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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.

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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.

27

1.   Introduction

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

2.1.   Sites and measurement methods

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

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).

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

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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

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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% yr^{-1} at Holme

234 Moss, -7.0% 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% 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

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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,

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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:

292   Orographic scavenging factor = $\frac{\text{(deposition at hill top – deposition upwind)}}{\text{(rain volume at hill top – rain volume upwind)}}$

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294

295   Deposition at the hill top

296   = (volume rain * rain concentration + volume scavenged cloud * cloud concentration)

297   = (volume rain * rain concentration + amount of aerosol scavenged)

298   Deposition upwind

299   = (volume rain * rain concentration + 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,

13

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   SO_2 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 NOx emissions in the U.K. over the

18

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

492 **7. Acknowledgements**

8.   References

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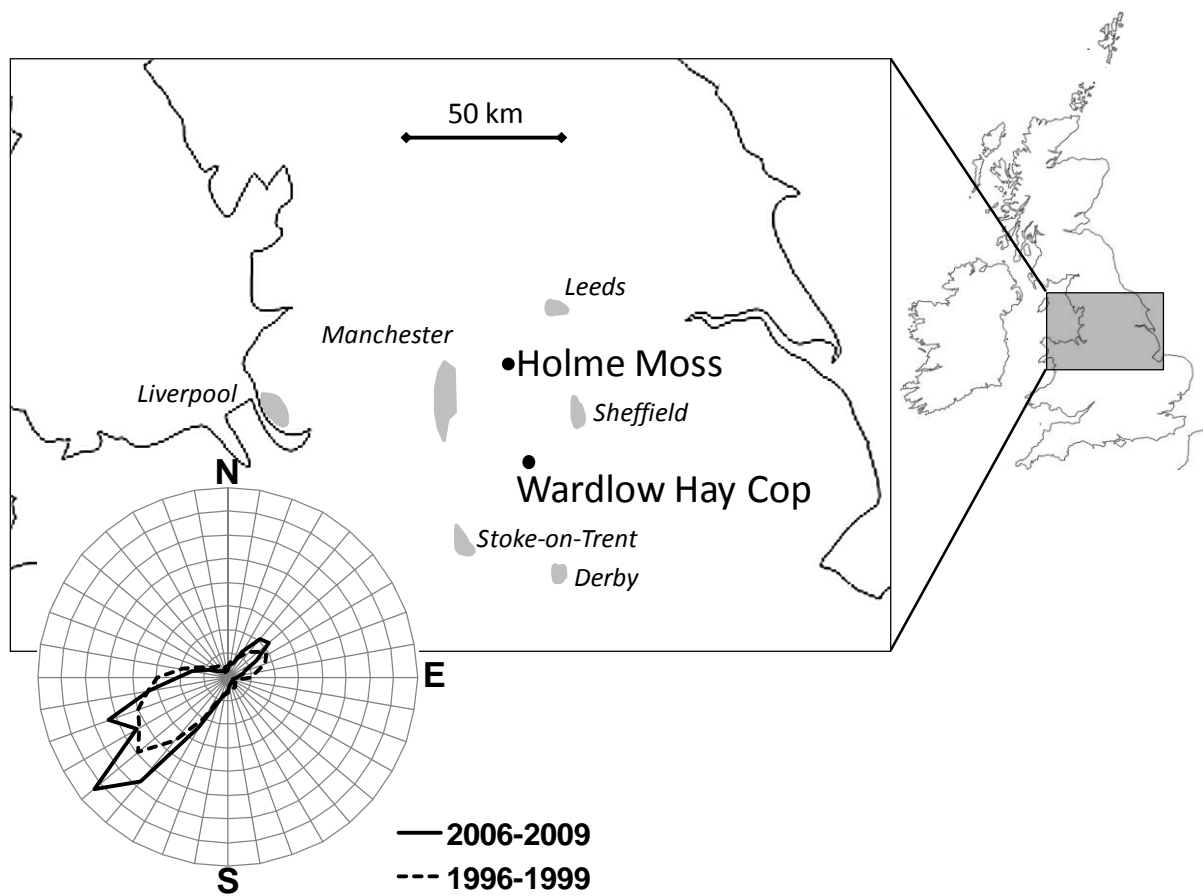
Figure 1. Location of the measurement sites in relation to major conurbations. The inset wind rose shows the average relative frequency of wind direction in 1996-1999 and 2006-2009 at Holme Moss.
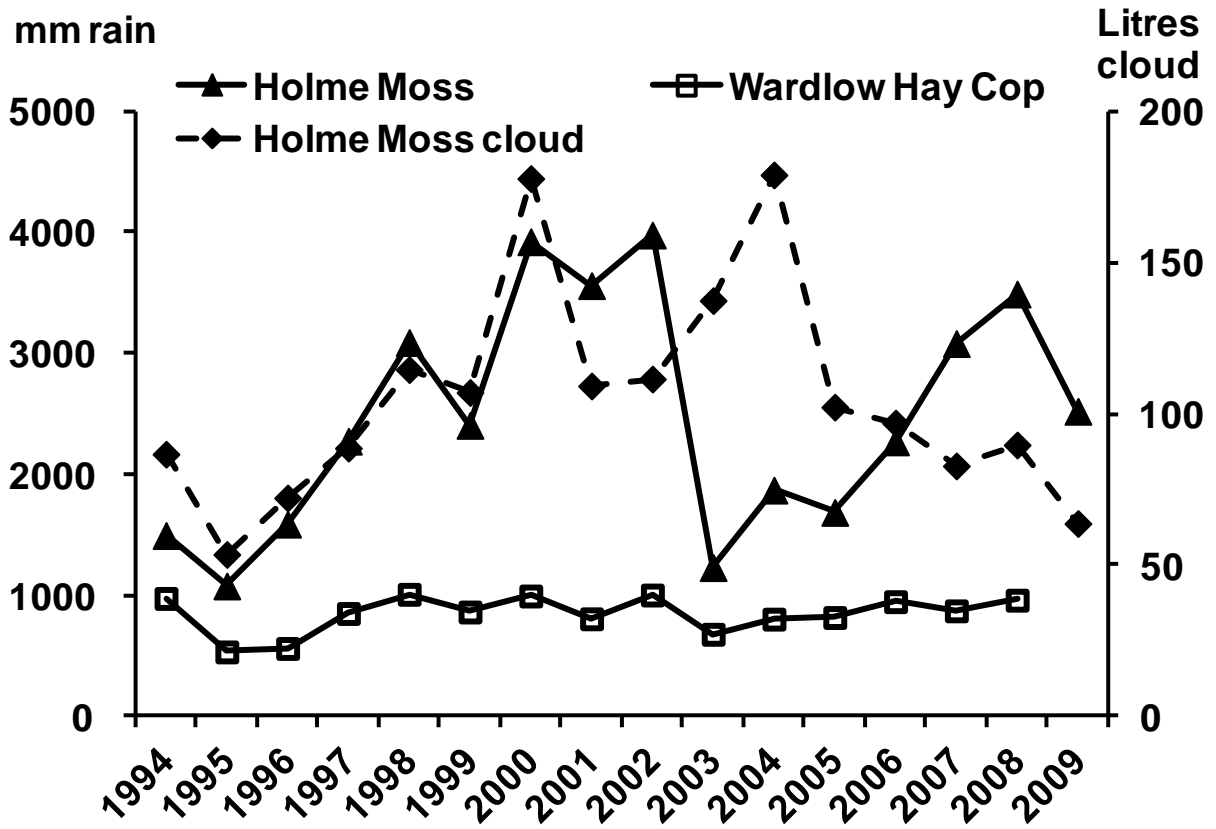
Figure 2. Rainfall amount measured at Wardlow Hay Cop and Holme Moss (LH axis), and volume of cloud water sampled at Holme Moss (RH axis), corrected for rainfall sampled by the cloud collector.
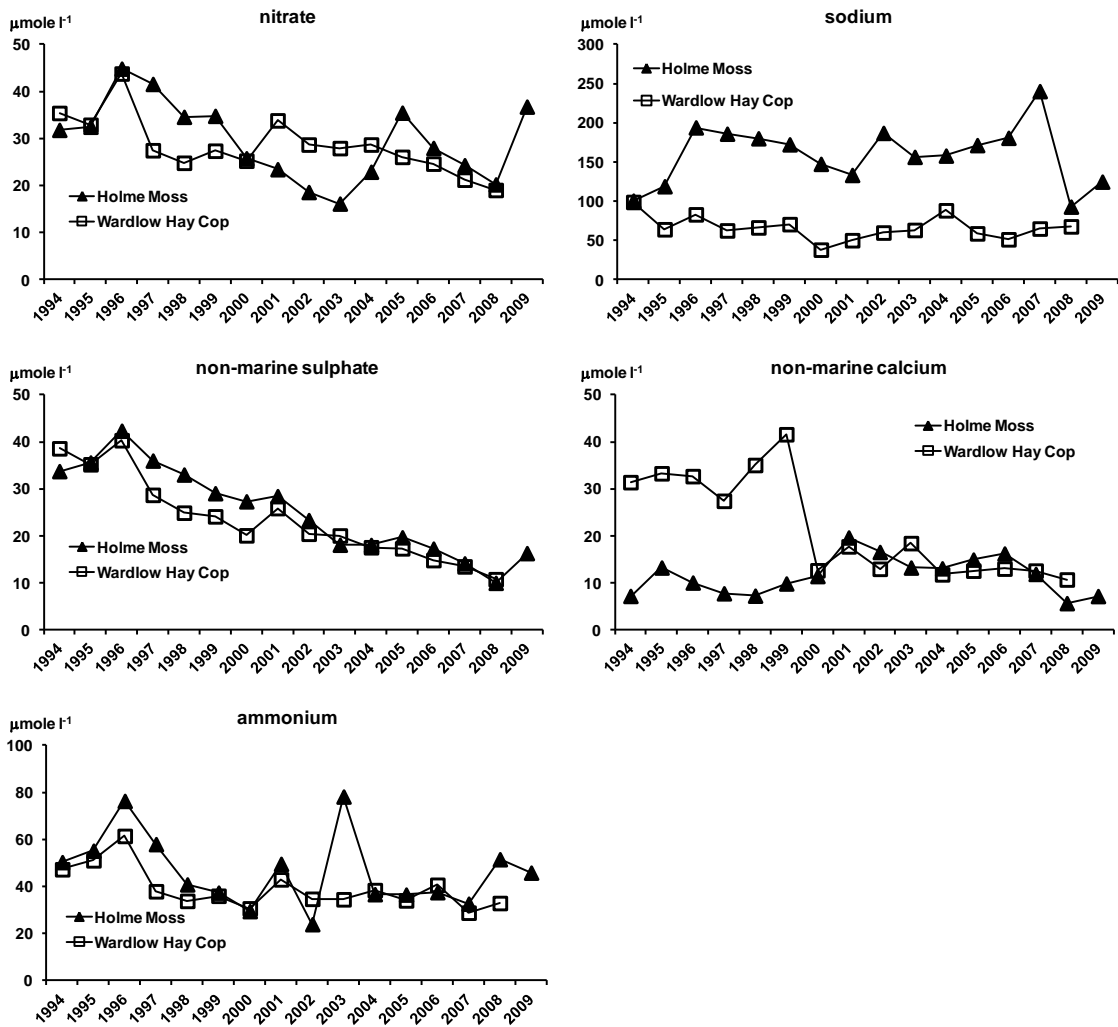
Figure 3. Trends in annual volume-weighted concentrations of major ions in rain at Holme Moss and Wardlow Hay Cop, based on matched samples. Note that the method for measuring Ca concentrations at Wardlow Hay Cop changed in 2000.
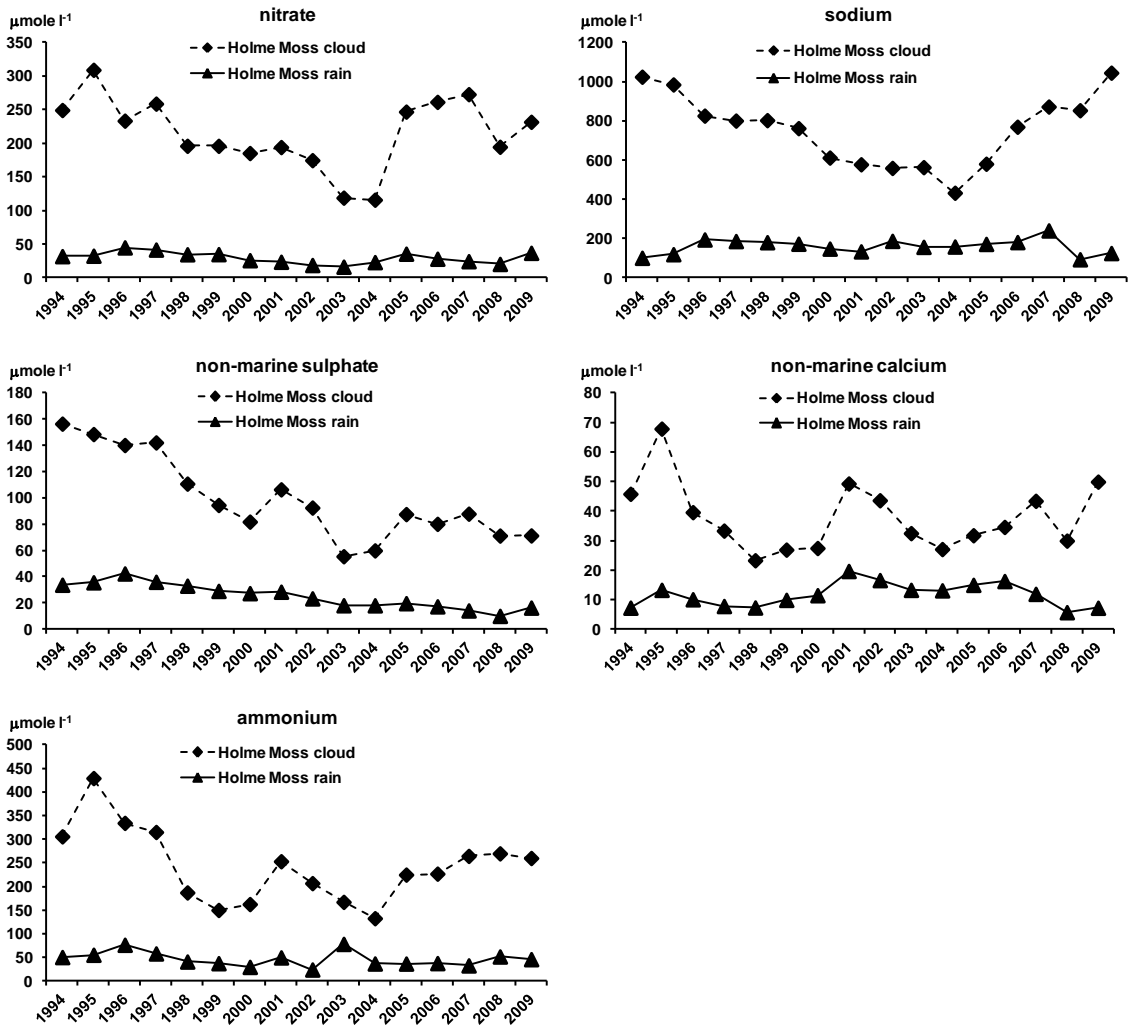
Figure 4. Trends in annual volume-weighted concentrations of major ions in cloud and rain at Holme Moss, based on matched samples
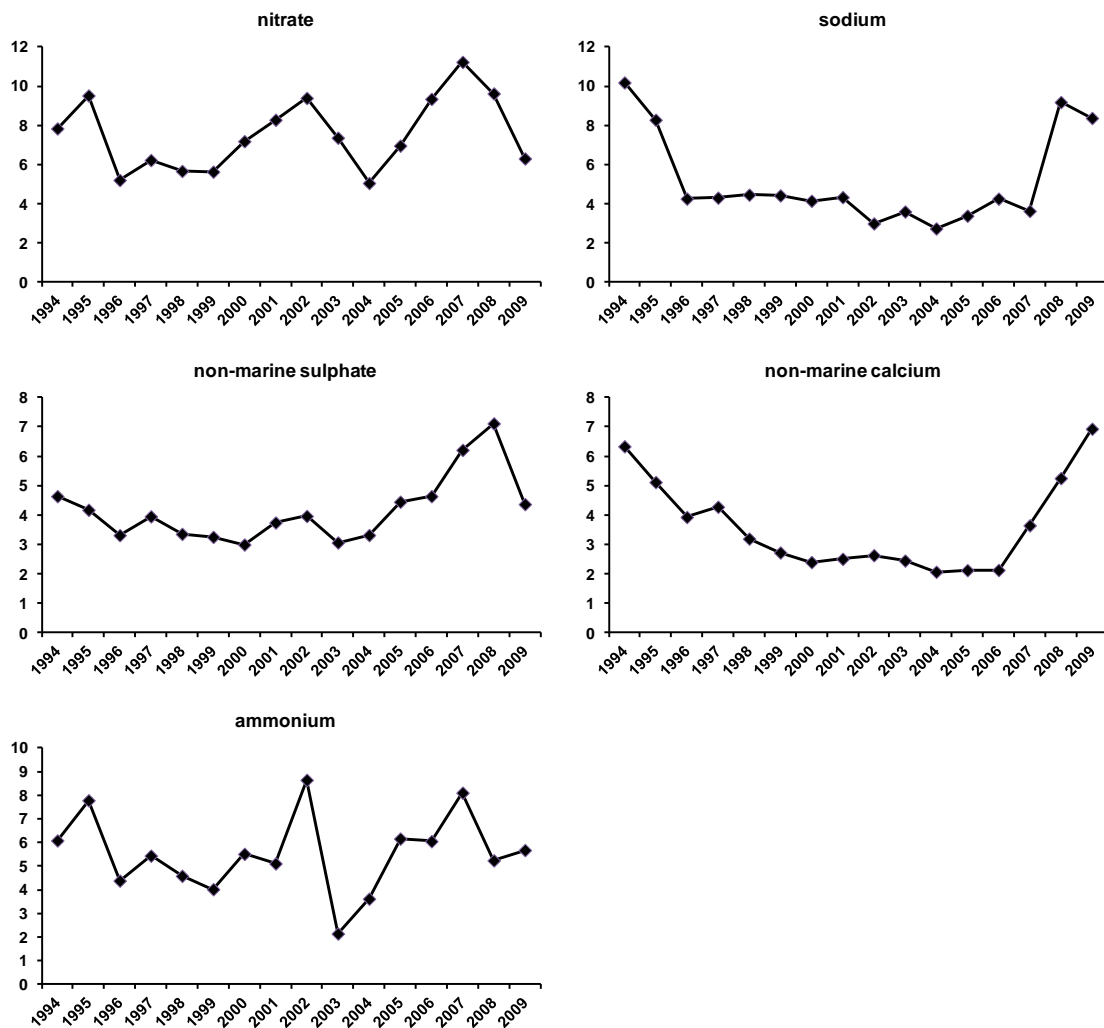
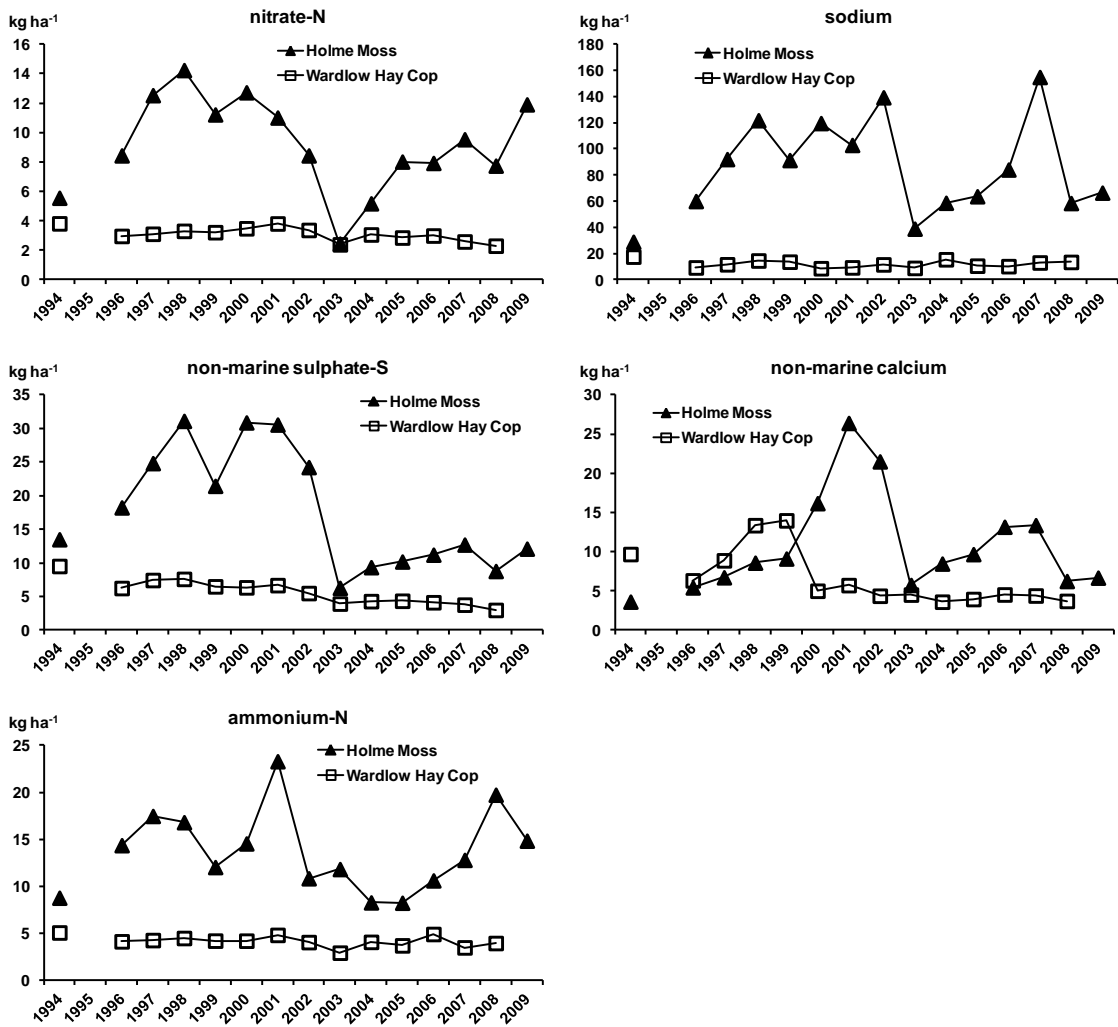Figure 5. Ratio of average concentrations of ions in cloud water to concentrations in rain water at Holme Moss.

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.
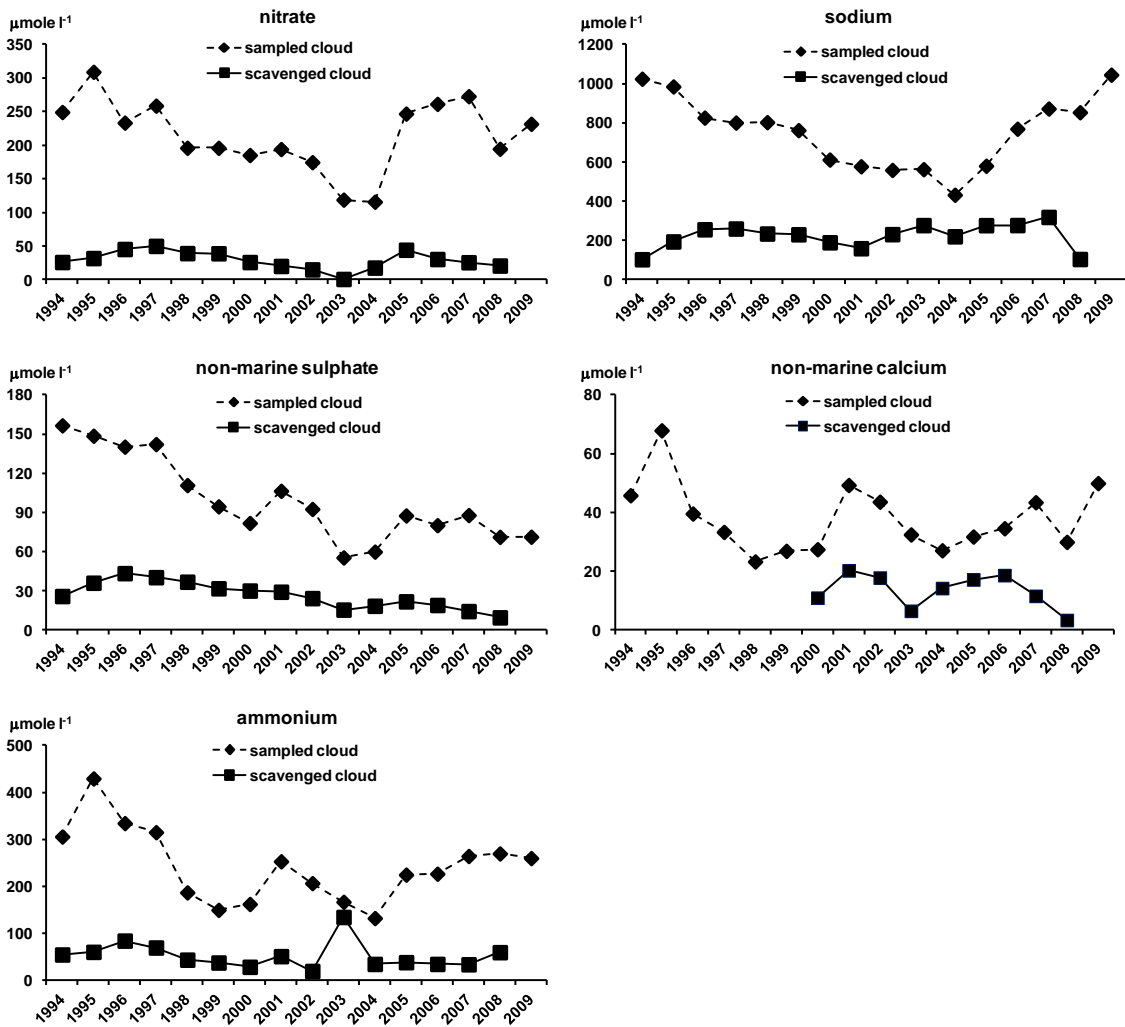
Figure 7. Concentrations of ions in scavenged cloud at Holme Moss, based on comparison with deposition at Wardlow Hay Cop. Concentrations measured in sampled cloud are also shown. Calcium data from Wardlow Hay Cop before 2000 are unreliable and have been omitted.
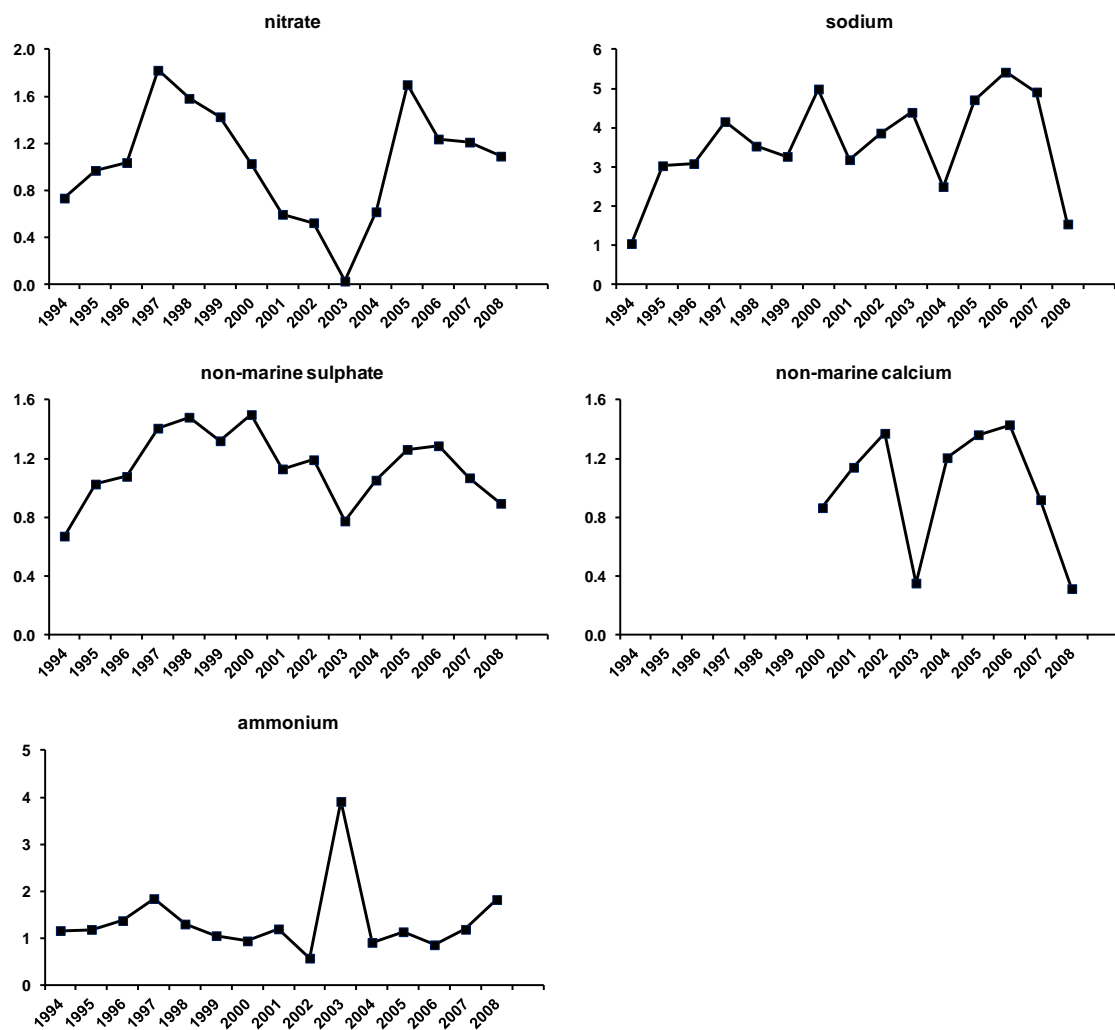
Figure 8. Time trend of the orographic scavenging factor, being the ratio of the cloud water concentration in scavenged cloud to the concentration in rain at Wardlow Hay Cop.
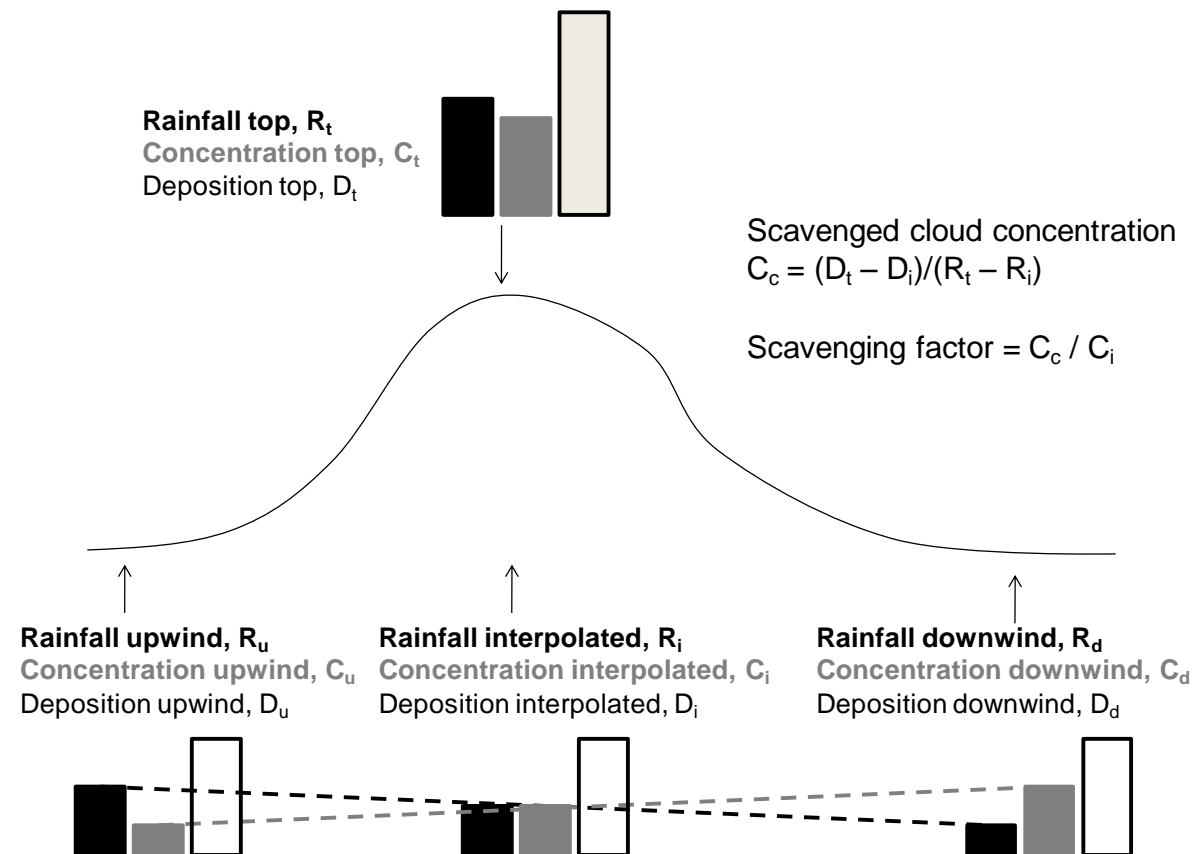
Rainfall top, R_t
Concentration top, C_t
Deposition top, D_t

Scavenged cloud concentration
$C_c = (D_t - D_i)/(R_t - R_i)$

Scavenging factor $= C_c / C_i$

Rainfall upwind, R_u
Concentration upwind, C_u
Deposition upwind, D_u

Rainfall interpolated, R_i
Concentration interpolated, C_i
Deposition interpolated, D_i

Rainfall downwind, R_d
Concentration downwind, C_d
Deposition downwind, D_d

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 $(R_t.C_t)-(R_i.C_i)$, 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 $C_c = (R_t.C_t - R_i.C_i)/(R_t - R_i)$, i.e. $C_t = C_i.(2 - R_i/R_t)$.

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.

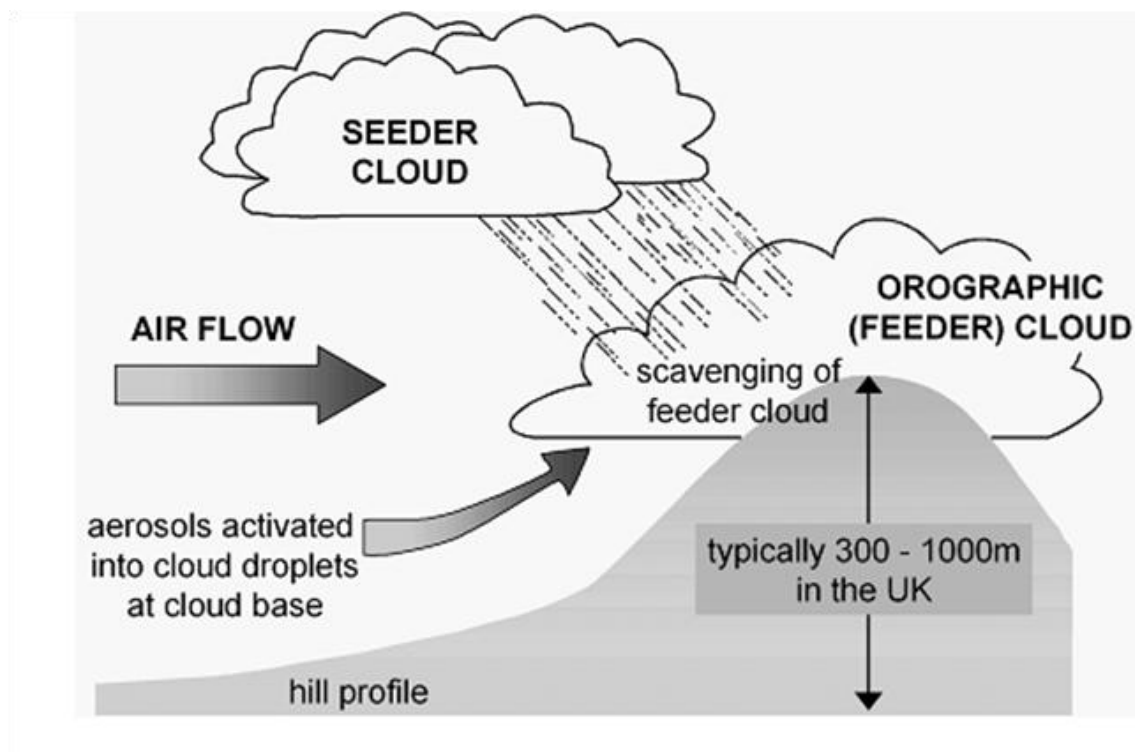| Year	Holme Moss rain	Holme Moss cloud	Wardlow Hay Cop rain
1994	83%	83%	79%
1995	48%	61%	56%
1996	85%	77%	86%
1997	95%	93%	95%
1998	95%	92%	94%
1999	96%	94%	97%
2000	90%	83%	99%
2001	94%	95%	100%
2002	81%	81%	84%
2003	88%	85%	90%
2004	86%	91%	95%
2005	96%	94%	96%
2006	89%	87%	91%
2007	91%	94%	100%
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.
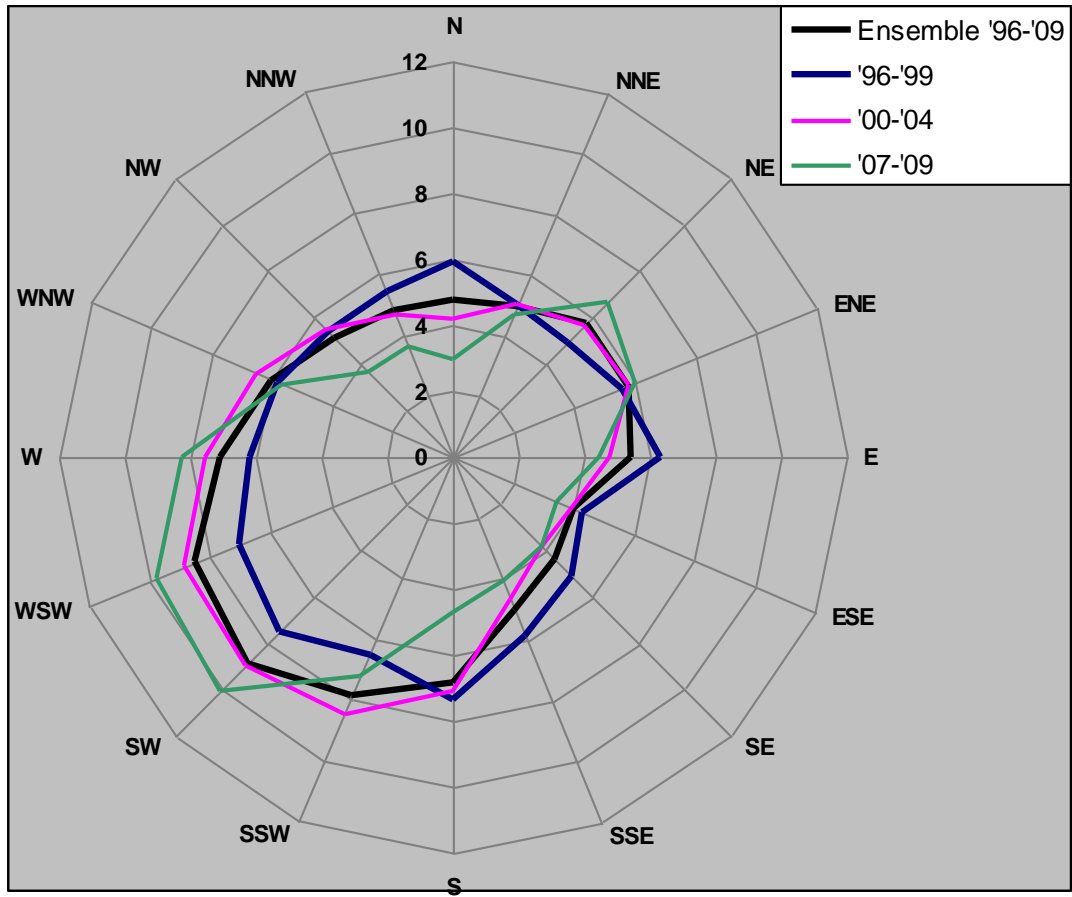
Figure S2. Variation of mean wind speed (m s^{-1}) with wind direction at Holme Moss during three periods: 1996-99, 2000-04, 2007-09
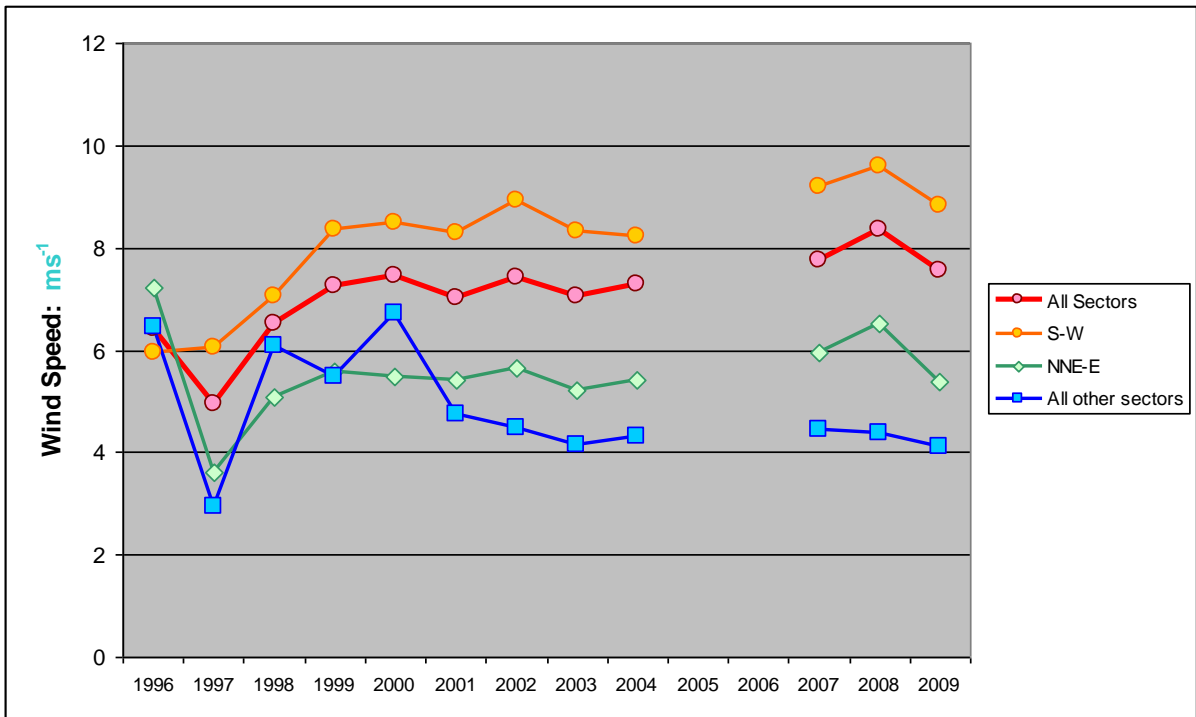
Figure S3. Long-term trends in mean wind speeds (m s^{-1}) at Holme Moss as a function of
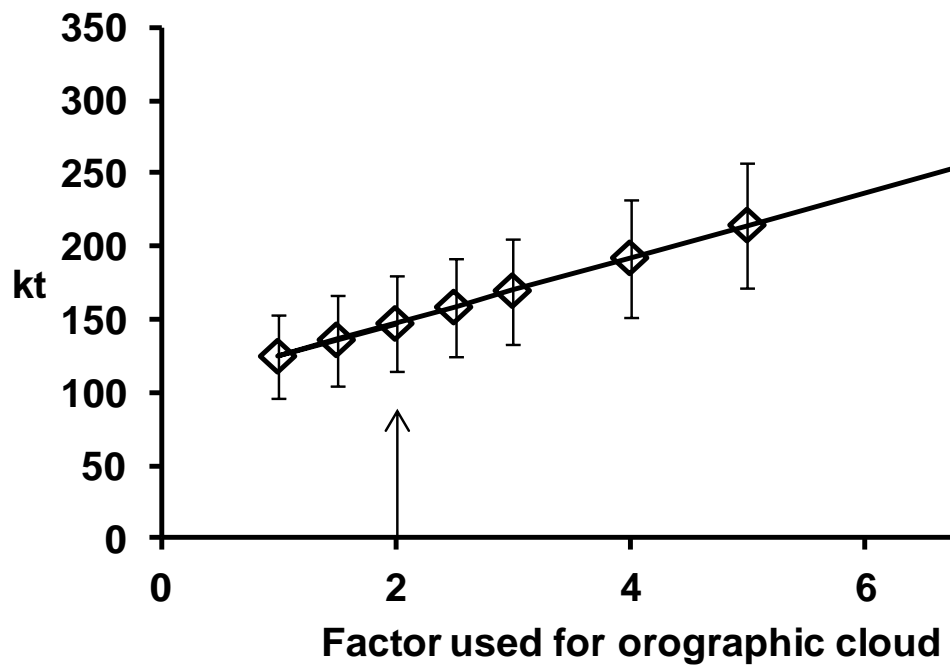
wind direction

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-}).