite the large temporal trends in concentration
451 and deposition for non-marine sulphate. Although direct cloud deposition may be locally
452 important, it makes a very small contribution to the U.K. budget, and even to estimates of
453 Critical Load exceedance. For orographic enhancement, the seeder-feeder model assumes that
454 enhancement of hill cap cloud concentrations arises from the activation and capture of
455 particulate material in cloud droplets that is not removed from the atmosphere by falling rain
456 upwind of the hill. This assumption is only met for material which exists only in the aerosol
457 phase, such as sea-salts. At Holme Moss the average orographic scavenging factor for
458 sodium, i.e. the ratio of the concentration of sodium in scavenged cloud to that in rainfall at

459 the nearby 'low-level' site of Wardlow Hay Cop, was 3.6, which is approximately twice the
460 default value of 2 used for all ions for calculating orographic enhancement across the U.K..
461 This means that the current model underestimates seeder-feeder enhancement of sea salts at
462 this site, and presumably also over the U.K. as a whole.

463 For pollutant-derived ions (sulphate, nitrate and ammonium) the assumptions of the seeder-
464 feeder model are not met in that some contribution from gas-phase species is to be expected.
465 If the gas-phase is not efficiently scavenged by falling rain then the effect on the seeder-
466 feeder calculation will be small, provided that there is no significant difference between gas-
467 phase concentrations at low and high-level sites. However, if there is a significant gas-phase
468 contribution to solutes at the low-level site, and systematically lower concentration in the gas-
469 phase at the elevated site, the orographic scavenging factor will be smaller than that observed
470 for sea-salts. This is clearly demonstrated in the data from Holme Moss, with the orographic
471 scavenging factors for non-sea sulphate, nitrate and ammonium close to 1, rather than the
472 default value of 2. It appears that at this site the presence of gas phase sulphur and nitrogen
473 compounds (SO_2 , NH_3 and HNO_3) has substantially reduced the measured orographic
474 scavenging factors, and that the sea-salt data provide a better test of the U.K. orographic
475 scavenging model.

476 In terms of potential bias in calculating U.K. budgets and Critical Load exceedances, the
477 likely maximum difference in the orographic scavenging ratio between the measurements and
478 the model contributes a relatively small uncertainty, well within the year-to-year variability.
479 However, this remains an uncertainty for the current model, because the orographic
480 scavenging factor is only measured at one site. Moreover, the location of Holme Moss, close
481 to some of the higher concentrations of gas-phase pollution in the U.K., suggests that the
482 contribution from gas-phase species is probably much greater here than at sites in the north-
483 west of Scotland, north Wales and the Lake District where orographic enhancement is

484 important. Consequently, the default factor of 2 used for the orographic scavenging factor
485 may still be appropriate over much of the northern and western uplands of the U.K.

486 The long-term data allow us to generalise about processes operating at the site without too
487 much emphasis on the year-to-year variability. Consequently, the problems with the seeder-
488 feeder assumptions can be investigated. The deviation caused by the presence of gas-phase
489 species is seen to dominate the value of the orographic scavenging factor at a site where gas-
490 phase concentrations are likely to be relatively large.

491

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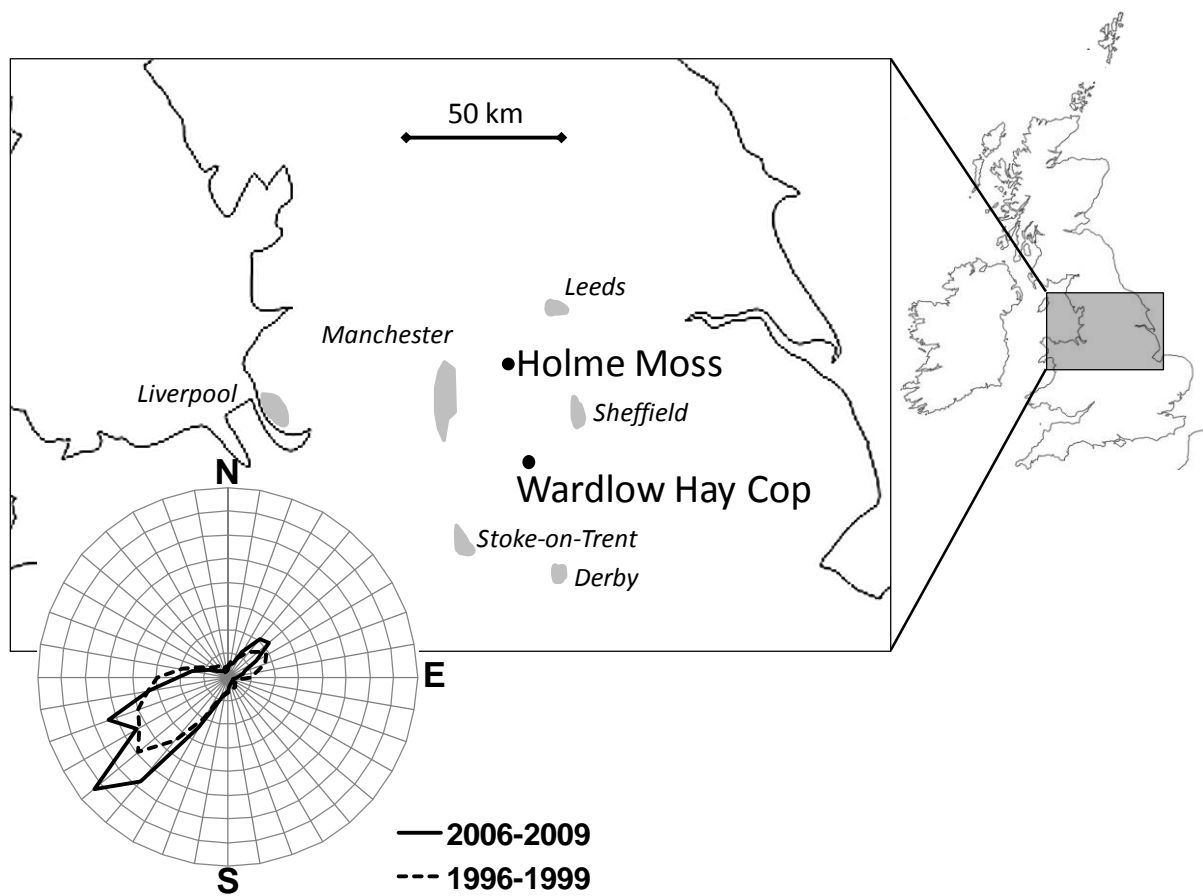


Figure 1. Location of the measurement sites in relation to major conurbations. The inset wind rose shows the average relative frequency of wind direction in 1996-1999 and 2006-2009 at Holme Moss.

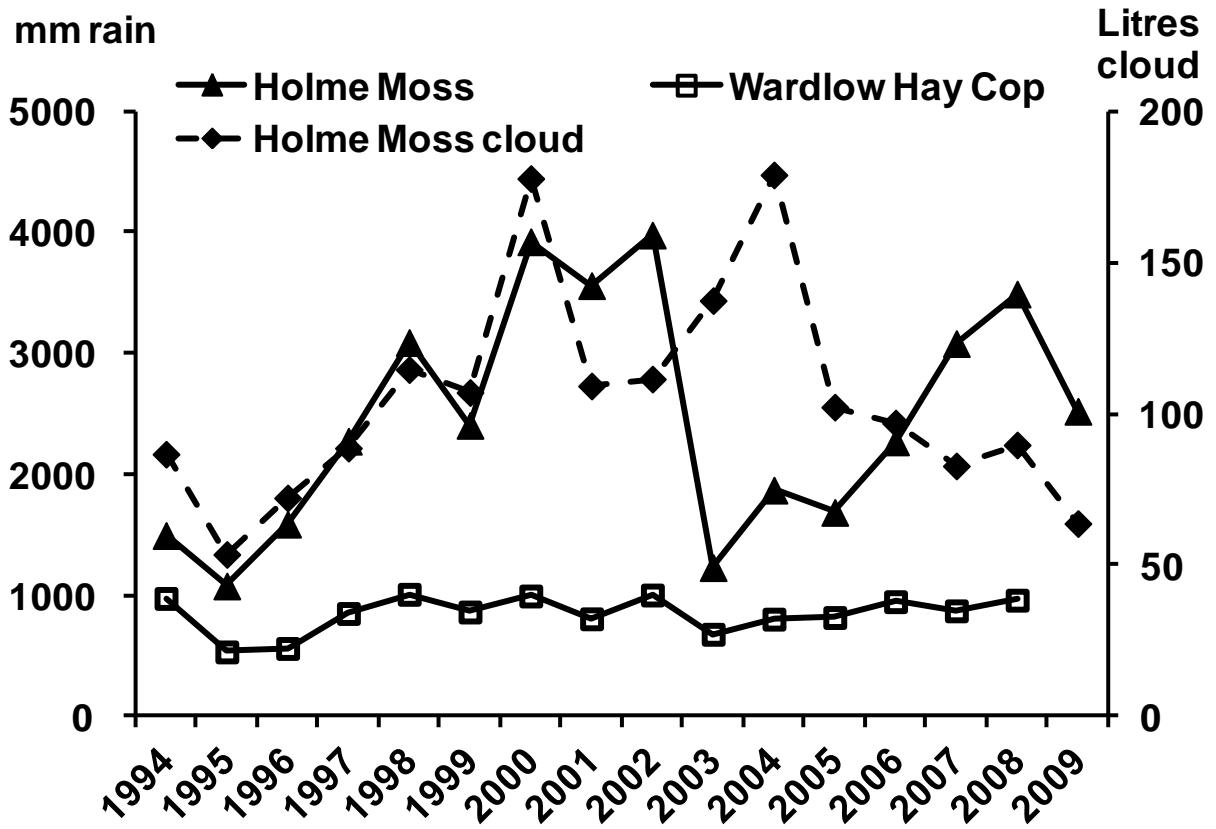


Figure 2. Rainfall amount measured at Wardlow Hay Cop and Holme Moss (LH axis), and volume of cloud water sampled at Holme Moss (RH axis), corrected for rainfall sampled by the cloud collector.

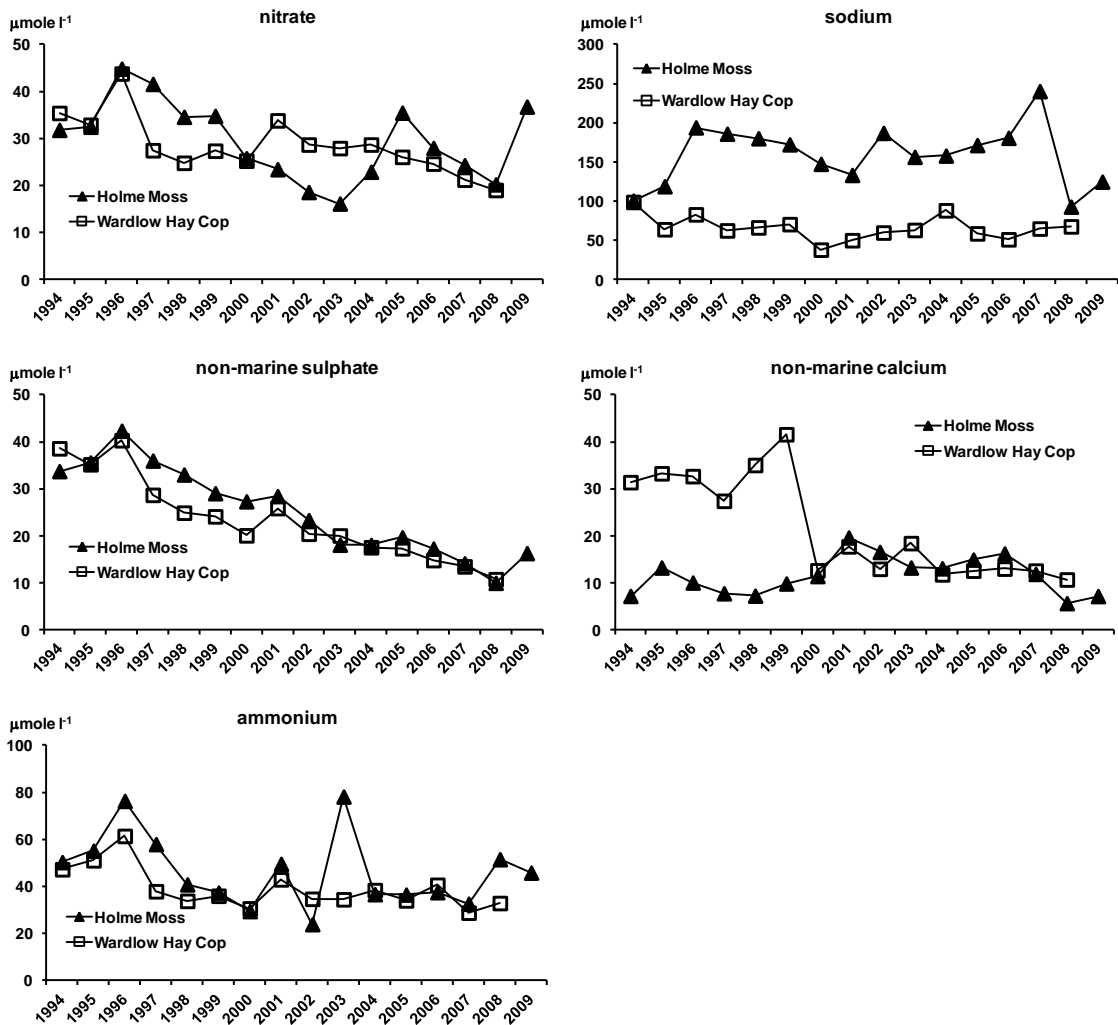


Figure 3. Trends in annual volume-weighted concentrations of major ions in rain at Holme Moss and Wardlow Hay Cop, based on matched samples. Note that the method for measuring Ca concentrations at Wardlow Hay Cop changed in 2000.

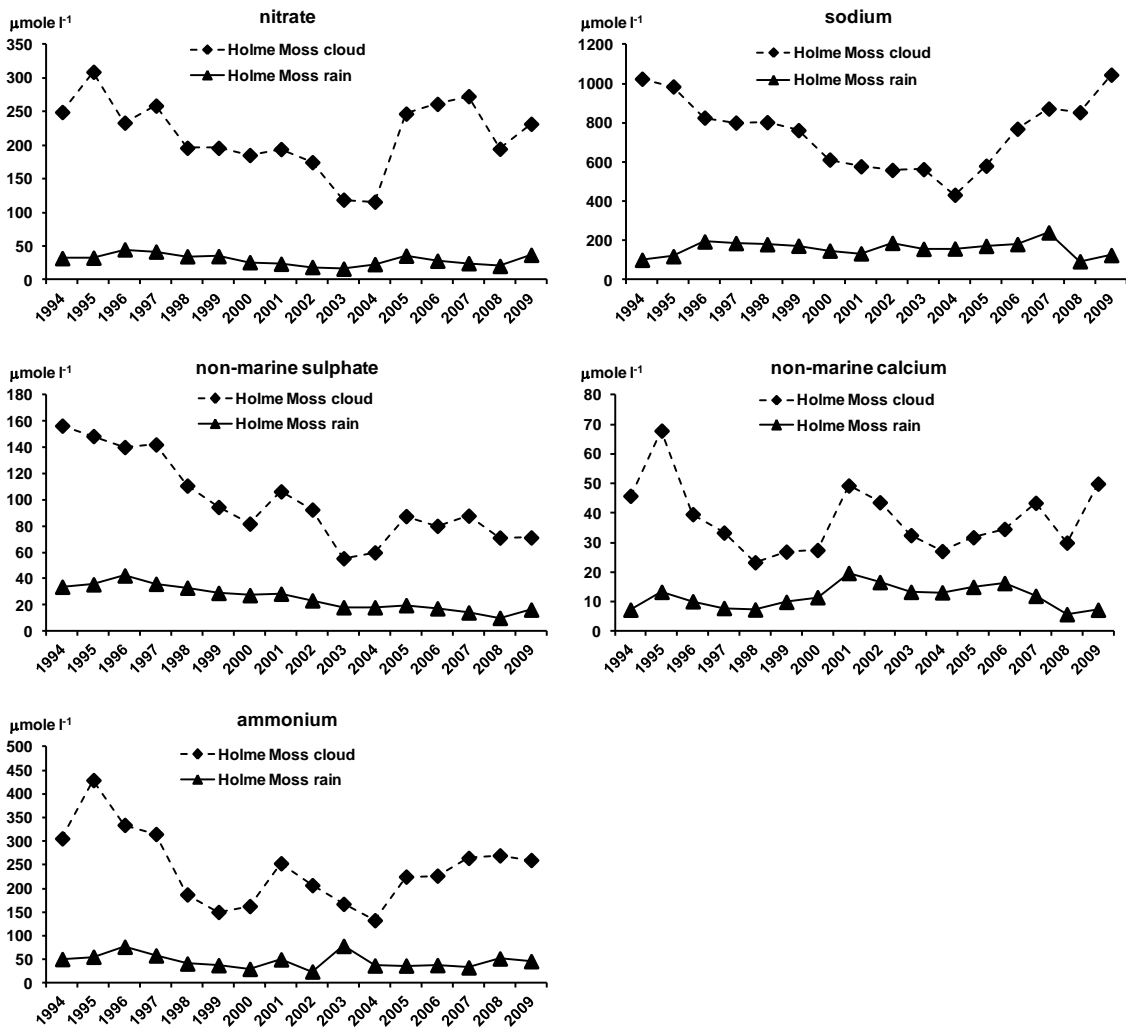


Figure 4. Trends in annual volume-weighted concentrations of major ions in cloud and rain at Holme Moss, based on matched samples

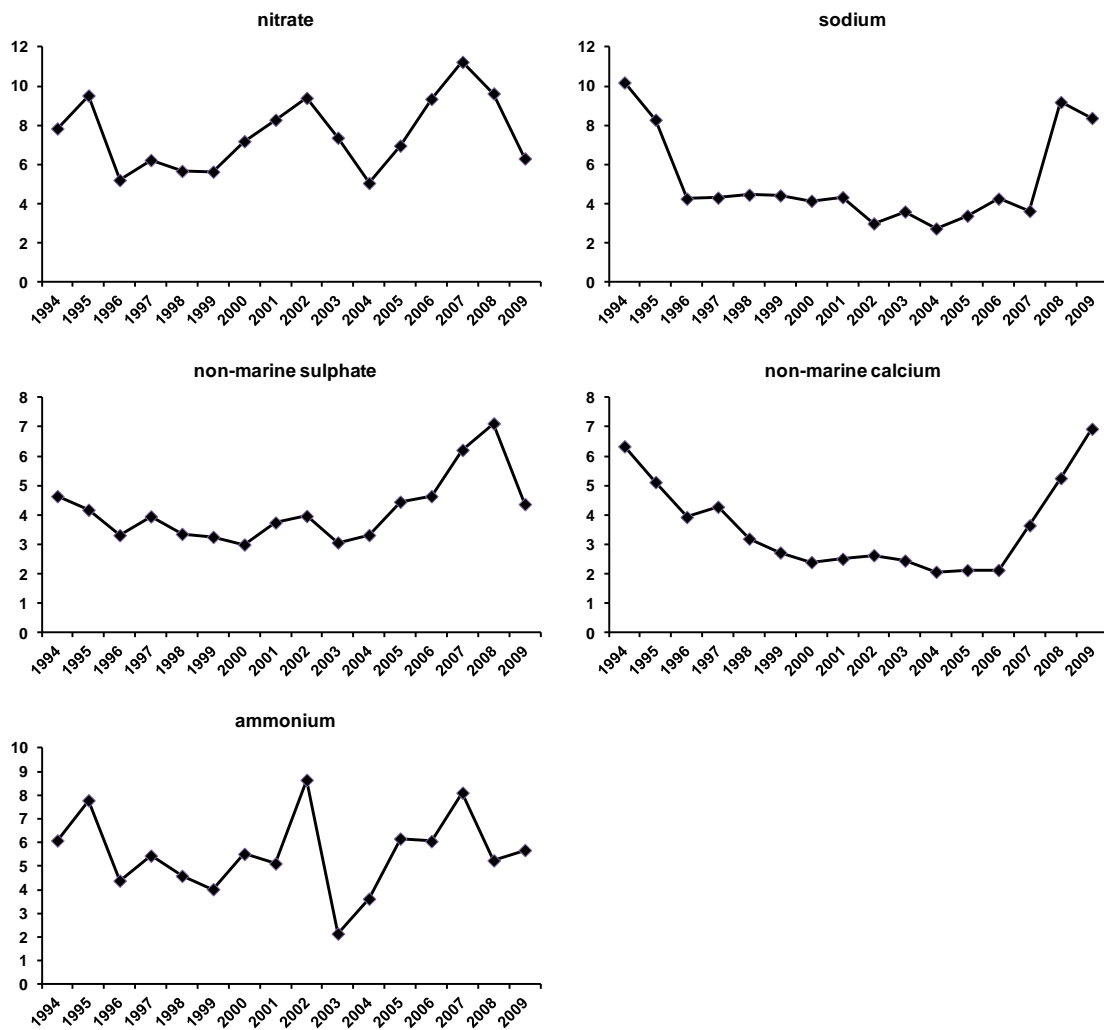


Figure 5. Ratio of average concentrations of ions in cloud water to concentrations in rain water at Holme Moss.

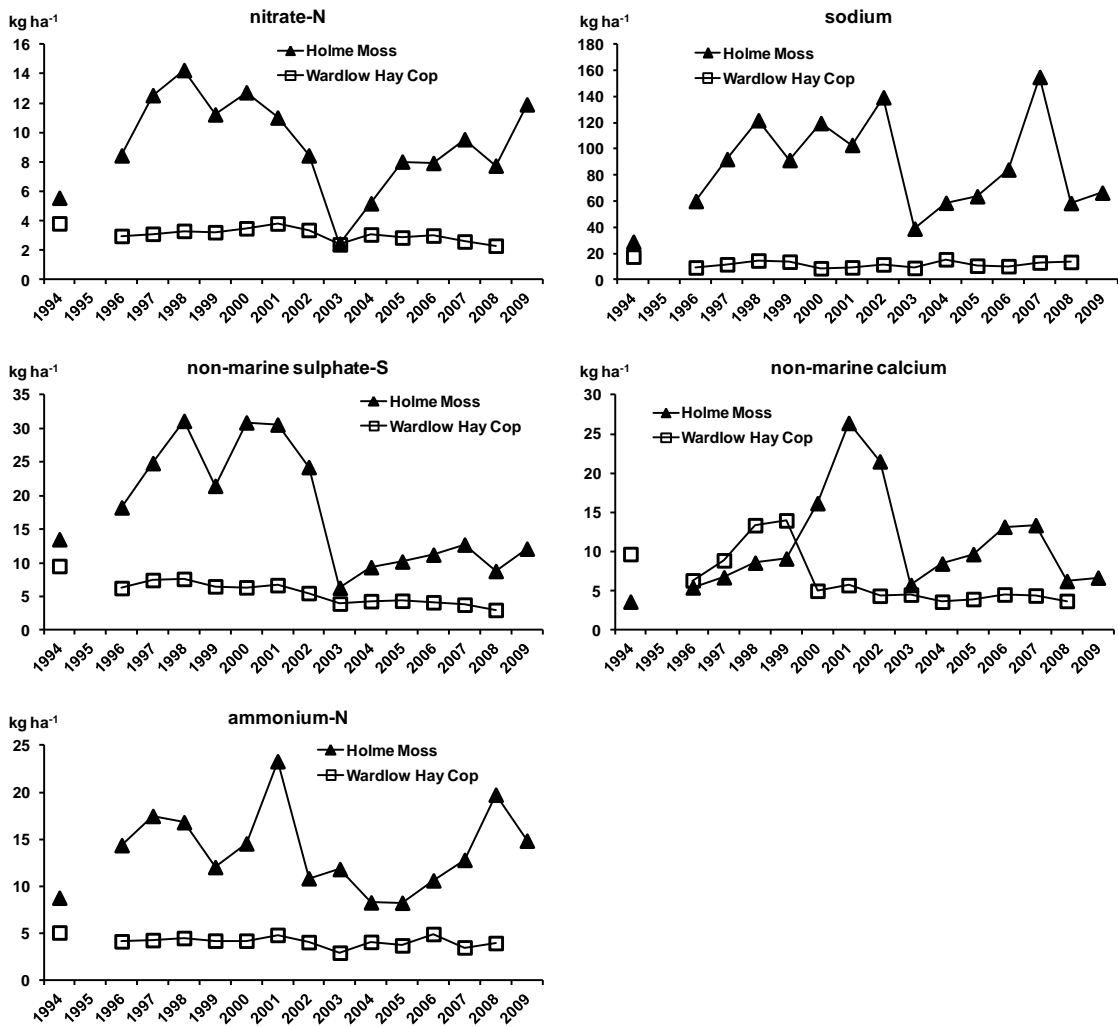


Figure 6. Wet annual deposition of ions in rain at Holme Moss and Wardlow Hay Cop. Data for 1995 are omitted because of poor data capture (see Table 1). Note that the method for measuring Ca concentrations at Wardlow Hay Cop changed in 2000.

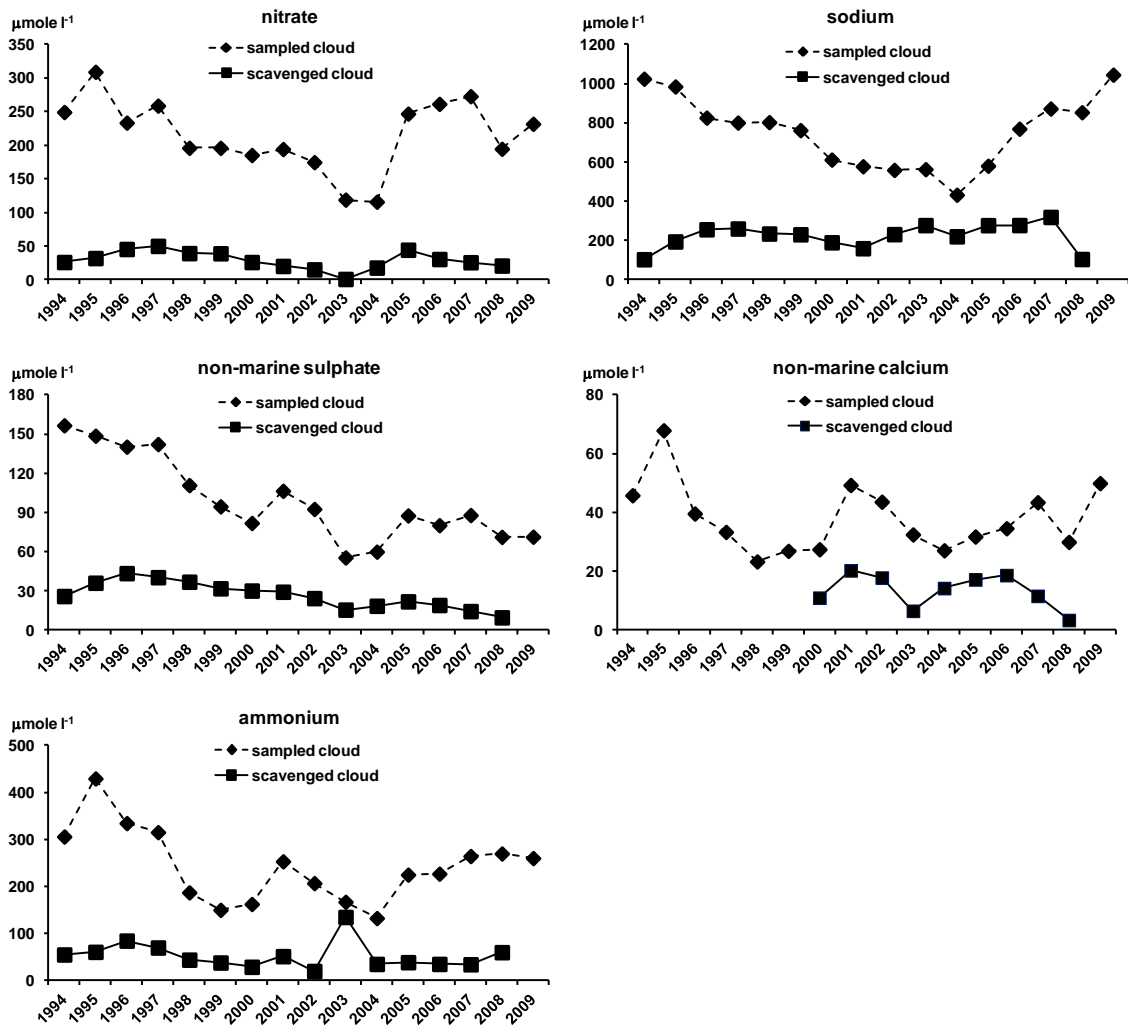


Figure 7. Concentrations of ions in scavenged cloud at Holme Moss, based on comparison with deposition at Wardlow Hay Cop. Concentrations measured in sampled cloud are also shown. Calcium data from Wardlow Hay Cop before 2000 are unreliable and have been omitted.

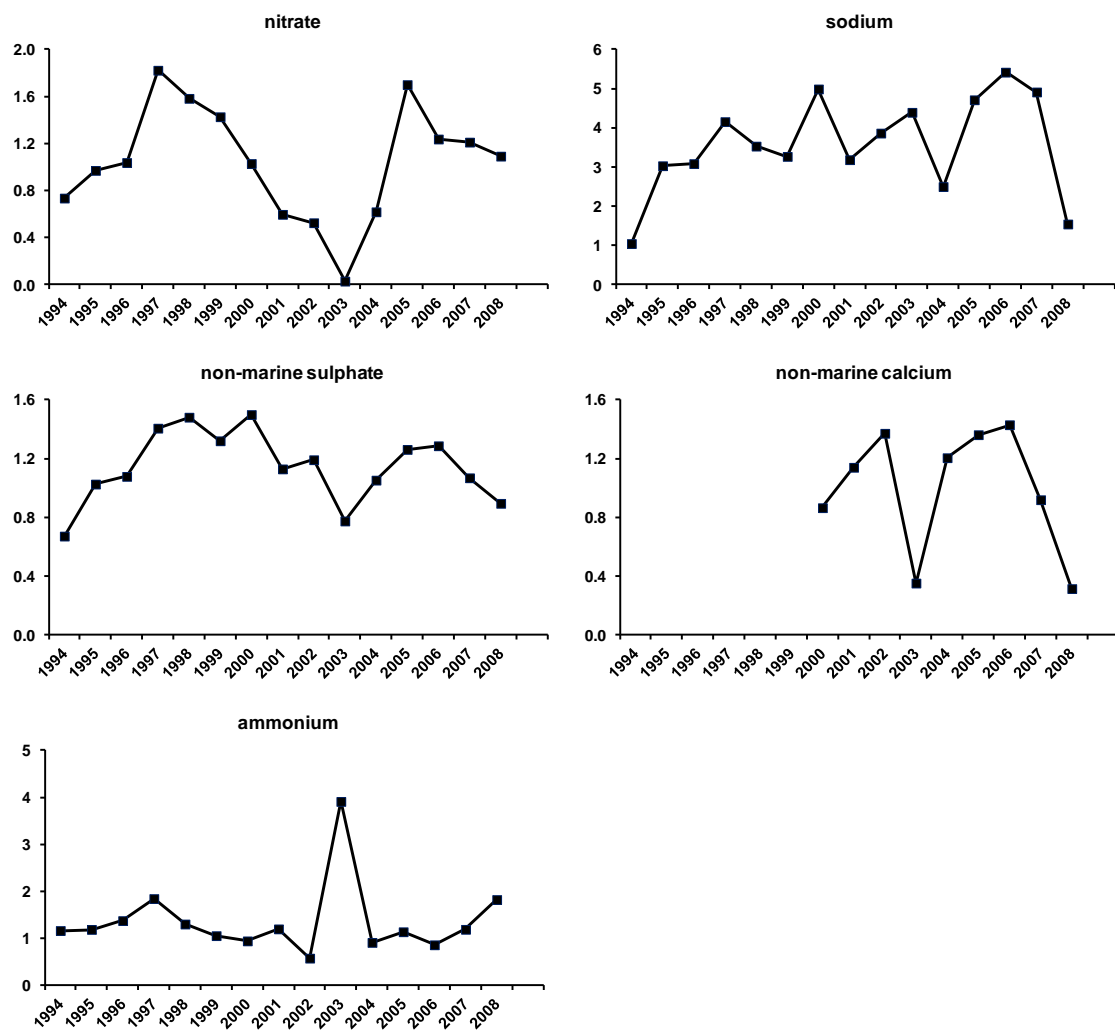


Figure 8. Time trend of the orographic scavenging factor, being the ratio of the cloud water concentration in scavenged cloud to the concentration in rain at Wardlow Hay Cop.

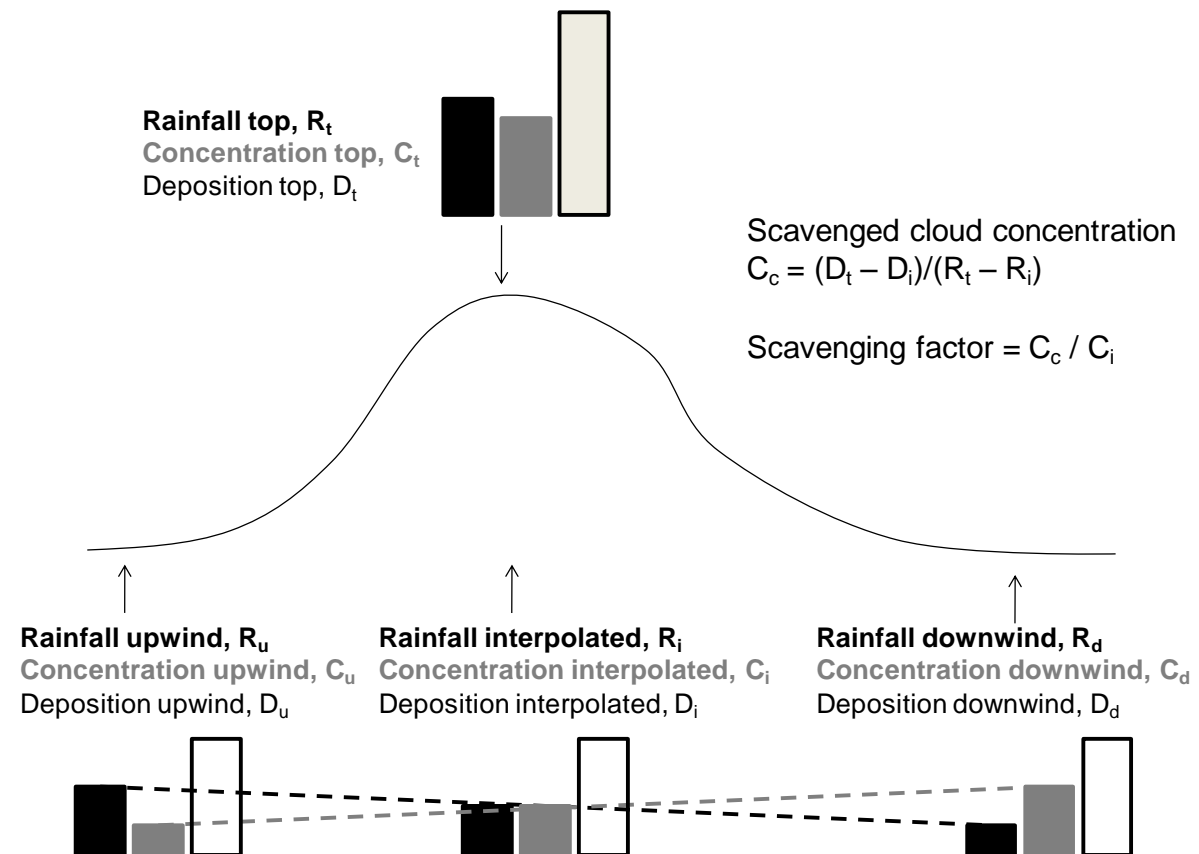


Figure 9. Schematic of the mapping process for calculating orographic enhancement of wet deposition across the UK. The amount of scavenged rain (water) is calculated as $R_t - R_i$, where R_i is interpolated from rainfall at low-elevation sites upwind and downwind, and R_t is measured or modelled based on altitude and location. The additional ion deposition is given by $(R_t \cdot C_t) - (R_i \cdot C_i)$, where the vertically integrated cap-cloud concentration (C_c) for a scavenging factor of 2 is $2C_i$, C_i is interpolated from the low-elevation sites upwind and downwind, and $C_c = (R_t \cdot C_t - R_i \cdot C_i) / (R_t - R_i)$, i.e. $C_t = C_i \cdot (2 - R_i/R_t)$.

Table 1: percentage by volume of valid simultaneous samples in each year in rain and cloud at Holme Moss and in rain at Wardlow Hay Cop.

Year	Holme Moss rain	Holme Moss cloud	Wardlow Hay Cop rain
1994	83%	83%	79%
1995	48%	61%	56%
1996	85%	77%	86%
1997	95%	93%	95%
1998	95%	92%	94%
1999	96%	94%	97%
2000	90%	83%	99%
2001	94%	95%	100%
2002	81%	81%	84%
2003	88%	85%	90%
2004	86%	91%	95%
2005	96%	94%	96%
2006	89%	87%	91%
2007	91%	94%	100%
2008	78%	84%	90%

Supplementary Figures

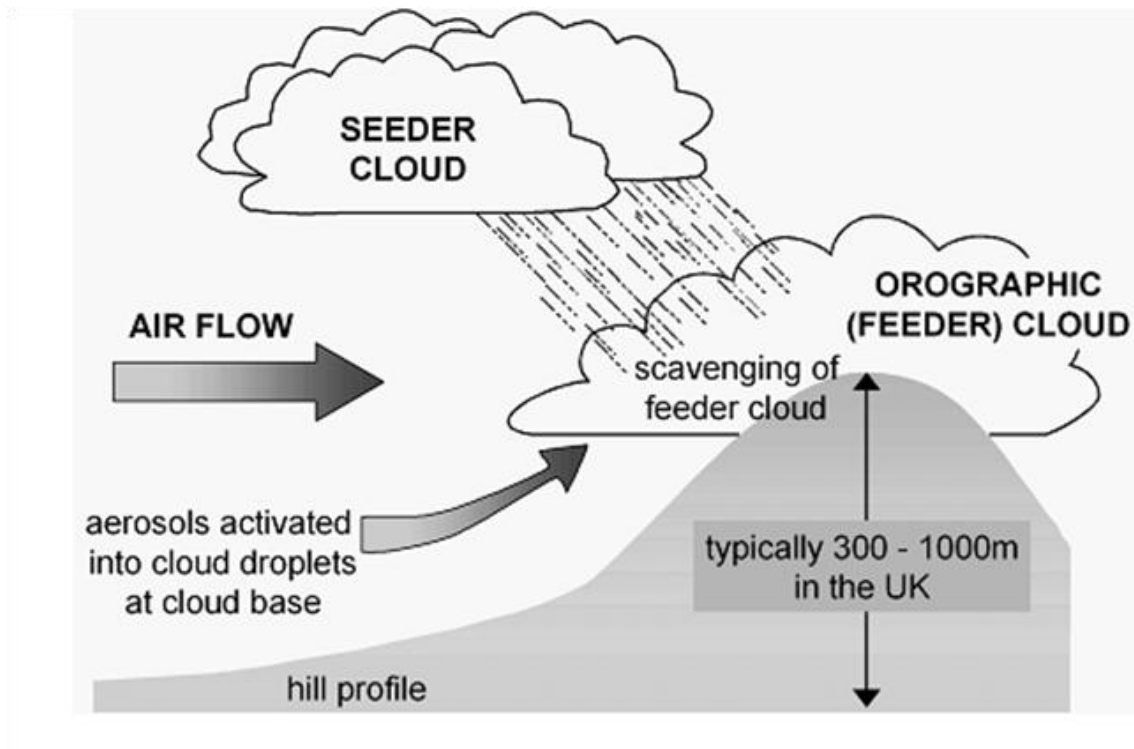


Figure S1. Schematic of the seeder-feeder process. Falling rain upwind of the hill cloud does not scavenge efficiently particles from the atmosphere. Once they are activated into cloud droplets in the cap cloud, particles are scavenged efficiently and deposited under the cap cloud, which also contributes additional water to deposition at the hill summit.

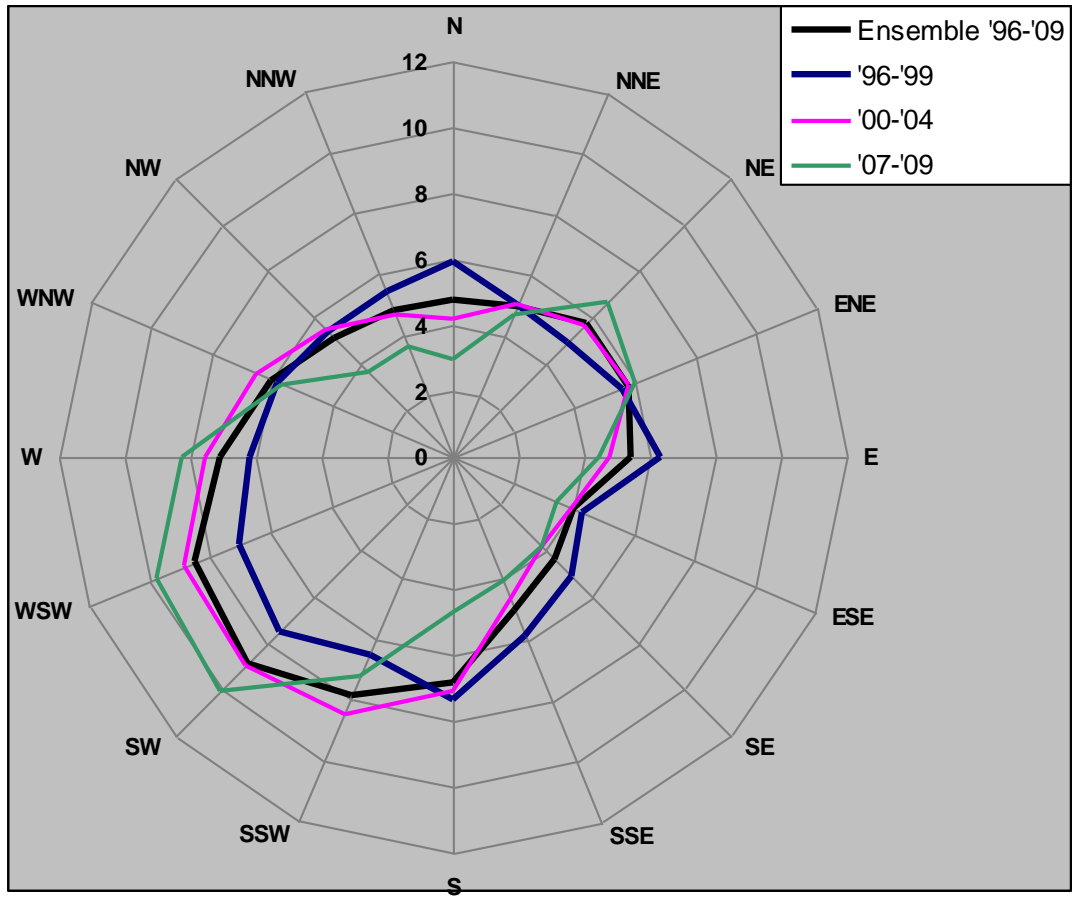


Figure S2. Variation of mean wind speed (m s^{-1}) with wind direction at Holme Moss during three periods: 1996-99, 2000-04, 2007-09

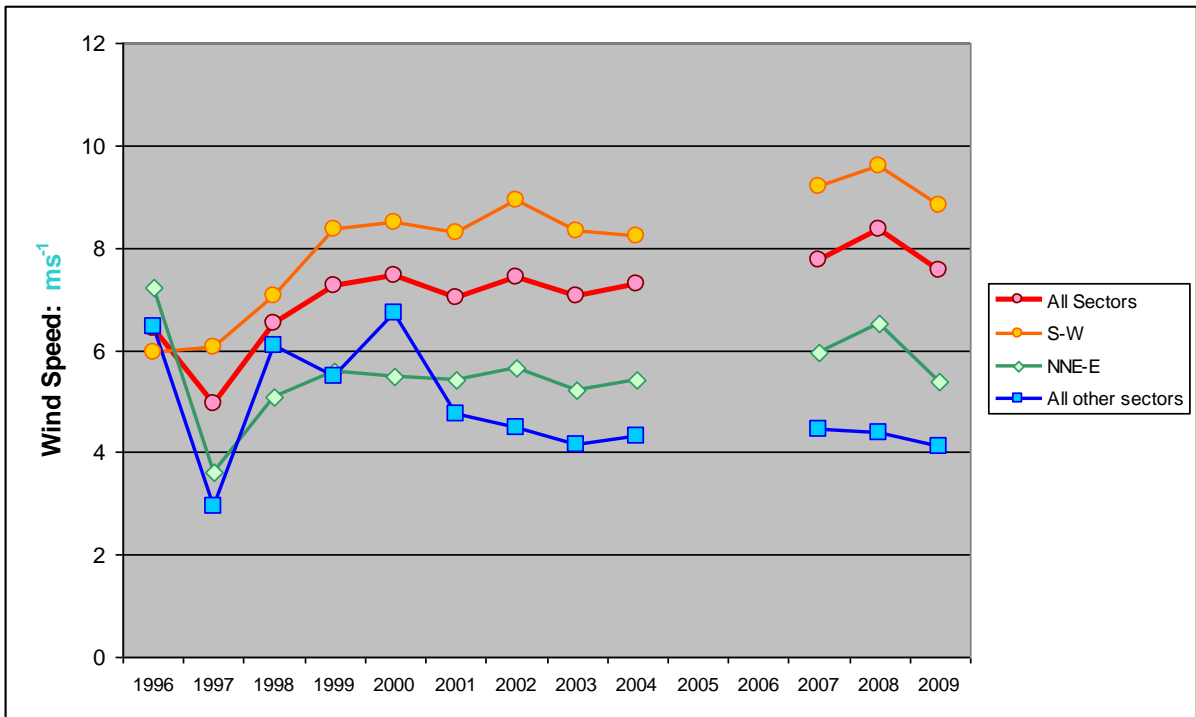


Figure S3. Long-term trends in mean wind speeds (m s^{-1}) at Holme Moss as a function of wind direction

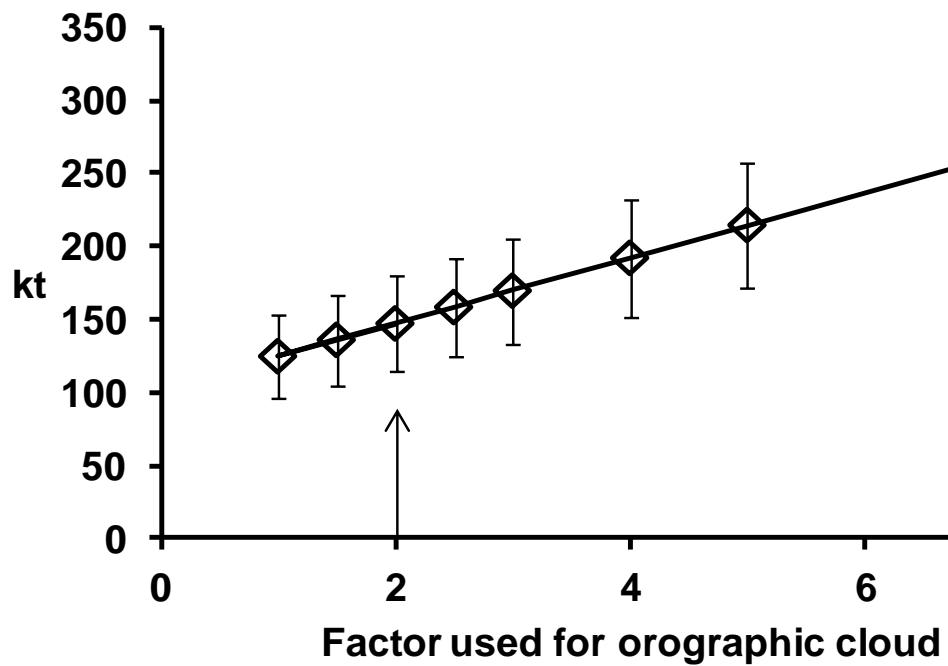


Figure S4. Average annual (wet+dry) deposition of S in the UK from 2000 to 2008 using different factors for the ratio of sulphate concentrations in scavenged cloud to the concentrations in the low-elevation rainfall at a site. The error bars show the year-to-year standard deviation. Data from this study suggest that the value of the factor may vary between 1 (where there are high gas-phase concentrations of SO_2) and 3.6 (for wholly particulate SO_4^{2-}).