

**Monitoring of acidifying and eutrophying deposition  
and ecological parameters at seven potentially  
vulnerable Natura 2000 sites in England and Wales.**

**Sixth report to the  
Power Station and Refinery Operators**

**Final Report  
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**Don Monteith, Lorna Sherrin,  
Heather Carter, Patrick Keenan, Sarah Thacker,  
Mhairi Coyle, Eiko Nemitz, and Ron Smith  
NERC Centre for Ecology & Hydrology  
Lancaster Environment Centre**

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# 1. Introduction

Operators of power stations and refineries in England and Wales who have “opted in” to the Large Plant Combustion Directive (LCPD) are required by the UK Environment Agency to undertake “a monitoring programme to assess changes in acidification and eutrophication deposition and ecological effects at appropriate Natura 2000 sites”, as part of the operating permit improvement conditions for plant. A formal response outlining this monitoring programme was submitted to, and accepted by, the Environment Agency in March 2008. The NERC Centre for Ecology and Hydrology were awarded a four year contract to implement the monitoring in 2011.

The monitoring programme is based on protocols for ecological and deposition monitoring at Natura 2000 sites approved by the Environment Agency in September 2010. Following discussions between the installation operators, the Environment Agency, Natural England and Countryside Council for Wales (CCW), seven Natura 2000 sites were selected for inclusion in the monitoring programme, including at least one site relevant to each of the 13 participating installations. As sulphur deposition remains the dominant issue associated with power station and refinery emissions, sites were selected on the basis of the installation’s modelled percentage contribution to the minimum site-relevant critical load for sulphur ( $CL_{maxS}$ ), plus the percentage contribution to total sulphur deposition and total acid deposition, while the absolute level of sulphur deposition arising from the installation was also taken into account.

Monitoring focuses on three components relating to the conservation objectives of the selected sites:

1. Prevailing levels of acidifying deposition and any changes in acidification deposition over the period of monitoring.
2. Prevailing levels of eutrophying deposition and any changes in eutrophication deposition over the period of monitoring.
3. Prevailing ecological condition and any changes in the ecological condition over the period of monitoring.

The monitoring programme provides supplementary monitoring information to complement a previous modelling assessment review conducted by the Environment Agency in relation to the Integrated Pollution Prevention and Control permitting for UK refineries and coal-fired power stations.

This report is the sixth data report to the power station and refinery operators and provides an update on chemistry data collected up to the end of 2014, thus covering the first three full calendar years of monitoring, and provides details of monthly measurements of wet deposition chemistry, gaseous concentrations and soil solution chemistry collated over 2014 particularly. Two dry deposition models that combine meteorological observations with gaseous concentration measurements have been used to produce monthly estimates of dry deposition. Monthly estimates of wet, dry and total deposition of oxidised sulphur, oxidised nitrogen, reduced nitrogen and acid chloride are provided for the seven sites, together with annual estimates of total deposition, (that also include estimates for nitric acid, and aerosol sulphate ( $SO_4$ ), nitrate ( $NO_3$ ) and ammonium ( $NH_4$ ) dry deposition) for the three years.

Following a review of the report presenting the results of the 2012 monitoring (Monteith et al., 2013), the England and Wales Environment Agency and Natural Resources Wales, provided comments outlining additional information that they felt would be useful for inclusion (Watkins, 2014). A response was prepared in consultation with CEH, submitted by the power station and refinery operators, and accepted by the regulators.

As a result of these discussions, the following additional information has been included in this report:

- Graphs of ammonia concentrations (in Section 6.1) and the measurements presented in the electronic appendix now include the three replicate samples. Previously these were reported as a single average result as a consequence of the application of the standard spreadsheet calculator deployed by the national ammonia network.
- As non-marine chloride deposition should be considered in the assessment of acid deposition against the MaxS critical load parameter, wet and dry non-marine chloride deposition has been calculated and included in the relevant sections summarising monthly and annual deposition. Wet non-marine chloride deposition has also been calculated for the 2012 data and included in the summary tables in Section 6.4.

## 2. Site selection

Seven Natura 2000 sites, listed in Table 2.1, were selected following discussions between the installation operators, the Environment Agency, Natural England and CCW, and a series of site-scoping visits by CEH and E.ON staff. These include at least one site relevant to each of the 13 participating installations. As sulphur deposition was considered the key issue associated with power station and refinery emissions, selection was based on the installation's modelled percentage contribution to the minimum site-relevant critical load for sulphur (CL<sub>maxS</sub>), plus the percentage contribution to total sulphur deposition and total acid deposition. The absolute level of sulphur deposition arising from the installation was also taken into account.

Wherever possible, ecological monitoring locations were selected on the basis of possession of the most sensitive designated features (i.e. those with the minimum site-relevant critical loads), using the "main habitat" data provided on the Natural England website for the associated SSSIs (<http://www.english-nature.org.uk/Special/sssi/search.cfm>). In practice, the most sensitive area was not always sufficiently accessible, nor was it always possible to find a secure area to base the associated Meteorological/deposition station. In these cases compromises were necessary, although, in all cases the selected habitats are considered to be ecologically very similar to the most sensitive habitats.

**Table 2.1 Monitoring sites and associated power station (PS) and refinery (RF) installations. SAC = Special Area of Conservation; SSSI = Site of Special Scientific Interest**

Installation(s)	Nature 2000 location and SSSI designation	Key monitored Natura 2000 habitat
Aberthaw PS	Usk Bat Sites SAC Mynydd Llangatwyg SSSI	Blanket Bogs
Ratcliffe PS, Cottam PS & West Burton PS	Thorne Moor SAC Thorne, Crowle & Goole Moors SSSI	Degraded Raised Bogs & Active Raised Bogs
Rugeley PS	Cannock Chase SAC/SSSI	European dry heaths
Fawley RF	The New Forest SAC/SSSI	European dry heaths
Drax PS, Eggborough PS & Ferrybridge PS	Skipwith Common SAC/SSSI	European dry heaths & Northern Atlantic wet heaths
Fiddler's Ferry PS & Stanlow RF	Manchester Mosses SAC Astley & Bedford Mosses SSSI	Degraded Raised Bogs
Milford RF* & Pembroke RF	Cleddau Rivers SAC Esgryn Bottom SSSI	Active Raised Bogs

\*Milford Haven Refinery closed at the end of 2014

### 3. Field Measurements and sample analysis

Monitoring protocols follow those outlined in the original project specification document based on the protocols agreed with the Environment Agency in September 2010 and are described in the following sections.

#### 3.1 Monitoring installation

Dates of the installation of the meteorological and deposition monitoring equipment at each site are provided in Table 3.1.

**Table 3.1 Dates of Met Site and sampler installation.**

SITE	Installation	
	Met site	Deposition samplers
Manchester Mosses SAC	12/10/2011	20/10/2011
Cannock Chase SAC	19/08/2011	13/10/2011
Skipwith Common SAC	26/08/2011	11/10/2011
Thorne Moor SAC	8/11/2011	08/11/2011
Cleddau Rivers SAC	18/08/2011	14/10/2011
Usk Bat Sites SAC	12/12/2011	06/12/2011
New Forest SAC	13/10/2011	13/10/2011

#### 3.2 Bulk wet deposition chemistry sampling and sample analysis

Two Warren Spring Laboratory (WSL) - type bulk rain gauges with a funnel diameter of 115 mm have been deployed since the Autumn of 2011 at each site by E.ON. The rims of the collection funnels are positioned 1.5 - 2.0 m above ground level to avoid sample contamination from the ground during heavy rain. A "bird guard", comprising a ring of vertically mounted cable ties, has been incorporated to discourage birds from perching on the rim of the funnel.

Collection bottles are deployed and replaced on a monthly basis. Weighed prior to deployment, retrieved bottles are placed in sample boxes, kept cool, and either sent by Royal Mail Special Delivery, or carried by CEH staff, within 24 hours to the CEH Lancaster laboratory where sample volumes are determined by reweighing and samples are analysed chemically. Providing sufficient volumes are collected, the following species are measured:

- Acid Anions: sulphate, nitrate, chloride (by ion chromatography)
- Base Cations: calcium, sodium, magnesium, potassium - by inductively coupled plasma emission spectroscopy (ICP-OES)
- pH - Fisherbrand Hydrus 400 pH meter buffered at pH
- Ammonium and phosphate- colorimetrically using a SEAL AQ2 discrete analyzer
- Specific conductivity – conductivity at 20° C

To date, sample volumes have always been sufficient to allow all the analyses above. However, in the case of any future samples being returned with insufficient volumes, the two samples will be bulked. If the bulked sample is still not sufficient the following priority will be given to the measurements performed:

1) ammonium + phosphate; 2) acid anions; 3) pH; 4) base cations; 5) conductivity.

Phosphate is prioritised here as it provides an indication of bird strikes, and thus whether the sample is viable for further analysis.

### **3.3 Gaseous concentrations sampling and sample analysis**

Concentrations of sulphur dioxide (SO<sub>2</sub>), nitrogen dioxide (NO<sub>2</sub>) and nitrogen oxides (NO<sub>x</sub>) are measured at each site on a monthly frequency using Gradko tubes fixed to an open frame at a height of around 1.5 m within the meteorological/deposition sampling enclosure. Sampling methodology follows Gradko protocols. Retrieved Gradko tubes are placed in the sample crate and returned to the CEH laboratory along with the other water samples where they are logged before being sent in monthly batches to Gradko for analysis. Concentrations of NH<sub>3</sub> are measured at CEH using Adapted Low-cost Passive High Absorption (ALPHA) samplers.

Accompanying each group of monthly samples, additional monthly sets of three Gradko (SO<sub>2</sub>, NO<sub>2</sub> and NO<sub>x</sub>) and five ALPHA samplers are kept in refrigerated conditions and analysed alongside the field deployed samples. All SO<sub>2</sub> and ammonia concentration data detailed and analysed in this report have been blank corrected, that is to say the appropriate monthly mean of blanks for these measurements has been subtracted from each field sample measurement. In accordance with advice to Defra (Targa & Loader, 2008), data for NO<sub>2</sub> and NO<sub>x</sub> blanks have been used to monitor potential contamination problems only and have not been subtracted from the values from the field samples, i.e. NO<sub>2</sub> and NO<sub>x</sub> data presented and analysed in this report have not been blank corrected.

### **3.4 Soil solution chemistry**

Within the vegetation sampling area, three soil solution sampling points were chosen amongst vegetation considered relatively homogenous and representative of the dominant vegetation type for the full vegetation survey area. The points were spaced within five metres of each other. At the heathland sites, Cannock Chase, Skipwith Common and New Forest, three pairs of Prenart suction samplers were installed at approximately 15 cm and 30 cm depth according to UK Environmental Change Network (ECN) soil solution monitoring protocols at each sampling point. A vacuum pump was used to apply a vacuum to the samplers, which were then left until the next monthly monitoring visit when they were emptied into acid-washed and distilled water rinsed polyethylene sample bottles before evacuating once more. The sample bottles were labelled and transferred to a storage box and kept cool before dispatching to the CEH Lancaster laboratory for analysis.

Most Prenart samplers at Skipwith Common and New Forest established strong vacuums from the outset and began to collect samples immediately following installation. Most of the samplers at Cannock Chase remained empty for the first two months of deployment but began to collect water during the winter months. It is not yet clear whether the absence of soil water in the early stages was due to the dryness of the soil, during what was a relatively dry autumn at the site, or due to a delay in the samplers “bedding in”.

At the four bog sites, three dipwell sampling tubes were installed in a similar spatial arrangement to the Prenart suction samplers. Unlike the heathland soils that show clear vertical zonation, only one sampling tube was necessary per sampling point due to the homogeneity of the peat at these sites. The tubes were inserted to a depth of 50 cm, and were

perforated with holes from 2 cm below the surface to 30 cm. On each monthly sampling visit a vacuum pump is used to empty the tubes into polyethylene sample bottles which are then treated as above.

When received by the CEH laboratory, individual sample bottles are first assessed to determine the volume collected. Samples are filtered through a 0.45 µm filter. Where sufficient volumes are collected, as is normally the case for dip well samples, the following measurements are performed:

- Acid Anions: sulphate, nitrate, chloride (by ion chromatography)
- Base Cations: calcium, sodium, magnesium, potassium and aluminium - by ICP-OES
- pH - Fisherbrand HydruS 400 pH meter buffered at pH
- Dissolved organic carbon (DOC)- Shimadzu TOC-Vcph analyser - samples acidified with 2M HCl and sparged with oxygen.
- Ammonium and phosphate- colorimetrically using a SEAL AQ2 discrete analyzer
- Specific conductivity – conductivity at 20° C

Separate sub-samples are required for various analyses. Where insufficient volumes are collected to allow all the analyses, as is sometimes the case for the heathland sites, upper and lower samples are bulked, and if the bulked samples are still not sufficient the following priority is given to the measurements performed:

1) Acid anions; 2) pH; 3) ammonium + phosphate; 4) DOC; 5) base cations; 6) alkalinity; 7) conductivity.

### **3.5 Meteorological monitoring**

At each meteorological monitoring location the following parameters are continuously sampled and processed into 15 minute averages:- Wind Speed – ( $\text{m s}^{-1}$ ); Wind Direction – (deg N); Ambient Air Temperature – ( $^{\circ}\text{C}$ ); Relative Humidity – (RH%); Photosynthetic Active Radiation (PAR;  $\mu\text{mol m}^{-2} \text{s}^{-1}$ ); Rainfall – (mm); and, Surface Wetness. Battery powered loggers relay the data via a mobile phone link to a data server. The meteorological monitoring sites are operated and maintained by E.ON Technologies, who are also responsible for the associated data collection.

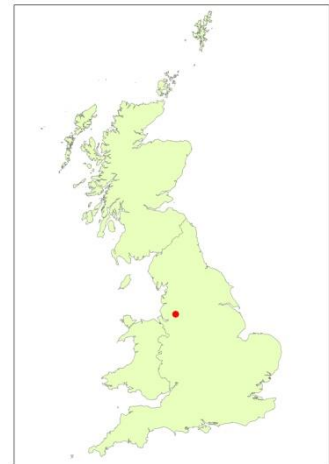


## **4. Site Descriptions**

This section provides details of the monitoring locations at the seven selected Natura 2000 sites. Soil solution monitoring was carried out in areas containing the key Natura 2000 habitat of interest and where possible the deposition and meteorological monitoring equipment was co-located with the soil monitoring. Where co-location of the deposition/meteorological equipment was not possible, due to physical constraints or security concerns, the nearest suitable location was selected.

#### 4.1 Manchester Mosses SAC - Astley Moss

Astley Moss, along with Bedford, Risley and Holcroft Mosses (together known as the Manchester Mosses) are areas of peat bog in Greater Manchester. They represent remnants of a much larger area of raised bog that once occupied a substantial area of south Lancashire north of the River Mersey. Astley Moss was designated a Site of Special Scientific Interest in 1989, while the Manchester Mosses were also designated as a Natura 2000 Special Area of Conservation in 2005. The mosses in this area originated as fen peat that was later colonised by Sphagnum that drove a change to an acidic raised bog. The key monitored Natura 2000 habitat at the monitoring location is 'degraded raised bogs'.



The area has been extensively drained to improve agricultural capacity in recent decades, leading to substantial degeneration of the peatlands. However, a recent restoration programme, overseen by the Wildlife Trust for Lancashire, Manchester & North Merseyside has resulted in a gradual rise in the water table across much of the site.

**Figure 4.1.1 Astley Moss and location of the Met/deposition station (red box)**



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**Figure 4.1.2 Aerial photograph (Google Earth) of the Astley Moss site. Locations for the Meteorological/Deposition, and soil water monitoring sites indicated by blue and red symbols respectively.**



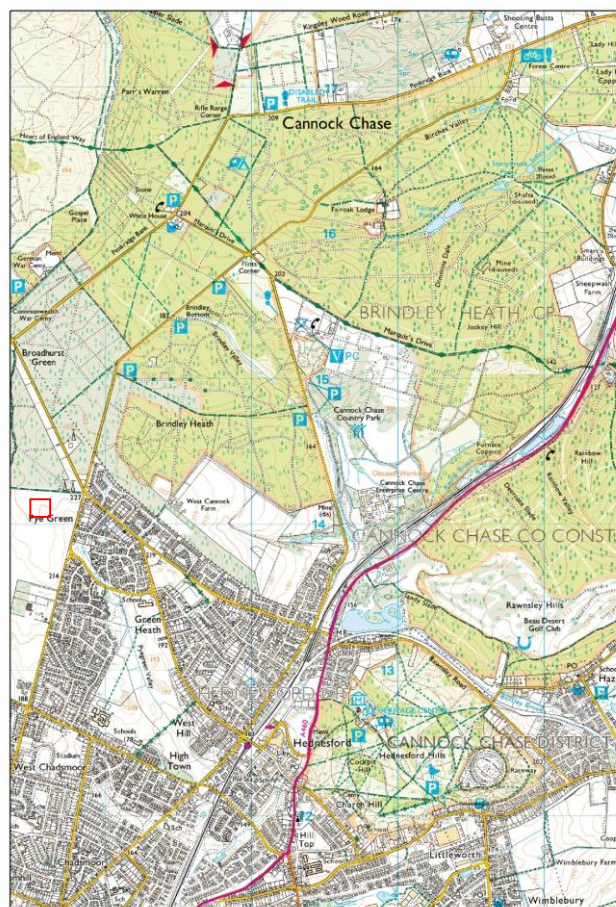


## 4.2 Cannock Chase SAC

The Cannock Chase SSSI is situated between Stafford, Rugeley, Lichfield and Cannock and comprises over 600 hectares of largely dwarf shrub heath. The site was designated as an SAC in 2005. The key monitored Natura 2000 habitat at the monitoring location is 'European dry heaths'. Concerns over security led to the siting of the meteorological and deposition apparatus in an open grazing area of a local equestrian centre, 700 metres to the west of soil solution monitoring area.



**Figure 4.2.1 Cannock Chase and location of the Met/deposition station (red box)**



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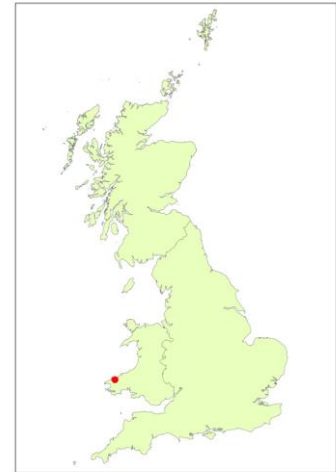
**Figure 4.2.2 Aerial photograph (Google Earth) of Cannock Chase site. Locations for the Meteorological/Deposition, and soil water monitoring sites indicated by blue and red symbols respectively.**





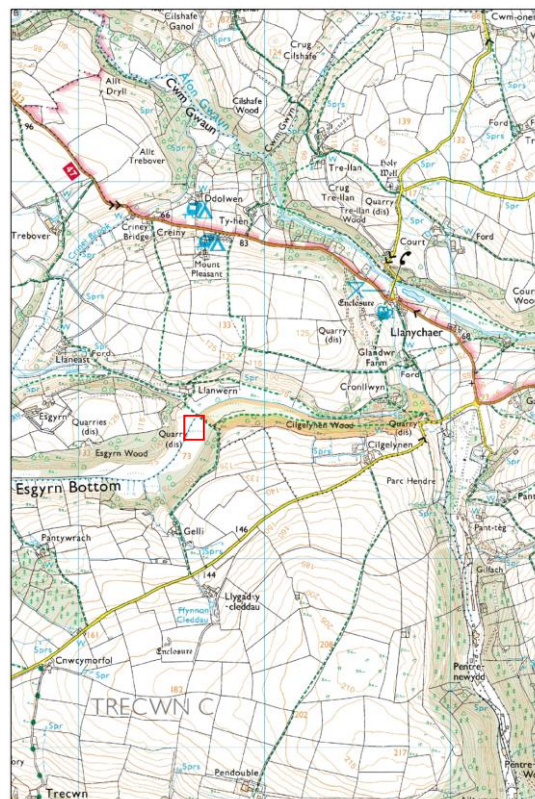
### 4.3 Cleddau Rivers SAC - Esgryn Bottom

Esgryn Bottom, 3 km south-south-east of Fishguard in south-west Wales and at an altitude of circa 80 m above sea level, is situated on the watershed between Afon Cleddau to the west and Afon Gwaun to the east. Cleddau Rivers was designated an SAC in 2004. The site lies within a melt-water channel system formed during the Late Pleistocene by sub-glacial stream erosion from melt-water. Much of the valley comprises thick peat deposits of up to 7 m depth that have formed over early Holocene lake-bed deposits thought to date from the early Holocene (9,000 - 10,000 years BP). The relatively small area of peatland has been subject to considerable degradation in the past as a result of peat cutting and drainage. The key monitored Natura 2000 habitat at the monitoring location is 'active raised bogs'.



For reasons of access and security, the meteorological/deposition station was sited in the vicinity of the residence at Llanwern, 200 m to the north of the soil solution monitoring area.

**Figure 4.3.1 Esgryn Bottom and location of the Met/deposition station (red box).**



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**Figure 4.3.2 Aerial photograph (Google Earth) of Esgryn Bottom site. Locations for the Meteorological/Deposition, and soil water monitoring sites indicated by blue and red symbols respectively.**





#### 4.4 Usk Bat Sites SAC - Mynydd Llangatwyg

Mynydd Llangatwyg comprises an undulating plateau rising to a height of circa 530 m overlooking the Usk Valley in the Brecon Beacons National Park. Most of the plateau is underlain by coarse sandstone, giving way in parts to underlying limestone. The site includes extensive areas of moorland and blanket bog and was designated a SAC in 2004. The key monitored Natura 2000 habitat at the monitoring location is 'blanket bogs'.

For reasons of security the meteorological/deposition station was sited 2.5 km to the south at Clydach Terrace. Precipitation at Clydach terrace is likely to be lower than on the plateau and for this reason a second "mountain rain gauge was established closer to the soil solution monitoring area to provide a short term comparison of inputs, and with a view to establishing a calibration factor. Unfortunately, the second gauge was stolen after only three months of deployment in 2013. A replacement was established in the summer of 2014. Currently there are insufficient data to be confident about the appropriate calibration factor, although, on average, precipitation measured on the plateau was around 10% higher than at Clydach Terrace. No adjustment has yet been made to the bulk deposition chemical flux estimates for this site.



Figure 4.4.1 Mynydd Llangatwyg and location of the Met/deposition station (red box)



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**Figure 4.4.2** Aerial photograph (Google Earth) of Mynydd Llangatwyg site. Locations for the Meteorological/Deposition, and soil water monitoring sites indicated by blue and red symbols respectively.



#### 4.5 The New Forest SAC

The New Forest National Park covers over 500 km<sup>2</sup> in Hampshire, southeast England, approximately 20% of which is either heathland or grassland. Overall the New Forest encompasses a very wide range of terrestrial and freshwater habitats and was designated an SAC in 2005. The heathland was determined to be the most sensitive habitat type for the purposes of this study. The key monitored Natura 2000 habitat at the monitoring location is 'European dry heaths'. For reasons of security, the meteorological/deposition monitoring station was established 600 m to the west on private farmland.

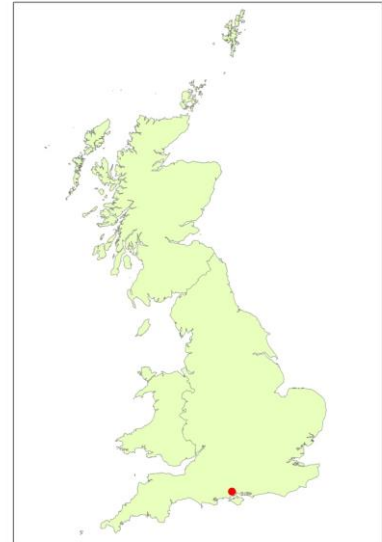


Figure 4.5.1 New Forest, Beaulieu site and location of the Met/deposition station (red box)



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**Figure 4.5.2** Aerial photograph (Google Earth) of New Forest, Beaulieu site. Locations for the Meteorological/Deposition, and soil water monitoring sites indicated by blue and red symbols respectively.



#### 4.6 Skipwith Common SAC

The Skipwith Common National Nature Reserve comprises circa 270 hectares of open heath, wetlands, woodland and scrub and was designated an SAC in 2005. The Common is largely owned by the Escrick Park Estate who also manage the site in partnership with Natural England (NE). The key monitored Natura 2000 habitats at the monitoring location are 'European Dry Heaths' and 'North Atlantic Wet Heaths'.

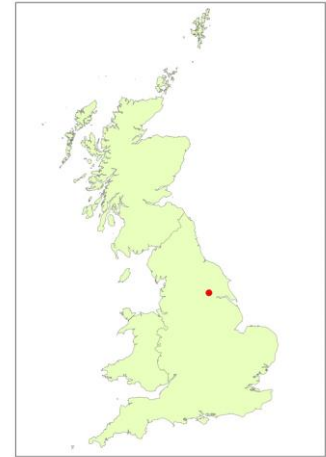


Figure 4.6.1 Skipwith Common and location of the Met/deposition station (red box)



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**Figure 4.6.2 Aerial photograph (Google Earth) of Skipwith Common site. Locations for the Meteorological/Deposition, and soil water monitoring sites indicated by blue and red symbols respectively.**



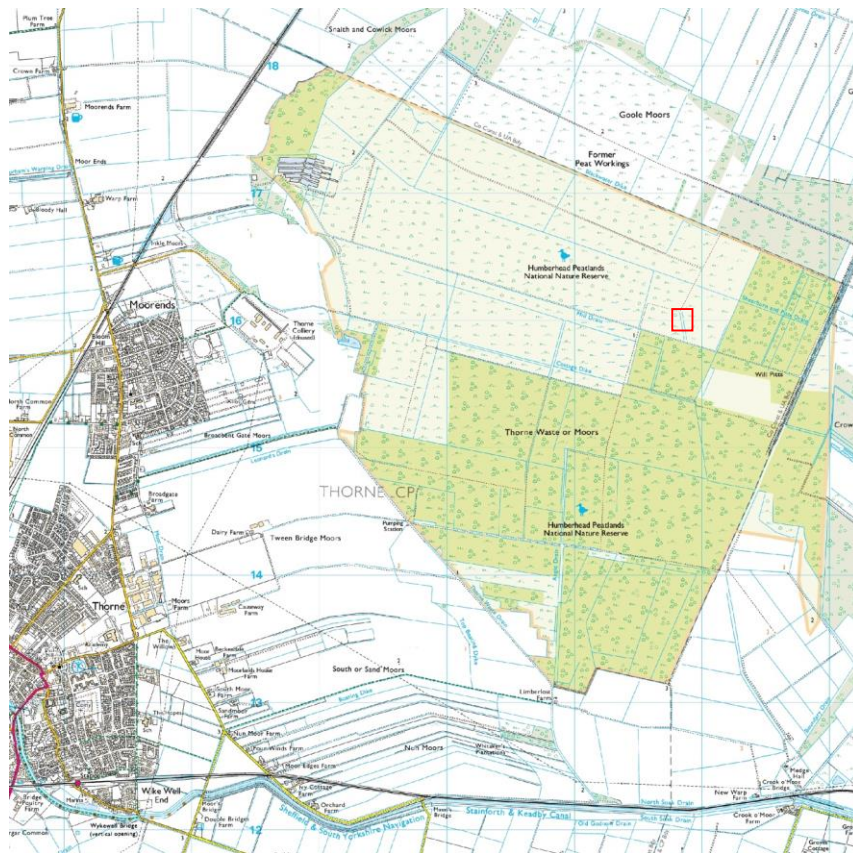
#### 4.7 Thorne Moor SAC

The Thorne Moor SSSI lies 8 km to the south of Goole in South Yorkshire. It comprises part of the Humberhead Peatlands National Nature Reserve - the largest area of raised bog wilderness in lowland Britain and was designated an SAC in 2005. A relic of the Humberhead wetlands, the site is characterised by substantial peat deposits that accumulated over millenia until peat became recognised as a major fuel resource in medieval times. In recent times peat from the site has been exploited for horticultural use. Extraction for horticulture became mechanised in the 1960s and continued until 2004. Over the last decade Natural England have overseen a process of rewetting with the aim of encouraging Sphagnum mosses and Cotton grasses and restoring the Moor as a fully functioning bog. The key monitored Natura 2000 habitats at the monitoring location are 'Degraded raised bogs' and 'Active raised bogs'.



For purposes of access, security and to provide a more stable platform for instruments masts and collectors, the meteorological/deposition site was established approximately 1 km to the north east, close to the main access track for the site.

**Figure 4.7.1 Thorne Moor and location of the Met/deposition station (red box)**



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**Figure 4.7.2 Aerial photograph (Google Earth) of the Thorne Moor site. Locations for the Meteorological/Deposition, and soil water monitoring sites indicated by blue and red symbols respectively.**



## 5. Data Analysis

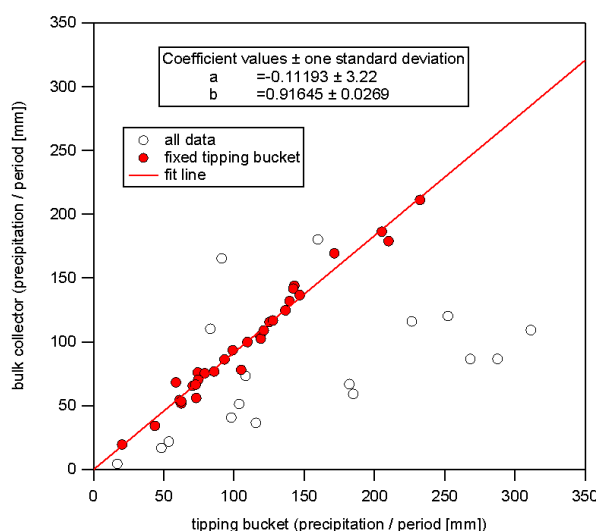
### 5.1 Bulk wet deposition

The atmospheric flux of chemical species collected by the WSL bulk rain gauges tends to be dominated by species in wet deposition, although some dry and particulate deposition onto the collector funnels is also incorporated. The net flux is often described as “bulk deposition”. However, to avoid confusion with “total deposition”, used later to represent the sum of deposition collected using this method and estimated dry deposition, we use the term “bulk wet deposition” to represent the bulk rain gauge deposition in this report.

Monthly bulk wet deposition loads of acid anions and base cations have been determined by multiplying concentrations of the monthly bulk samples by total precipitation recorded for the month. While bulk wet deposition gauges provide a robust measurement of the chemical precipitation composition, their aerodynamic properties are not ideal to quantify precipitation amount accurately. Over the first few months of deployment, problems were encountered with the automatic (tipping-bucket) rain gauges apparently over-recording rainfall at some sites. This was eventually attributed to “reed-switch bounce”, whereby the electrical contacts that come together on each tip of the tipping-bucket mechanism, bounce apart one or more times before making steady contact. This results in repeated electrical pulses for individual tips of the bucket, a consequent over-counting of the actual number of tips, and hence an over-estimate of the precipitation received. An adjustment was subsequently made to the recording software to eliminate this effect.

Comparison of monthly rainfall, as recorded by the rain gauges, with monthly bulk wet deposition volumes demonstrates that the software adjustment was effective in eliminating the problem. This is illustrated in Figure 5.1.1 with the red dots representing samples collected in the months following the adjustment.

**Figure 5.1.1. Relationship between monthly precipitation recorded by the bulk collectors and the automatic rain gauges. Open circles and red circles represent the pre- and post-adjustment periods respectively. The red line represents a linear regression through the post-adjustment points**





The slope of the relationship between rain gauge and bulk collector precipitation for the post-adjustment period (red line) was then used to infer monthly precipitation for the pre-adjustment samples, i.e. estimated monthly precipitation = bulk collector precipitation/0.916. The strength of the relationship confirms the high consistency of the dataset.

Monthly bulk wet deposition flux estimates were calculated separately for the two bulk collectors at each site. The estimates presented in Section 6 represent the mean of the two samples collected from each site over each month. Annual bulk non-seasalt SO<sub>4</sub> fluxes were determined from the annual seasalt SO<sub>4</sub> flux (following the common assumption that the entire annual sodium flux was derived from seasalt, and that the molar ratio of SO<sub>4</sub> to sodium in seasalt has a constant value of 0.0602) and subtracting this from the annual bulk SO<sub>4</sub> deposition flux. Annual bulk non-marine chloride fluxes were estimated using the same approach as above, but this time using a molar ratio of chloride to sodium in seasalt of 1.17. Monthly bulk wet deposition results for non-marine SO<sub>4</sub>, NO<sub>3</sub>, NH<sub>4</sub> and non-seasalt chloride, are presented in Section 6.3. Where small negative monthly bulk wet non-seasalt chloride estimates are recorded these could simply reflect the accuracy of measurement. However, persistently negative values are likely to reflect atmospheric processes. Seasalt NaCl can undergo dechlorination by nitric acid in the atmosphere via the substitution reaction  $\text{NaCl} + \text{HNO}_3 \rightarrow \text{NaNO}_3 + \text{HCl}$ . Differences in deposition rates of HCl and NaCl result in differences in their atmospheric lifetime and transport distance. As a consequence some Cl originating from seasalt may be deposited as dry HCl, resulting in an apparent Cl deficit in wet deposition (relative to Na). However, as total acid deposition is conserved, while the primary objective is to determine the total acid deposition flux, it was considered appropriate to treat both positive and negative non-seasalt chloride values as “real”. Thus a very small negative annual estimate at Thorne Moor was deducted from the total acidity estimate for the site rather than re-setting this value to zero.

## 5.2 Dry deposition

### 5.2.1 Dry deposition models

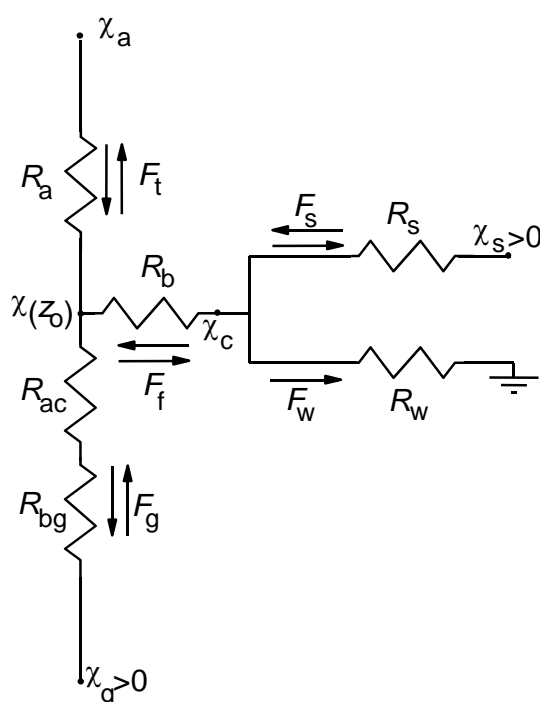
Dry deposition of gases, through the exchange of gases between the atmosphere and the land surface, can be inferred on the basis of measured gaseous concentrations above the surface of interest coupled with assumptions about the rate of transfer between the two systems derived from meteorological data and information on the state of the vegetation canopy. Ideally, high time-resolution concentration data (e.g. 1-hour) would be combined with measured information on turbulence, atmospheric stability, other meteorological parameters and the vegetation morphology.

In this report gaseous concentration data, derived from Gradko (diffusion) tubes or, in the case of NH<sub>3</sub>, Alpha samplers, have been used in combination with meteorological measurements to determine the exchange using two “Big Leaf”-based modelling routines: UK CBED (Smith et al., 2000; Vieno, 2005), and EMEP as used to inform the UNECE Convention of Long Range Transboundary Air Pollution (CLRTAP; Simpson et al., 2006). While most of the pollutants are thought to be only deposited, the CBED routine accounts for the bi-directional nature of NH<sub>3</sub>

exchange. However, over semi-natural vegetation the net exchange is thought to be from the atmosphere towards the ecosystem (via dry deposition).

The combination of monthly concentration data and half-hourly meteorological data mainly follows the approach of Flechard et al. (2011), who also provided a review of the structure and performance of UK CBED, EMEP, and two further, dry deposition models, as summarised briefly below. All surface-vegetation-atmosphere transfer (or SVAT) models are based on an electrical analogy that relates electrical current to potential difference and electrical resistance. Figure 5.2.1 shows the generic resistance framework that underpins the parameterisations used here.

**Figure 5.2.1. Big-leaf resistance framework for prediction of bi-directional exchange between vegetation and the atmosphere, allowing for two parallel exchange pathways with the vegetation (bi-directional exchange through the stomata and deposition to leaf surfaces (cuticles)), and bi-directional exchange with the ground.**



Essentially, the gas deposition flux is determined as the product of concentration at a reference height and a theoretical deposition velocity. Deposition velocity, in turn, is determined as the reciprocal of the sum of the resistances imposed by the key pathways from the atmosphere to surfaces and into plant foliage. These include the atmospheric aerodynamic resistance ( $R_a$ ) (characterising the efficiency of turbulent transfer), the resistance of a laminar sublayer of air surrounding a vegetated surface ( $R_b$ ), and resistance to uptake by the surface, or canopy ( $R_c$ ), as represented by a theoretical “big leaf”. For the gases considered here,  $R_c$  can be broken down further: exchange with the canopy is via two parallel pathways: deposition to the leaf surface (cuticle) via the cuticular resistance ( $R_w$ ) and exchange with the apoplastic

liquid within the leaf, through the stomatal bulk resistance ( $R_s$ ), which is sometimes modelled to act in series with a further (mesophyll) resistance. In addition, deposition to other plant parts (e.g. stems and bark) and ground surfaces may offer a further parallel pathway.

Calculation of aerodynamic resistance and sublayer resistance is determined in a similar manner across all models. The dry deposition calculations presented in this report assume neutral stratification throughout. This is consistent with the national application of the CBED model for the mapping of UK dry deposition on the grounds that the predominantly windy conditions over the UK mean that atmospherically “neutral” conditions normally dominate.

Most models do incorporate atmospheric stability corrections in the calculation of aerodynamic resistance which can be applied if suitable stability measurements are available (allowing, for example, for effects of stagnant surface conditions during temperature inversions). Sonic anemometer measurements of turbulence and sensible heat flux from which the atmospheric stability can be derived, are useful in this respect. These measurements were, however, not identified as critical during the scoping of the project.

Stomatal resistance is expressed per unit leaf area and is normally calculated using a light-response function, since stomatal opening and closing is strongly influenced by the availability of photosynthetically active radiation (PAR). In addition to PAR, this function is also dependent on the vapour pressure deficit of the atmosphere, plant water stress and air temperature. There is little consensus to date over the parameterisation of non-stomatal resistances, reflecting challenges of measurement and relatively large uncertainties. There are substantial differences between models in the way in which non-stomatal resistance to  $\text{NH}_3$  transfer is calculated, largely reflecting the different ecosystems and pollution climates in which  $\text{NH}_3$  flux measurements have been made. Indeed CBED employs a constant canopy resistance (of  $20 \text{ s m}^{-1}$ ) for forest and moorland canopies, while incorporating a variable water film resistance for grasslands and crops.

Exchange of  $\text{NO}_2$  in both the models applied here is modelled to be through downward transfer (i.e. deposition) only, and is mostly, or in the case of CBED, wholly, controlled by stomatal opening. There is ongoing debate whether there is a stomatal compensation point for  $\text{NO}_2$  and a non-zero  $\text{NO}_2$  concentration may exist in plant canopies, caused by the reaction of soil NO with  $\text{O}_3$ ; both effects limit deposition at low ambient concentrations. In the absence of a mechanistic model description, in the EMEP routine, the  $\text{NO}_2$  dry deposition flux is therefore assumed to fall to zero when ambient concentration falls below 4 ppb. For the purposes of this study monthly  $\text{NO}_2$  dry deposition flux estimates were derived from monthly mean concentration data and no allowance was made for periods during the diurnal cycle when concentrations might have exceeded this threshold. For sites and months when mean monthly EMEP  $\text{NO}_2$  concentrations are less than 4 ppb, application of a diurnally varying concentration field would be likely to result in non-zero, although small, flux estimates. Consequently, the mean for the two models (see Section 5.2.3) for such data points would also be slightly higher were a diurnal approach to be taken. In the dry deposition figures presented in Section 6, months where concentration data are missing are indicated with an asterisk in order to distinguish them from months where the EMEP model returned a flux of zero.

Both models used in this report use constant parameters for canopy height (measured during the vegetation surveys of summer 2011) and constant values of Leaf Area Index (LAI). Average canopy height for individual sites ranged from 9 cm to 33 cm with a mean of 20 cm

(Table 5.2.1). The LAI in this analysis has been set to 2.05 independent of season. This value was taken from the heavily studied moorland site at Auchencorth Moss, which is dominated by similar ericoid/graminoid vegetation to that found at the habitat monitoring sites.

**Table 5.2.1. Mean canopy heights (hc) recorded during the 2011 vegetation surveys.**

Site	Habitat	mean canopy height (hc) (cm)
Manchester Mosses SAC	bog	33
Cannock Chase SAC	heath	14
Cleddau Rivers SAC	bog	30
Usk Bat Sites SAC	bog	9
New Forest SAC	heath	10
Skipwith Common SAC	heath	15
Thorne Moor SAC	bog	29

### 5.2.2 Gap filling of meteorological data

Meteorological data are required to parameterise dry deposition modelling routines. During 2014 some stations experienced periods of battery power failure and some sensor failures - mostly the relative humidity (RH) and temperature (T) sensors, but also intermittently wind speed and direction.

Installation of more robust tipping bucket rain gauges, weekly data screening and site integrity inspections have improved the coverage of rainfall data in 2014, relative to previous years. Where tipping-bucket precipitation data were incomplete for any month at any site (Manchester Mosses, January 2014), precipitation for the month was estimated using the approach set out in Section 5.1. With respect to the other parameters listed in Table 5.2.2, we have adopted a similar approach to gap filling to that outlined in the 2012 and 2013 deposition reports using data obtained from the Skylink network (<http://skylinkweather.com/metar/metarmapindex.php>). The Skylink network provides air temperature, relative humidity, wind speed and wind direction for nearby locations that are essentially directly comparable with Habitats Monitoring Network meteorological measurements.

**Table 5.2.2. Local Skylink meteorological monitoring site used for gap filling, missing parameter and period of data loss with respect to 2014 data collection only.**

Project site	Corresponding Skylink network site	Parameter	Period of data loss
Manchester Mosses SAC	n/a	Precipitation	1/1/2014 to 13/1/2014
Cleddau Rivers SAC	n/a	Precipitation	1/1/2014 to 2/1/2014
Cleddau Rivers SAC	Milford Haven	All parameters – battery failure	9/12/2014 to 12/12/2014
Cleddau Rivers SAC	Milford Haven	Relative humidity and temperature	14/12/2014 to 31/12/2014
Cleddau Rivers SAC	Milford Haven	Wind speed and direction	7/7/2014 to 3/9/2014
New Forest	Southampton	All parameters – battery failure	26/11/2014 to 8/12/2014
Usk Bat Sites SAC	Rhymney Valley	Relative humidity	5/2/2014 to 5/3/2014
Usk Bat Sites SAC	Rhymney Valley	Relative humidity and temperature	5/12/2014
Usk Bat Sites SAC	Rhymney Valley	Wind speed and direction (Intermittent fault)	Throughout period
New Forest	Southampton Eastleigh	Relative humidity and temperature (Intermittent fault)	4/8/2014 to 7/11/2014
All sites		Various short term anomalies	Throughout period

Of the standard measurements provided by the habitats monitoring network weather stations, air temperature, relative humidity, windspeed and wind direction analogous measurements are covered by Skylink. Surface wetness, PAR and rainfall are not covered by Skylink sites. However, Skylink measurements are accompanied by “weather comments. Of these the following: 'T-STORM', 'DRIZZLE', 'DRIZZLE/RAIN', 'DRIZZLE/SNOW', 'FLURRIES', 'FOG', 'FOGGY', 'FR/DRIZ', 'MIST', 'FRZ.RAIN', 'GND FOG', 'H/DRIZZLE', 'H/RAIN', 'H/SNOW', 'HVY.RAIN', 'L/FOG', 'L/RAIN', 'L/SNOW', 'LGT.RAIN', 'LGT.SNOW', 'A FLURRY', 'A SHOWER', 'RAIN', 'RAIN AND SNOW', 'RAIN/DRIZZLE', 'RAIN/SNOW', 'SNOW', 'SNOW/DRIZZLE', 'SNOW/FOG', 'SNOW/RAIN', and 'DNS FOG', were interpreted as the weather being "Wet"; Whereas, 'CLOUDY', 'M/CLOUDY', 'P/CLOUDY', 'M/CLEAR', 'CLEAR', 'M/SUNNY', 'SUNNY', 'P/SUNNY', 'SOME CLOUDS', and 'CLOUDS AND SUN' were interpreted as the weather being "Dry".

To inform solar radiation intensity: 'T-STORM', 'CLOUDY', 'DNS FOG', 'DRIZZLE', 'DRIZZLE/RAIN', 'DRIZZLE/SNOW', 'FLURRIES', 'FOG', 'FOGGY', 'FR/DRIZ', 'MIST', 'FRZ.RAIN', 'GND FOG', 'H/DRIZZLE', 'H/RAIN', 'H/SNOW', 'HVY.RAIN', 'L/FOG', 'L/RAIN', 'L/SNOW', 'LGT.RAIN', 'LGT.SNOW', 'A FLURRY', 'A SHOWER', 'RAIN', 'RAIN AND SNOW', 'RAIN/DRIZZLE', 'RAIN/SNOW', 'SNOW', 'SNOW/DRIZZLE', 'SNOW/FOG', and 'SNOW/RAIN' were interpreted as the weather being "Dull"; 'M/CLOUDY' and 'P/CLOUDY'; as “Partial”;

'M/CLEAR' and 'CLEAR'; as "Other"; and 'M/SUNNY', 'SUNNY', 'P/SUNNY', 'SOME CLOUDS', and 'CLOUDS AND SUN'; were interpreted as indicating "Bright" conditions.

As with the processing of the data for previous years, gap filling of missing air temperature, wind speed, direction and relative humidity data for 2013 was achieved by deriving site-specific monthly linear regression relationships between each Skylink and Habitats Monitoring Network parameter.

i.e. Parameter for network site in month-n = Skylink Parameter in month-n x gradient + intercept.

The gradients and intercepts were then used to derive the parameter for the Habitats Monitoring Network sites, when missing, using data from the local Skylink site. In the case of wind direction – data were replaced directly and not modelled, on the assumption that wind direction data are likely to be regionally consistent.

Mean PAR data for Habitats Monitoring Network sites was related to month (1-12), hour of the day (1-24) and brightness determined at the local Skylink site (i.e. Bright, Partial, Dull, Other). Where missing, PAR was then modelled as the mean value recorded for each combination of comparable conditions (i.e. month, time of the day and brightness as described on Skylink).

Similarly, average Surface Wetness values recorded at Habitats Monitoring Network sites was determined for each combination of Dry/Wet, Brightness, RH (to nearest 10%), Air Temperature (to nearest 5 °C) recorded at the local Skylink site, and gaps were then filled accordingly. Average surface wetness values (Range from 0 to 100) greater than 50 were taken to indicate Wet (100) conditions. Values of less than 50 were taken to indicate no surface wetness (0). Where surface wetness data were not available a value was inferred from on the basis of relative humidity, air temperature and brightness.

Skylink data are only available on an hourly frequency whereas the dry deposition calculation spreadsheets require data at half hourly frequency. Half hourly data for the gap filling exercise were therefore interpolated as the mean of the immediately preceding and following hourly values.

### 5.2.3 Dry deposition estimates

The CBED and EMEP models were parameterised within a Microsoft Excel Spreadsheet. Gaseous concentrations (based on blank corrected NH<sub>3</sub> and SO<sub>2</sub>, and uncorrected NO<sub>2</sub>) are measured at each site in triplicate at monthly intervals. The means of these replicated monthly concentrations for each chemical compound were combined with the 30-minute meteorological data to compute monthly flux estimates. SO<sub>2</sub> samples recorded at below the limit of detection were set to half the detection limit (set at 0.4 ppb) prior to calculation of monthly mean concentrations. The methodology followed the approach by Flechard et al. (2011), except that, due to more limited input parameters,

- a) turbulence (parameterised by friction velocity,  $u_*$ ) was estimated from a combination of measured wind speed and canopy height using the relationship:  
$$u_* = u(z-d) \times k / \ln[(z-d)/z_0]$$
 where  $u$  is the measured wind speed,  $z$  is the measurement

height,  $d$  is the zero plane displacement height (estimated as  $2/3 \times h_c$ ) and  $z_0$  is the roughness height (estimated as  $0.1 \times h_c$ ); and

b) stability was assumed to be neutral.

Average monthly half hourly estimates of  $\text{SO}_2$ ,  $\text{NH}_3$  and  $\text{NO}_2$  deposition were generated for both models, from which single monthly mean fluxes were calculated in units of  $\text{ng m}^{-2} \text{s}^{-1}$ . For the monthly dry deposition calculations presented in Section 6.2, estimates were then scaled up to provide monthly deposition estimates in units of  $\text{kg ha}^{-1}$  and  $\text{keq ha}^{-1}$ . To simplify this procedure each month of the year was treated as representing an equal number of days (i.e.  $365.25/12 = 30.4$  days).

The bar plots in Section 6.2 represent the monthly means of the CBED and EMEP models. In common with the 2012 data there was reasonably good agreement between CBED and EMEP models for  $\text{SO}_2$  and  $\text{NH}_3$  deposition, with CBED deriving larger deposition for  $\text{NH}_3$ , but considerably smaller deposition for  $\text{SO}_2$  than the EMEP routine. This can be traced to the differences in the parameterisation of the cuticular resistance, which is lower in the EMEP routine overall. In addition, in the EMEP model the cuticular resistance for  $\text{SO}_2$ , and also for  $\text{NH}_3$ , depends on the annual average air concentration ratio of  $\text{SO}_2 / \text{NH}_3$  and therefore differs between sites. This effect on the chemical climate of the site reflects the potential of deposited  $\text{SO}_2$  to be neutralised by  $\text{NH}_3$  (and *vice versa*) which counteracts the tendency for deposition to be self-limiting by reducing (or increasing) the leaf water pH. The  $\text{SO}_2/\text{NH}_3$  ratio ranged from 0.5 at Cannock Chase to 1.9 at the New Forest site, where the EMEP model predicted the  $\text{SO}_2$  deposition that was most similar to the CBED routine.

Estimates for  $\text{NO}_2$  deposition differed more significantly between the two parameterisations. As discussed in Section 5.2.1, there is substantial debate about the presence of a plant compensation point for  $\text{NO}_2$  deposition which would reduce uptake of  $\text{NO}_2$  by the plant. In addition,  $\text{NO}$  emitted from the soil can be converted chemically to  $\text{NO}_2$  by reaction with ozone ( $\text{O}_3$ ), resulting in a non-zero concentration of  $\text{NO}_2$  in the canopy, which reduces transport of atmospheric  $\text{NO}_2$  towards the plant. To account for these effects the EMEP parameterisation sets the deposition to zero for  $\text{NO}_2$  concentrations below 4 ppb, whereas CBED does not. This leads to a smaller deposition predicted at sites where this level is not reached during individual months. This discrepancy is consistent with the model comparison of Flechard et al. (2011) and reflects the scientific uncertainty in modelling  $\text{NO}_2$  deposition.

Comparisons of monthly mean  $\text{SO}_2$  concentrations determined by Gradko diffusion tubes with mean monthly hourly  $\text{SO}_2$  gas analyser measurements at the Bottesford air quality monitoring site indicated that the diffusion tube measurements were consistently lower – of an order of circa 50%. This discrepancy was apparent throughout the three years of data available which included periods where Gradko measurements were above the detection limit and more recently when measurements fell below detection and were, therefore, adjusted to 0.2 ppb. It was also noted that similar differences were observed when Gradko-based  $\text{SO}_2$  concentrations for the seven Habitats Monitoring Network sites were compared with estimates generated by the UK Air Pollution Information system (APIS) – which are based on spatial extrapolations of CEH DELTA (DENuder for Long Term Atmospheric sampling) gas sampler measurements made on the UK Automatic Urban and Rural Network (AURN). To allow, therefore, for potential underestimates of  $\text{SO}_2$  deposition at HMN sites resulting from the use of diffusion tubes, Section 6.7 of this report provides alternative estimates of total sulphur

deposition and total acid deposition upwards adjustment of SO<sub>2</sub> dry deposition estimates using a fixed factor of 2.0.

### 5.3 Annual deposition calculation

Annual (2012-2014) bulk wet deposition fluxes of SO<sub>4</sub>, NO<sub>3</sub> and NH<sub>4</sub> and Cl, and annual dry deposition fluxes of SO<sub>2</sub>, NO<sub>2</sub> and NH<sub>3</sub> have been calculated by summing the monthly flux values. Where monthly measurements were missing, e.g. in the case of the June 2012 NO<sub>2</sub> values that were invalid due to a faulty batch of diffusion tubes provided by the manufacturer, flux data for the available months were summed before the resulting value was scaled up to represent a full year's deposition (i.e. multiplied by 12/11 when data for one month was missing). Annual non-seasalt SO<sub>4</sub> and Cl deposition estimates were derived from the annual fluxes of SO<sub>4</sub>, Cl and Na using the ratios between the former two ions and Na in seasalt stated in Section 5.1.

For purposes of comparison of the contributions of wet, dry, oxidised and reduced deposition the mean of CBED and EMEP estimates was used to represent the dry fluxes. Deposition fluxes based on the use of either CBED or EMEP dry deposition are provided in Appendix 1. Results in Section 6.4 are presented both in terms of deposited acidity (keq ha<sup>-1</sup> yr<sup>-1</sup>) (non-marine sulphur and nitrogen species) and deposited nitrogen (kg N ha<sup>-1</sup> yr<sup>-1</sup> and keq ha<sup>-1</sup> yr<sup>-1</sup>), and included modified fluxes following application of a correction factor of 2.0 to dry SO<sub>2</sub> estimates.

Section 6.4 includes annual estimates of nitric acid (HNO<sub>3</sub>), SO<sub>4</sub>, NO<sub>3</sub> and NH<sub>4</sub> aerosol deposition. Concentrations of gaseous HNO<sub>3</sub> and aerosol SO<sub>4</sub>, NO<sub>3</sub> and NH<sub>4</sub> are not measured at the target sites. However, these compounds are not emitted directly, but rather are formed in the atmosphere through the oxidation of NO<sub>x</sub> and SO<sub>x</sub>, and through reactions of these oxidation products with NH<sub>3</sub>. Thus, concentration fields of these secondary products are less variable than those of primary emissions. Monthly concentrations of these compounds at the target sites can therefore be reasonably estimated by interpolation of the monthly measurements from the national monitoring network (AGANET).

Measurements of HNO<sub>3</sub> and aerosol SO<sub>4</sub>, NO<sub>3</sub> and NH<sub>4</sub> are made using the CEH DELTA (DENuder for Long-Term Atmospheric sampling) system (see [http://pollutantdeposition.defra.gov.uk/ammonia\\_methodology](http://pollutantdeposition.defra.gov.uk/ammonia_methodology) for more details). The system is based around the concept of a single bore glass denuder for sampling trace gases (Ferm 1979). When a laminar air stream passes through the denuder coated on the inside with an acid coating such as citric acid, ammonia is captured by the acid walls (to be later extracted in the laboratory), while aerosols pass through and can be collected by aerosol filters placed downstream of the denuder. Conversely, an alkaline coating on the denuders will collect acid gases such as HNO<sub>3</sub> and HCl. The separation of aerosol from gaseous components is achieved due to the much more rapid diffusion of gaseous species to the tube wall compared with that of particles. It is important to note that recent investigations suggest that DELTA denuder HNO<sub>3</sub> measurement may be subject to overestimation by up to a factor of 2 in some circumstances as a result of cross interference from nitrogen oxides. Under a Defra-funded contract CEH are currently carrying out a comparison of the standard denuder coating with a KCl coating, which does not generate interference but is not appropriate for measurement of HCl.



Dry deposition estimates of the aerosol,  $\text{HNO}_3$  and  $\text{HCl}$  species were obtained by driving a similar dry deposition model as used for  $\text{NH}_3$ ,  $\text{NO}_2$  and  $\text{SO}_2$  with these monthly concentration values. The general parameterisations implemented in the CBED and EMEP models (Flechard et al., 2011) were used, but differ from the parameterisations of  $\text{NH}_3$ ,  $\text{NO}_2$  and  $\text{SO}_2$  to take into account different deposition mechanisms. Rates of deposition of  $\text{NH}_3$ ,  $\text{SO}_2$  and  $\text{NO}_2$  to leaf surfaces and through leaf stomata depend on species-specific solubility, reactivity and molecular diffusivity.  $\text{HNO}_3$  is usually assumed to deposit to leaf surfaces very efficiently, with a near-zero canopy resistance. Particles have additional mechanisms with which they can overcome the sub-laminar boundary layer that forms around all surface elements, i.e. interception, impaction and gravitational settling. These processes are approximated in different ways in the CBED and EMEP routines (Flechard et al., 2011).  $\text{HCl}$  is modelled analogously to  $\text{HNO}_3$  using a very low  $R_c$  value. The  $R_b$  term for  $\text{HCl}$  is adjusted to account for the difference in the molecular diffusivities of  $\text{HCl}$  and  $\text{HNO}_3$ .

## 5.4 Tabulation of additional results

As required by the deposition monitoring protocol approved by the Environment Agency in September 2010, the following results are presented in Table 6.1.1.

- Monthly SO<sub>2</sub> concentrations
- Monthly NO<sub>x</sub>, NO<sub>2</sub> and NO concentrations
- Monthly NH<sub>3</sub> concentrations

The annual average values of these parameters for each site are shown in Table 6.1.2.

Further to the requirements of the ecological monitoring protocol, the monthly averages of the following soil solution chemistry measurements are presented in Section 6.5.

- Sulphate
- Nitrate
- Base cations (sodium, potassium, calcium and magnesium)
- pH
- Dissolved organic carbon
- Chloride
- Ammonium
- Aluminium
- Phosphorus

The annual average values of these parameters for each site are shown in Table 6.5.2.

An electronic appendix is also provided, containing the full set of monitoring results, namely:

- Individual diffusion tube measurements of gaseous concentrations of SO<sub>2</sub>, NO<sub>x</sub> and NO<sub>2</sub>, and ALPHA sampler measurements for NH<sub>3</sub> for each month
- Individual bulk wet deposition chemistry concentration measurements of sodium, potassium, calcium, magnesium, chloride, nitrate (as nitrogen), ammonium (as nitrogen), sulphate (as sulphur) and phosphate (as phosphorus), together with measurements of pH and conductivity.
- Individual soil solution chemistry concentration measurements , as listed above with reference to Section 6.5, together with conductivity measurements.
- Individual tipping bucket and bulk collector precipitation measurements

The appendix also provides details of data rejected due to contamination or identified as clearly erroneous.

## 6. Results

In the following sections raw data and bulk and dry deposition estimates for habitat monitoring sites for 2013 are presented for sulphur and nitrogen species in addition to soil solution chemistry parameters. These include:

Section 6.1. Monthly gaseous concentration measurements for 2014 comprising: nitrogen dioxide ( $\text{NO}_2$ ); nitrogen oxides ( $\text{NO}_x$ ); nitric oxide (NO) (calculated as the difference between  $\text{NO}_x$  and  $\text{NO}_2$ ); blank corrected sulphur dioxide ( $\text{SO}_2$ ), in parts per billion; and, blank corrected ammonia ( $\text{NH}_3$ ) in microgrammes per metre cubed.

Section 6.2. Monthly modelled dry deposition fluxes (using CBED and EMEP dry deposition modelling routines) for 2014 expressed graphically in terms of monthly flux ( $\text{keq ha}^{-1} \text{ month}^{-1}$ ) and ( $\text{kg N ha}^{-1} \text{ month}^{-1}$ ).

Section 6.3. Monthly bulk wet deposition for 2014 expressed graphically in terms of monthly flux ( $\text{keq ha}^{-1} \text{ month}^{-1}$ ) and ( $\text{kg N ha}^{-1} \text{ month}^{-1}$ ) calculated by multiplying monthly mean concentrations by estimated precipitation.

Section 6.4. Graphical (2013 only) and tabulated (2012-2014) summaries of the relative contributions of wet and dry deposition to total annual nitrogen, sulphur and chloride fluxes, and a comparison of the relative contributions of sulphur, nitrogen and chloride deposition to total acidity.

Section 6.5. Soil solution chemistry analysis for 2014 comprising: pH; and concentrations of nitrate (as nitrogen), ammonium (as nitrogen), sulphate (as sulphur), phosphate (as phosphorous), chloride, sodium, calcium, potassium, magnesium, aluminium and dissolved organic carbon (DOC), in milligrams per litre.

The full results are tabulated in the electronic Appendix that accompanies this report.

Section 6.6 provides a qualitative comparison of summary deposition and soil solution chemistry data for the three years of complete data, and considers possible reasons for any clear differences between the two years.

Section 6.7 considers flux estimate uncertainties associated with a possible underestimation of  $\text{SO}_2$  concentrations using diffusion tubes, and potential implications of diurnal variation in  $\text{SO}_2$  and  $\text{NO}_2$  concentrations

## 6.1 Gaseous concentrations

**Table 6.1.1 Monthly mean concentrations of gaseous concentrations for 2014**

n.b. NO derived from difference between NO<sub>x</sub> and NO<sub>2</sub> (negative values set to zero for calculation of monthly means). No data are available for oxidised N gas species for Thorne Moor for the period September to November 2013 due to an infestation of the Gradko tubes with spiders. Individual SO<sub>2</sub> samples recorded as below limit of detection set to 0.2 ppb (i.e. half the detection limit) for calculation of monthly means. Data for SO<sub>2</sub> and NH<sub>3</sub> have been blank corrected (see Section 3.3)

Site	Month	NO <sub>2</sub> (ppb)	NO <sub>x</sub> (ppb)	NO (ppb)	SO <sub>2</sub> (ppb)	NH <sub>3</sub> (ug/m3)
Manchester Mosses	Jan-14	11.12	13.63	2.51	0.200	0.575
Manchester Mosses	Feb-14	9.58	13.32	3.74	0.227	1.202
Manchester Mosses	Mar-14	10.87	12.16	1.29	0.247	1.550
Manchester Mosses	Apr-14	4.56	9.54	4.98	0.200	1.927
Manchester Mosses	May-14	6.42	9.26	2.84	0.200	0.882
Manchester Mosses	Jun-14	7.19	10.95	3.76	0.200	0.876
Manchester Mosses	Jul-14	5.35	8.07	2.72	0.200	0.603
Manchester Mosses	Aug-14	5.73	8.41	2.67	0.210	1.114
Manchester Mosses	Sep-14	9.27	13.17	3.90	0.367	0.812
Manchester Mosses	Oct-14	7.90	11.88	3.98	0.200	1.001
Manchester Mosses	Nov-14	13.23	19.58	6.35	0.200	0.562
Manchester Mosses	Dec-14	9.58	13.33	3.75	0.200	0.419
Cannock Chase	Jan-14	11.53	15.07	3.54	0.200	0.550
Cannock Chase	Feb-14	9.04	14.18	5.14	0.200	0.792
Cannock Chase	Mar-14	9.62	12.96	3.34	0.200	2.506
Cannock Chase	Apr-14	6.45	7.90	1.45	0.200	2.426
Cannock Chase	May-14	5.79	9.19	3.40	0.200	lost sample
Cannock Chase	Jun-14	5.38	10.27	4.89	0.597	1.140
Cannock Chase	Jul-14	5.40	8.41	3.01	0.200	1.902
Cannock Chase	Aug-14	5.13	6.71	1.58	0.200	1.895
Cannock Chase	Sep-14	7.72	11.34	3.62	0.827	1.752
Cannock Chase	Oct-14	10.48	12.48	2.00	0.200	0.989
Cannock Chase	Nov-14	14.53	16.66	2.12	0.200	0.600
Cannock Chase	Dec-14	8.33	10.50	2.17	0.200	0.627
Cleddau Rivers	Jan-14	1.49	3.29	1.80	0.200	0.274
Cleddau Rivers	Feb-14	0.94	2.79	1.85	0.200	0.350
Cleddau Rivers	Mar-14	1.86	5.13	3.27	0.200	1.084
Cleddau Rivers	Apr-14	1.11	3.53	2.42	0.200	0.813
Cleddau Rivers	May-14	1.39	5.62	4.23	0.200	0.580
Cleddau Rivers	Jun-14	1.10	6.28	5.18	0.200	1.052
Cleddau Rivers	Jul-14	1.11	4.02	2.91	0.200	1.062
Cleddau Rivers	Aug-14	0.82	4.18	3.36	0.200	0.612
Cleddau Rivers	Sep-14	1.47	4.61	3.14	0.503	0.617
Cleddau Rivers	Oct-14	1.09	3.85	2.76	0.200	0.335
Cleddau Rivers	Nov-14	3.77	5.10	1.33	0.200	0.289
Cleddau Rivers	Dec-14	0.78	2.39	1.61	0.200	0.274
Usk Bat Sites	Jan-14	6.09	7.54	1.44	0.200	0.140
Usk Bat Sites	Feb-14	5.14	6.76	1.63	0.200	0.099
Usk Bat Sites	Mar-14	4.53	7.64	3.11	0.200	0.813
Usk Bat Sites	Apr-14	3.02	6.47	3.44	0.200	0.629
Usk Bat Sites	May-14	3.29	8.21	4.93	0.200	0.367
Usk Bat Sites	Jun-14	2.41	7.25	4.84	0.200	lost sample
Usk Bat Sites	Jul-14	2.22	5.28	3.06	0.200	0.499
Usk Bat Sites	Aug-14	2.28	5.97	3.69	0.200	0.219
Usk Bat Sites	Sep-14	2.96	6.75	3.79	1.110	0.704
Usk Bat Sites	Oct-14	4.65	5.77	1.11	0.200	0.197
Usk Bat Sites	Nov-14	5.25	8.97	3.72	0.200	0.148

Usk Bat Sites	Dec-14	5.55	4.27	-1.28	0.470	0.042
New Forest	Jan-14	5.91	8.06	2.15	0.200	0.145
New Forest	Feb-14	3.57	5.83	2.25	0.200	0.224
New Forest	Mar-14	9.04	14.68	5.64	0.200	1.092
New Forest	Apr-14	5.13	7.74	2.61	0.200	1.283
New Forest	May-14	4.69	7.03	2.34	0.200	0.652
New Forest	Jun-14	4.45	8.07	3.61	0.263	0.753
New Forest	Jul-14	3.60	6.08	2.48	0.297	0.857
New Forest	Aug-14	3.70	6.83	3.13	0.200	0.675
New Forest	Sep-14	7.00	11.63	4.63	0.937	0.429
New Forest	Oct-14	3.85	6.64	2.80	0.200	0.287
New Forest	Nov-14	10.77	14.65	3.87	0.200	0.213
New Forest	Dec-14	3.82	5.24	1.42	0.200	0.148
Skipwith Common	Jan-14	12.69	13.67	0.99	0.513	0.754
Skipwith Common	Feb-14	9.94	11.02	1.08	0.643	1.008
Skipwith Common	Mar-14	7.66	8.93	1.27	0.333	3.051
Skipwith Common	Apr-14	4.90	8.28	3.38	0.200	1.932
Skipwith Common	May-14	4.38	8.72	4.34	0.200	1.259
Skipwith Common	Jun-14	3.45	7.25	3.81	0.463	1.028
Skipwith Common	Jul-14	3.44	6.04	2.59	0.460	1.412
Skipwith Common	Aug-14	3.78	6.44	2.66	0.200	1.422
Skipwith Common	Sep-14	5.25	8.43	3.18	0.337	1.273
Skipwith Common	Oct-14	8.05	10.66	2.62	0.377	1.196
Skipwith Common	Nov-14	10.79	13.53	2.74	0.200	0.365
Skipwith Common	Dec-14	9.69	11.87	2.17	0.493	0.737
Thorne Moor	Jan-14	12.12	13.92	1.80	0.200	0.287
Thorne Moor	Feb-14	8.63	12.28	3.65	0.200	0.574
Thorne Moor	Mar-14	9.34	12.18	2.84	0.513	2.444
Thorne Moor	Apr-14	5.02	8.64	3.61	0.200	1.862
Thorne Moor	May-14	5.25	8.19	2.94	0.200	0.667
Thorne Moor	Jun-14	4.65	4.87	0.23	0.603	0.832
Thorne Moor	Jul-14	4.43	6.60	2.18	0.637	1.321
Thorne Moor	Aug-14	4.27	7.11	2.83	0.393	0.710
Thorne Moor	Sep-14	6.46	10.66	4.20	0.873	1.736
Thorne Moor	Oct-14	7.59	9.77	2.18	0.200	0.615
Thorne Moor	Nov-14	10.35	12.65	2.31	0.200	0.907
Thorne Moor	Dec-14	10.47	10.71	0.24	0.393	0.282

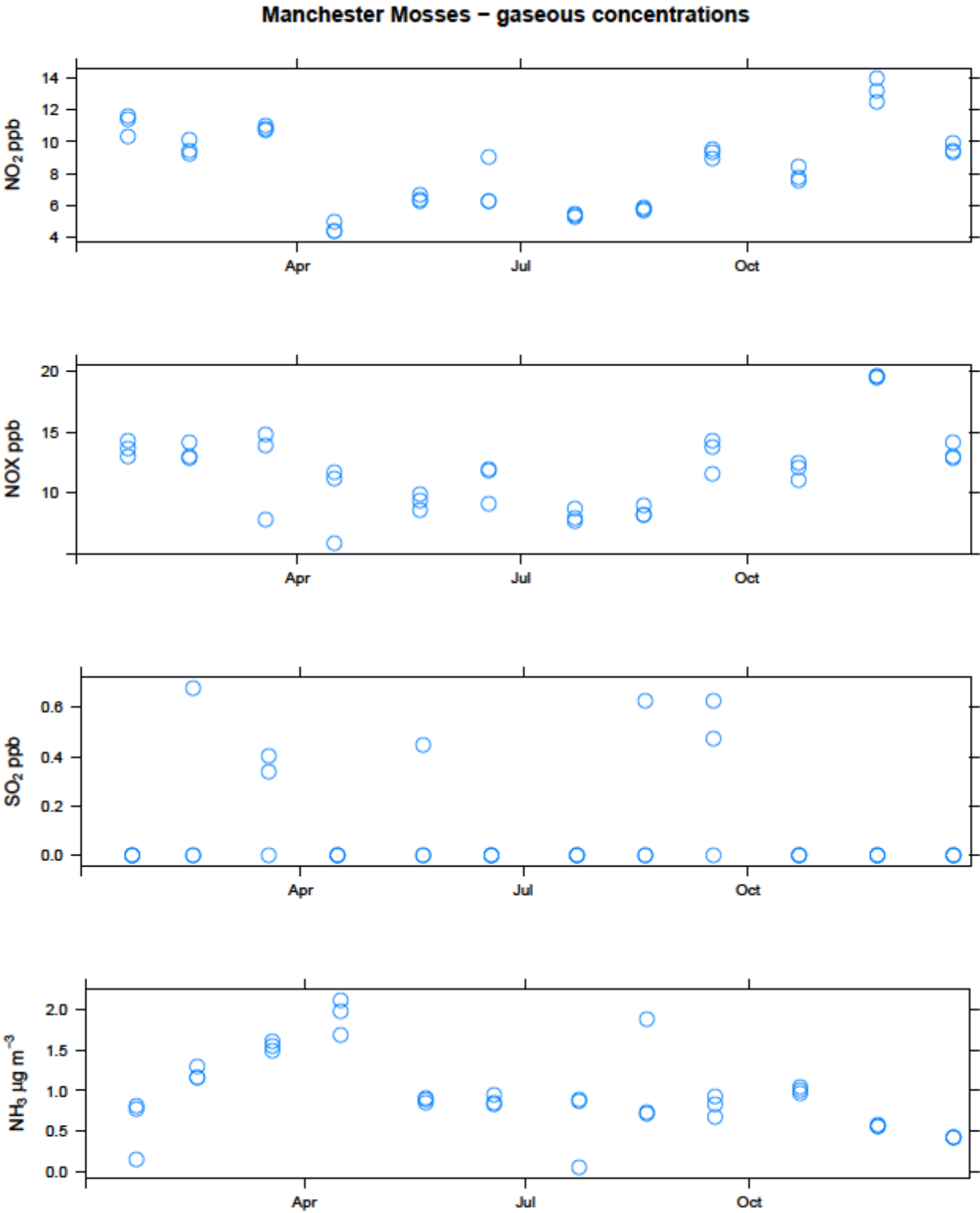
**Table 6.1.2 Annual mean concentrations of gaseous concentrations 2012-2014**

Derived from monthly mean data. n.b. NO derived from difference between NO<sub>x</sub> and NO<sub>2</sub> (negative values set to zero for calculation of annual means). Individual SO<sub>2</sub> samples recorded as below limit of detection set to 0.2 ppb (i.e. half the detection limit) for calculation of annual means.

Project site	Year	SO <sub>2</sub> (ppb)	NO <sub>2</sub> (ppb)	NO <sub>x</sub> (ppb)	NO (ppb)	NH <sub>3</sub> (µg m <sup>-3</sup> )
Manchester Mosses SAC	2012	0.39	9.47	13.7	4.23	0.83
	2013	0.37	8.42	12.42	4.00	1.18
	2014	0.22	8.40	11.94	3.54	0.96
Cannock Chase SAC	2012	0.33	9.14	12.14	3.04	1.18
	2013	0.37	8.95	11.37	2.42	1.64
	2014	0.29	8.28	11.31	3.02	1.38
Cleddau Rivers SAC	2012	0.32	1.72	4.52	2.81	0.57
	2013	0.24	1.92	4.23	2.31	0.72
	2014	0.23	1.41	4.23	2.82	0.61
Usk Bat Sites SAC	2012	0.39	3.83	6.56	2.73	0.32
	2013	0.26	3.49	6.40	2.91	0.35
	2014	0.30	3.95	6.74	2.79	0.35
New Forest SAC	2012	0.54	5.85	8.37	2.58	0.43
	2013	0.50	6.37	9.15	2.78	0.58
	2014	0.28	5.46	8.54	3.08	0.56
Skipwith Common SAC	2012	0.47	6.80	9.46	2.78	1.24
	2013	0.66	6.43	9.22	2.79	1.12
	2014	0.37	7.00	9.57	2.57	1.29
Thorne Moor SAC	2012	0.74	8.31	11.40	3.09	0.92
	2013	0.49	6.80	9.50	2.70	0.81
	2014	0.38	7.38	9.80	2.42	1.02

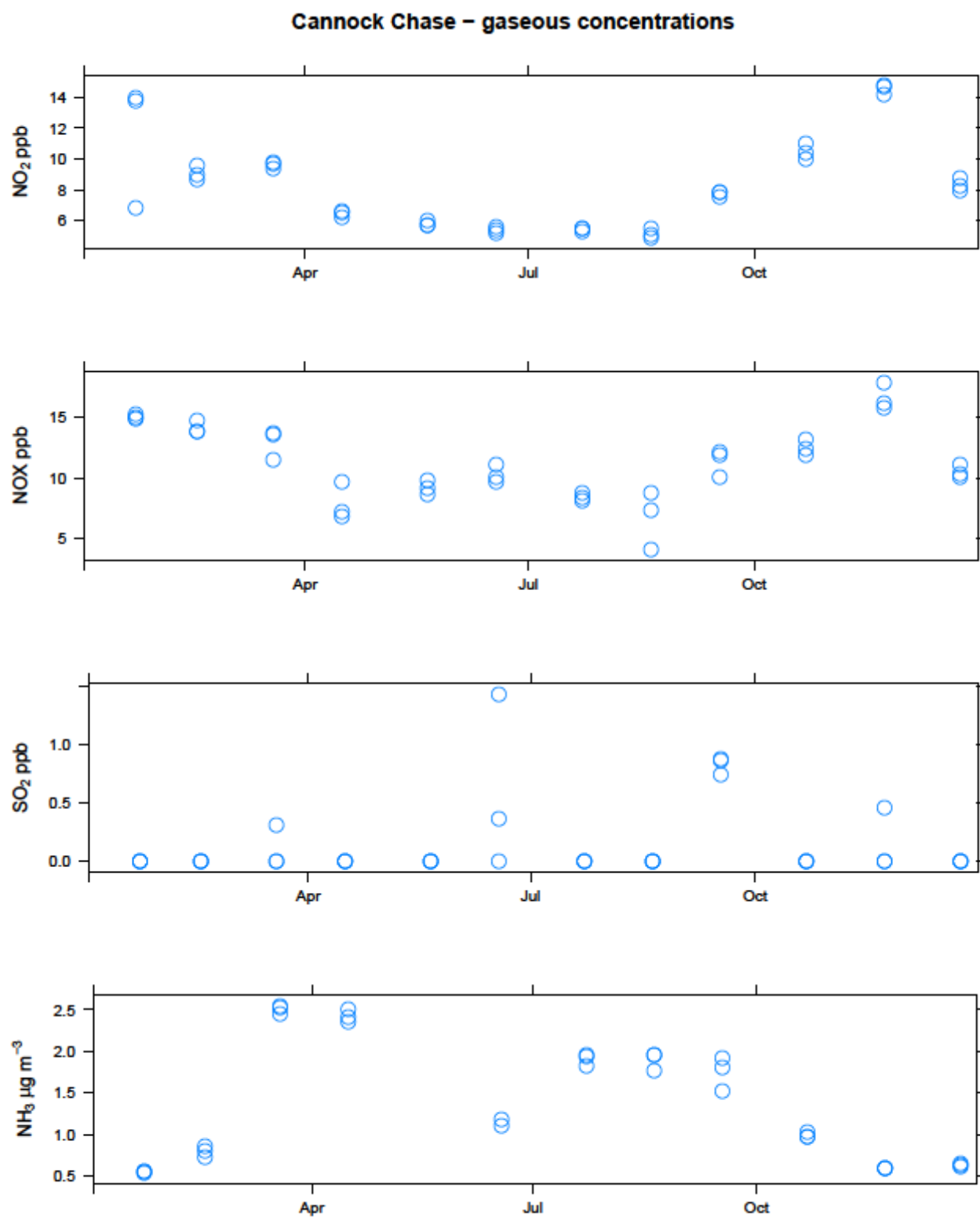
Figure 6.1.1 Gaseous concentrations (2014): Manchester Mosses SAC

SO<sub>2</sub> samples recorded as below limit of detection set to zero.



**Figure 6.1.2 Gaseous concentrations (2014): Cannock Chase SAC**

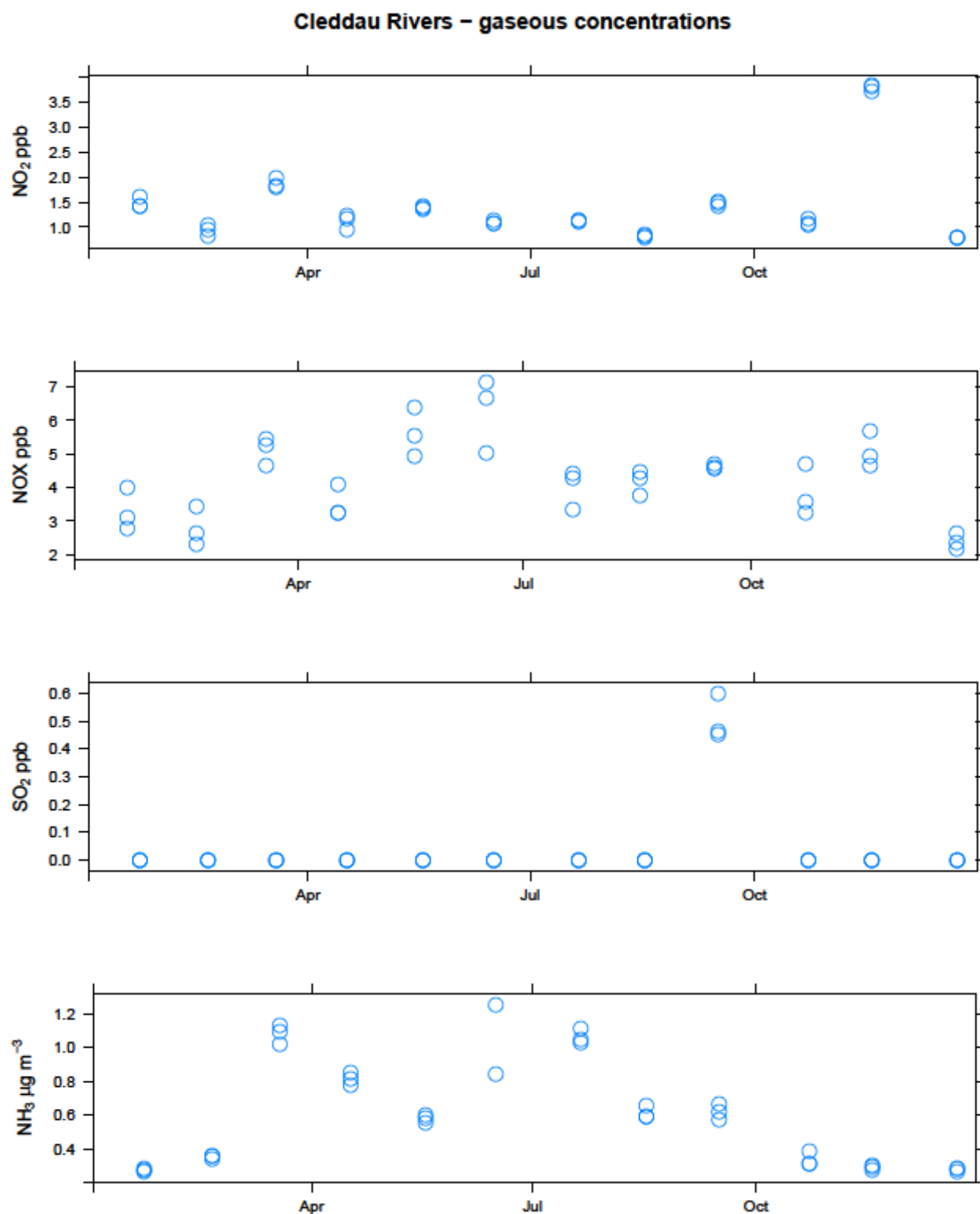
SO<sub>2</sub> samples recorded as below limit of detection set to zero.





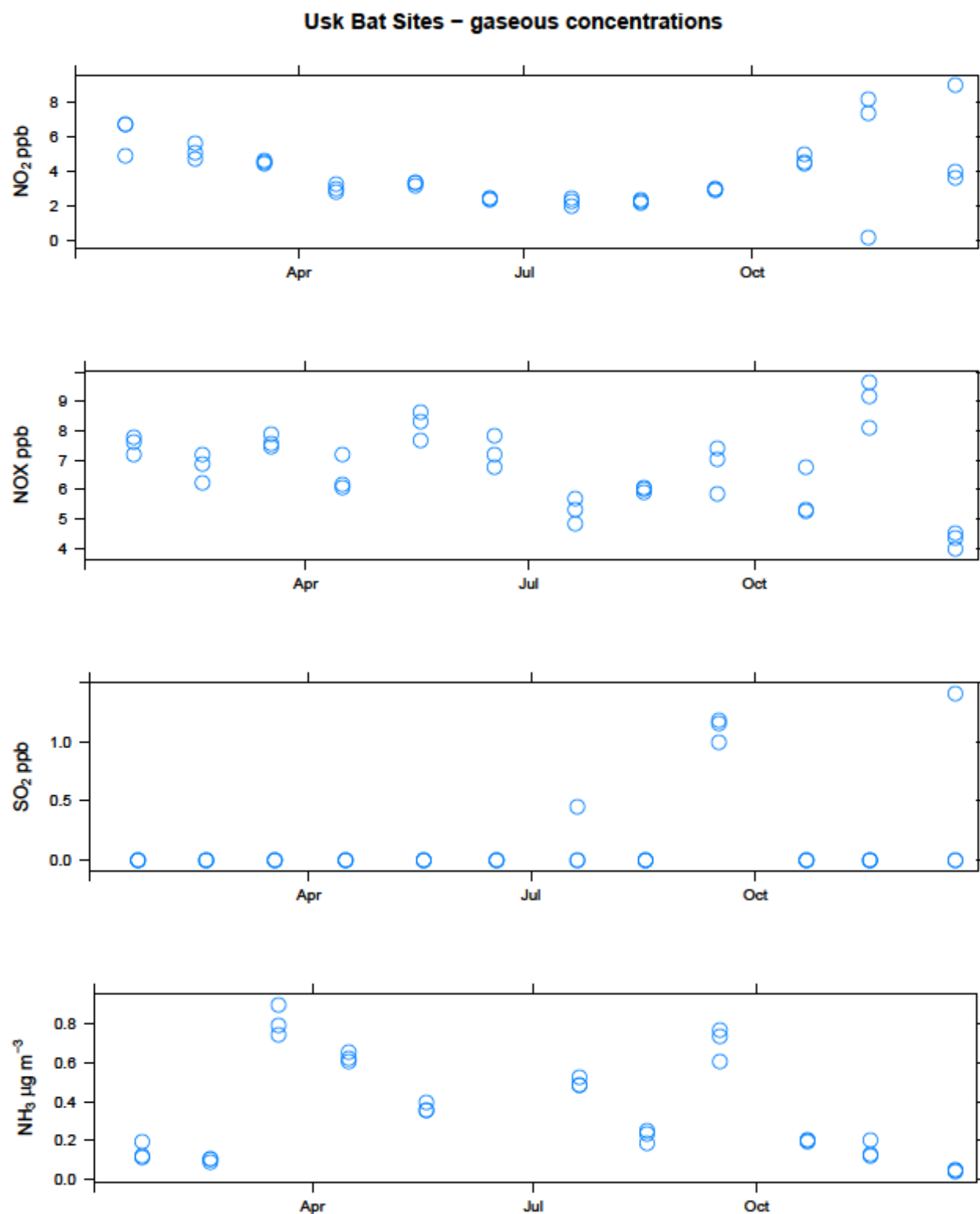
**Figure 6.1.3 Gaseous concentrations (2014): Cleddau Rivers SAC**

SO<sub>2</sub> samples recorded as below limit of detection set to zero.



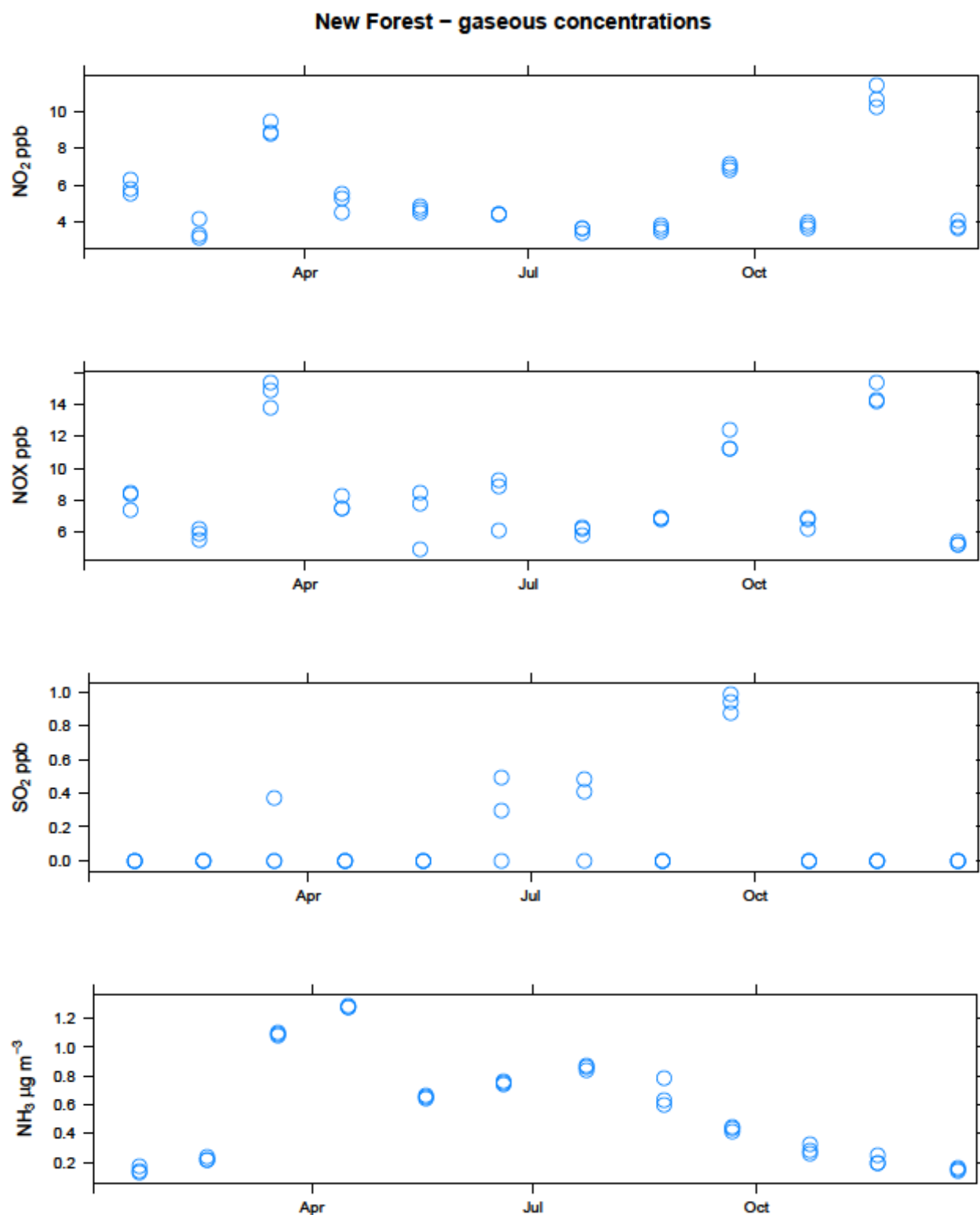
**Figure 6.1.4 Gaseous concentrations (2014): Usk Bat sites SAC**

SO<sub>2</sub> samples recorded as below limit of detection set to zero.



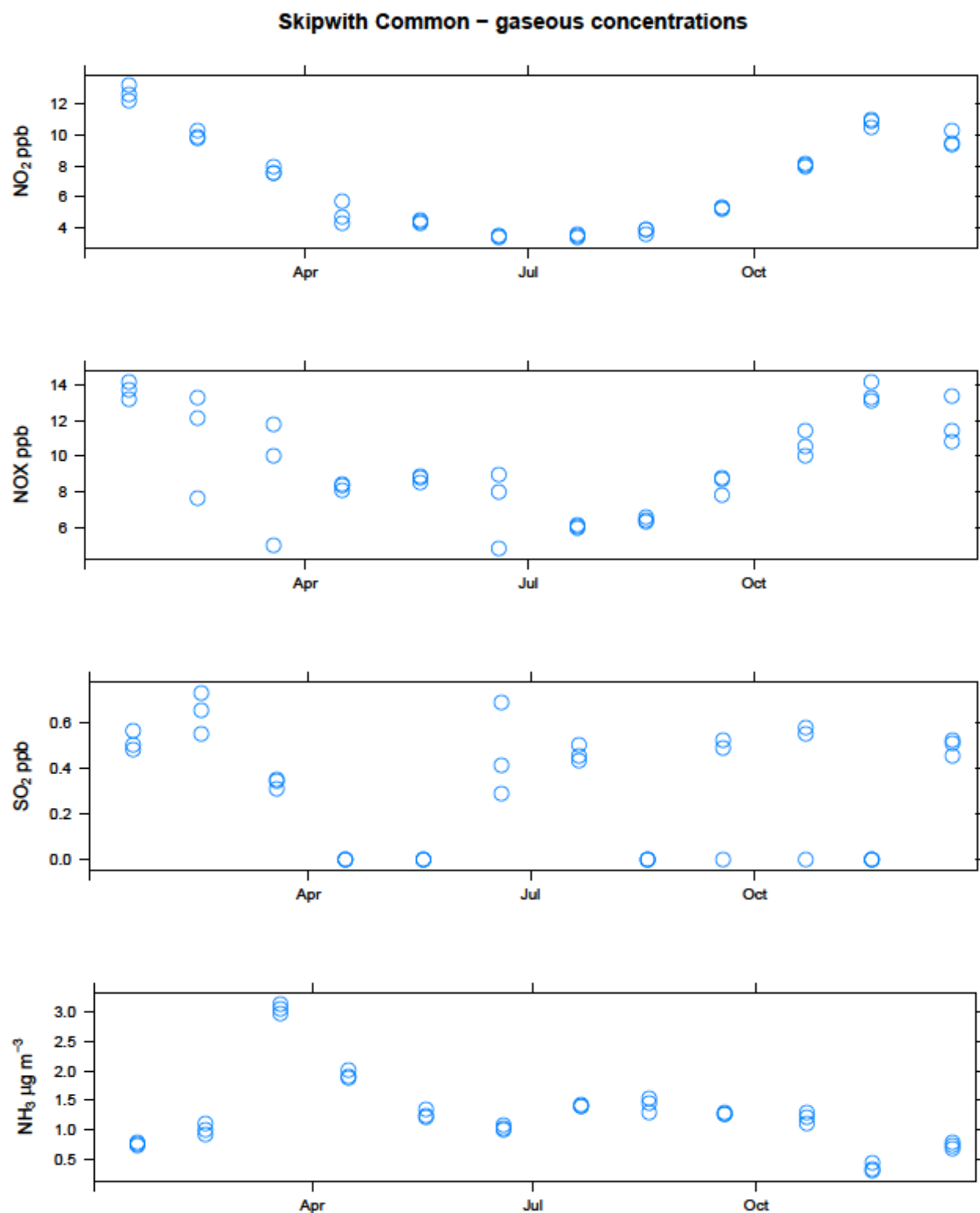
**Figure 6.1.5 Gaseous concentrations (2014): New Forest SAC**

SO<sub>2</sub> samples recorded as below limit of detection set to zero.



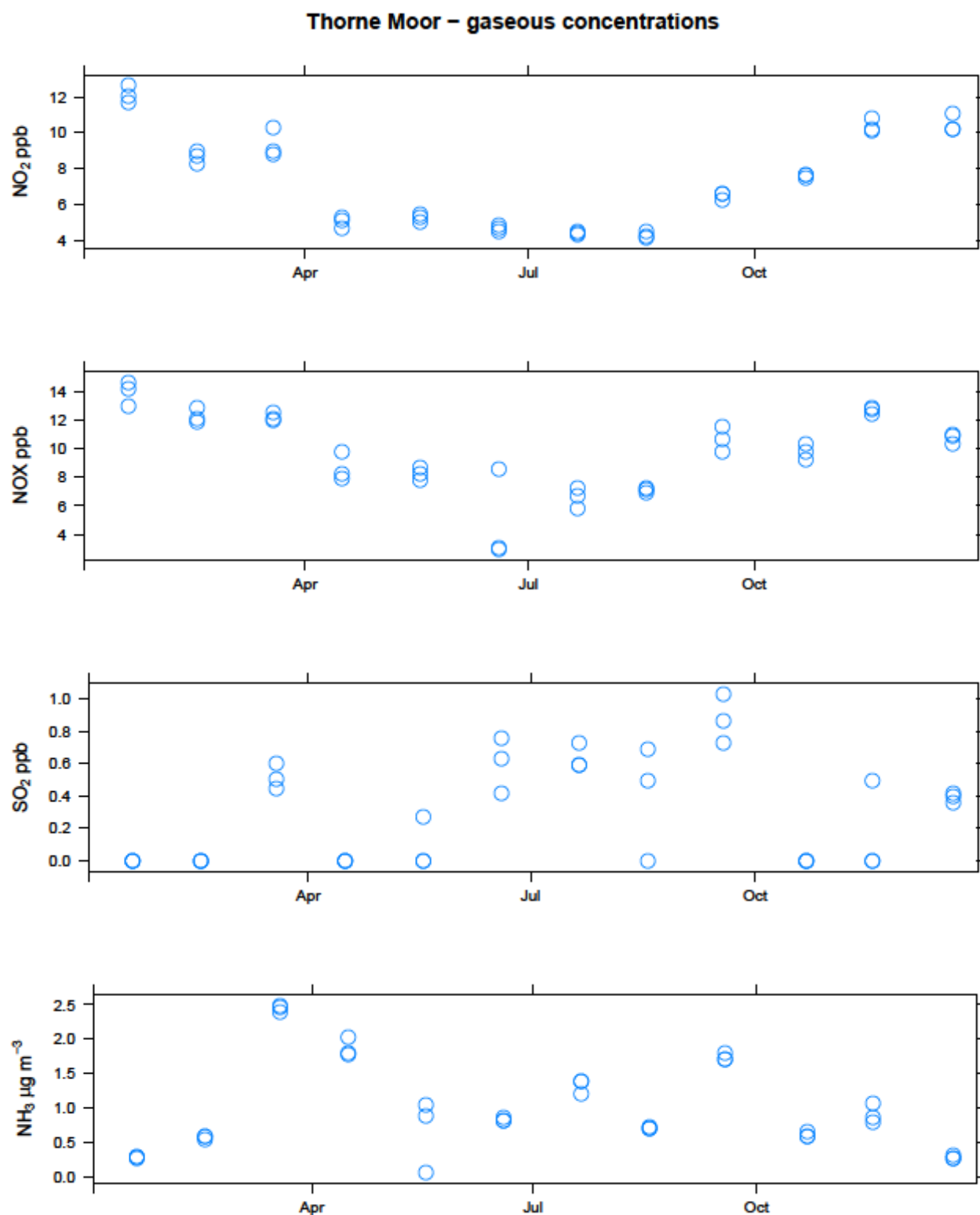
**Figure 6.1.6 Gaseous concentrations (2014): Skipwith Common SAC**

SO<sub>2</sub> samples recorded as below limit of detection set to zero.



**Figure 6.1.6 Gaseous concentrations (2014): Thorne Moor SAC**

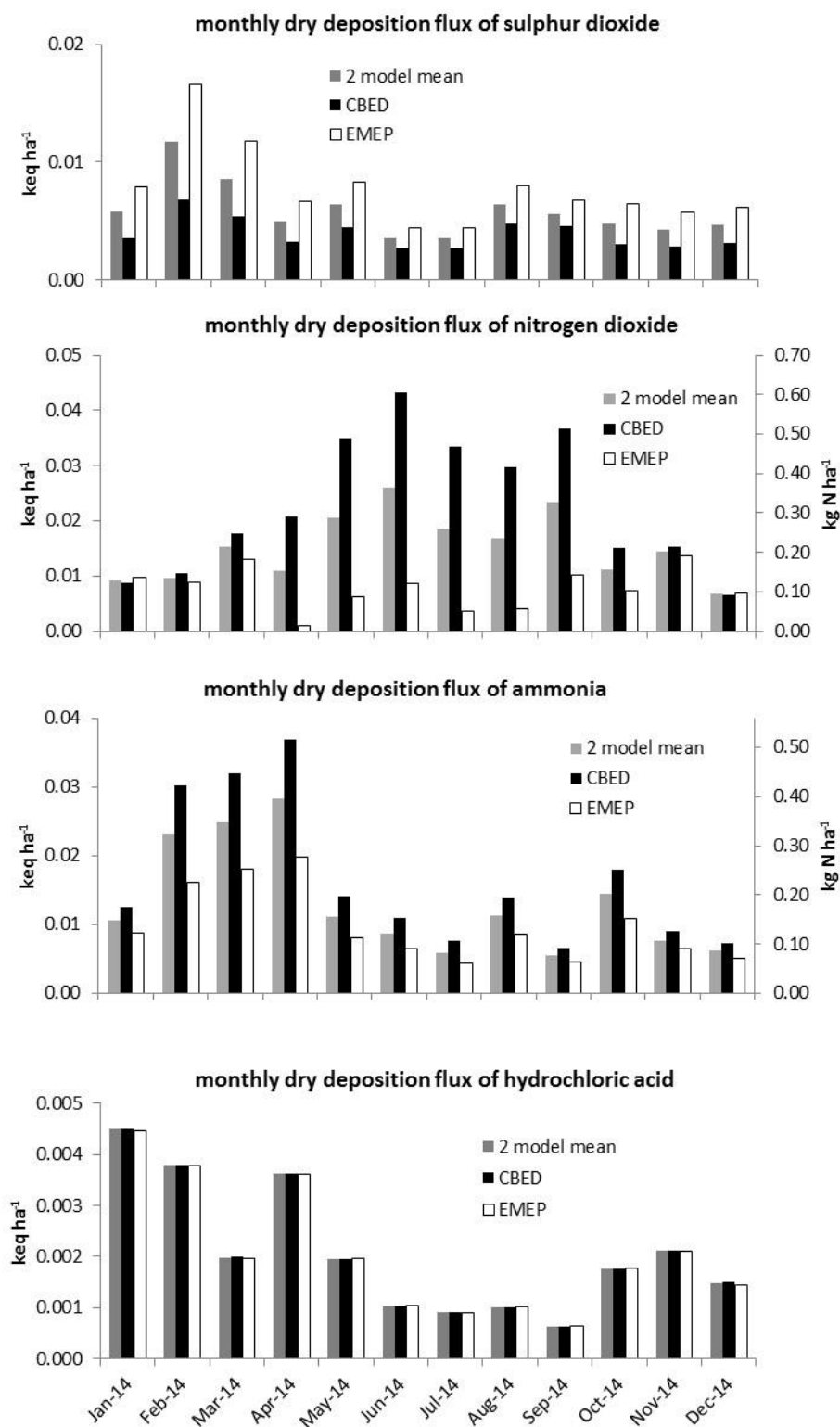
SO<sub>2</sub> samples recorded as below limit of detection set to zero.



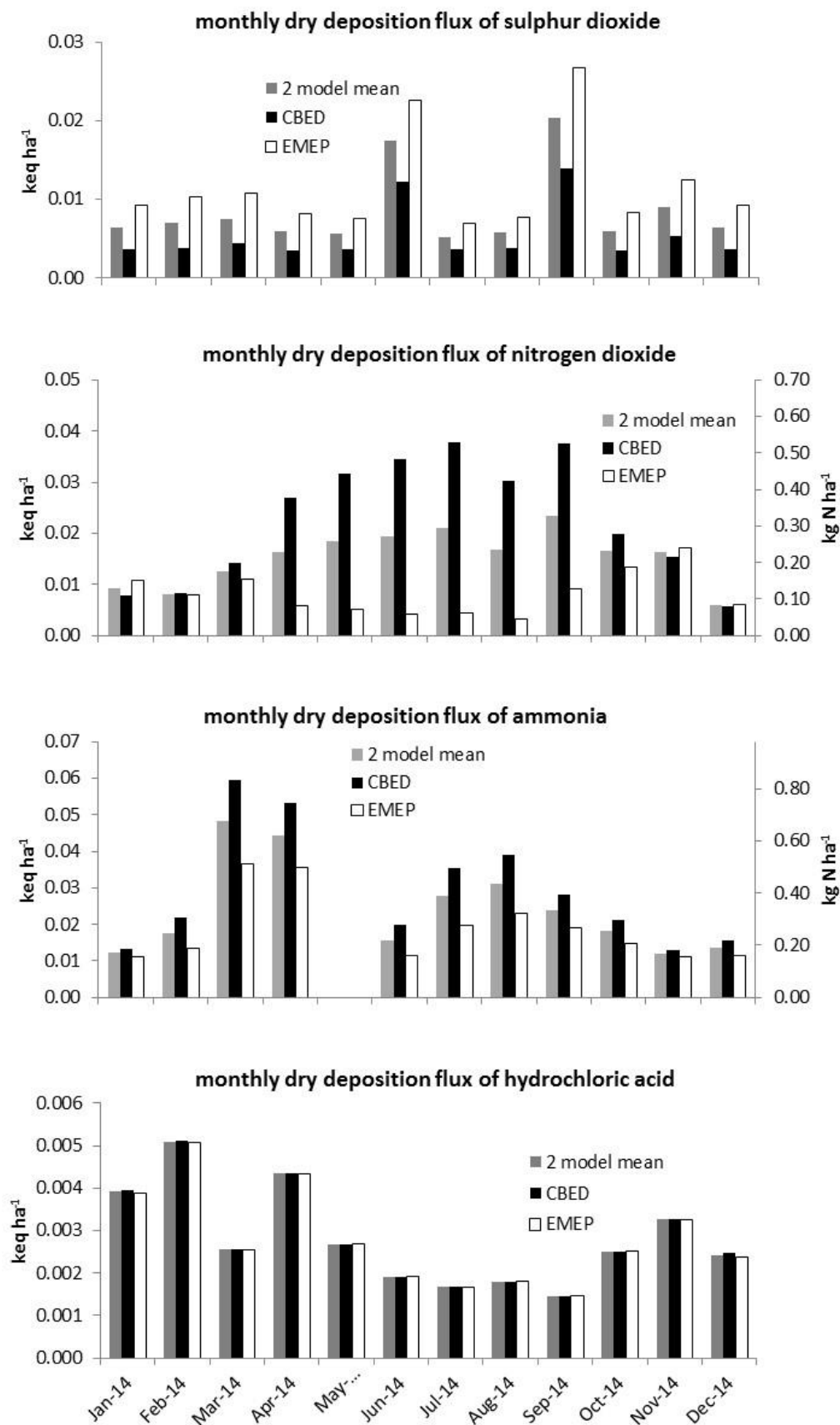
## 6.2 Dry deposition estimates - 2014

n.b. Asterisk indicates missing dry deposition data due to faulty sample batch. Individual SO<sub>2</sub> samples recorded as below limit of detection set to half detection limit prior to calculation of monthly mean concentrations

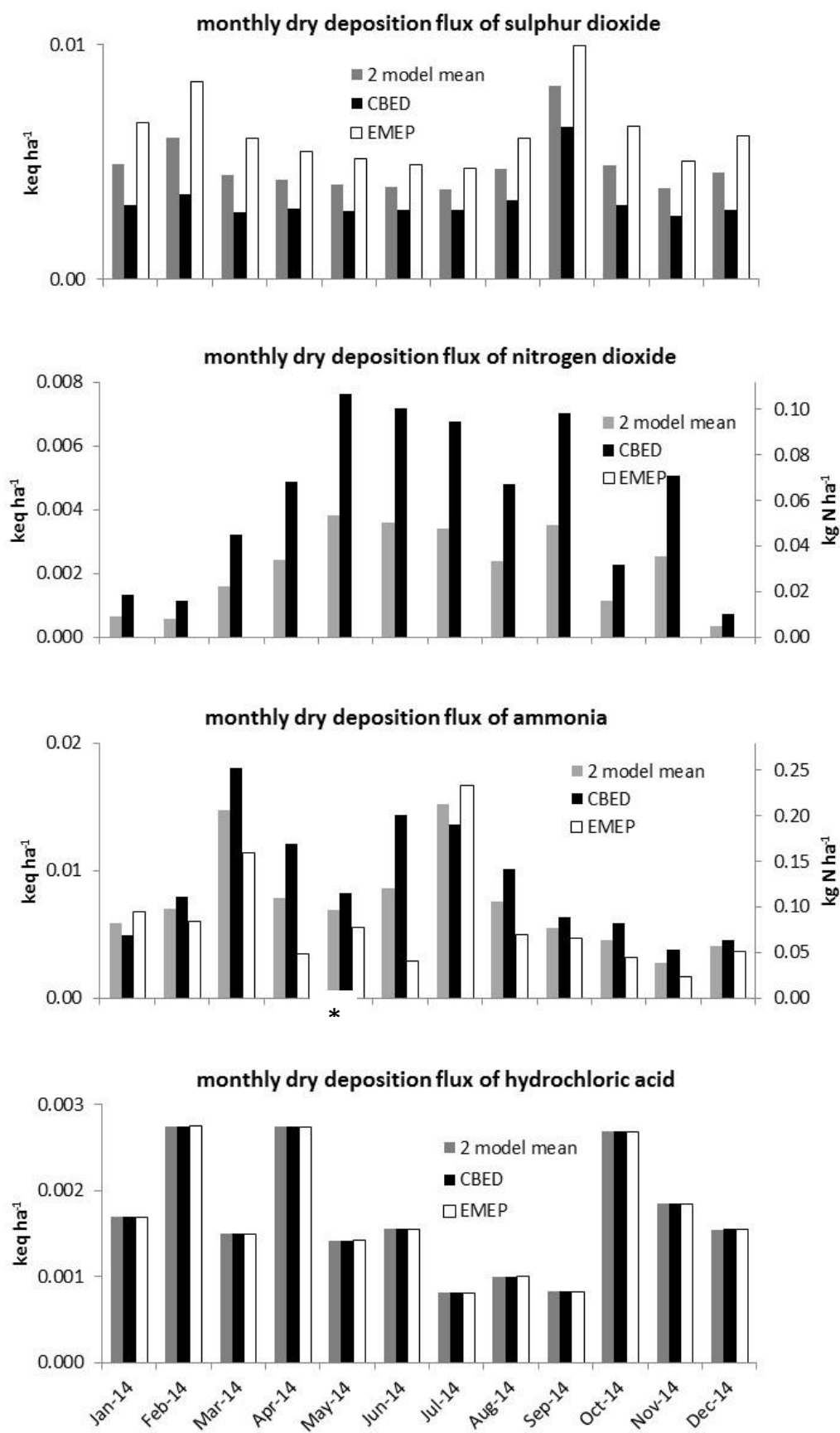
Figure 6.2.1 Monthly dry deposition estimates: Manchester Mosses SAC



**Figure 6.2.2 Monthly dry deposition estimates: Cannock Chase SAC**



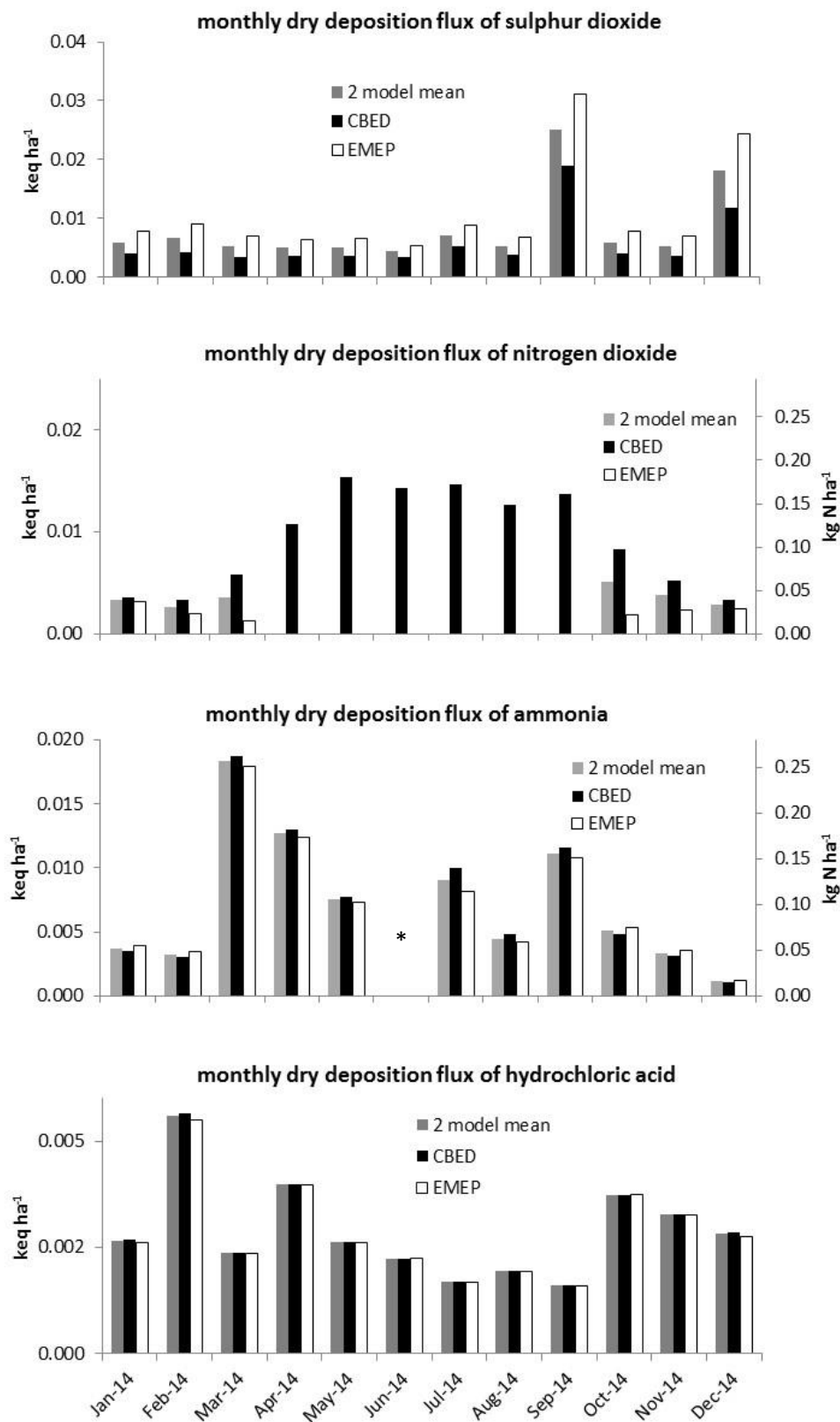
**Figure 6.2.3 Monthly dry deposition estimates: Cleddau Rivers SAC**





**Figure 6.2.4 Monthly dry deposition estimates: Usk Bat sites SAC**

• = lost sample



**Figure 6.2.5 Monthly dry deposition estimates: New Forest SAC**

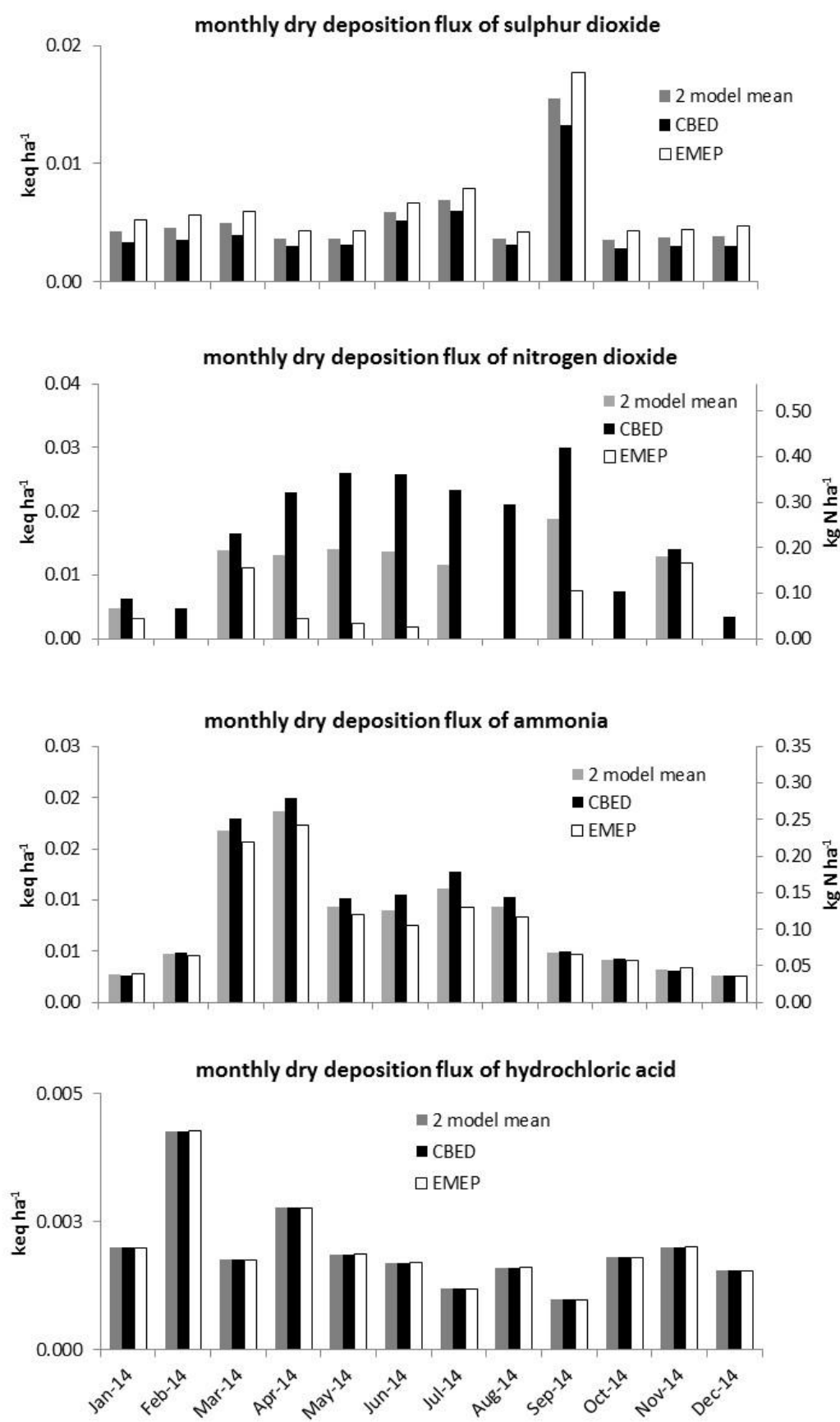
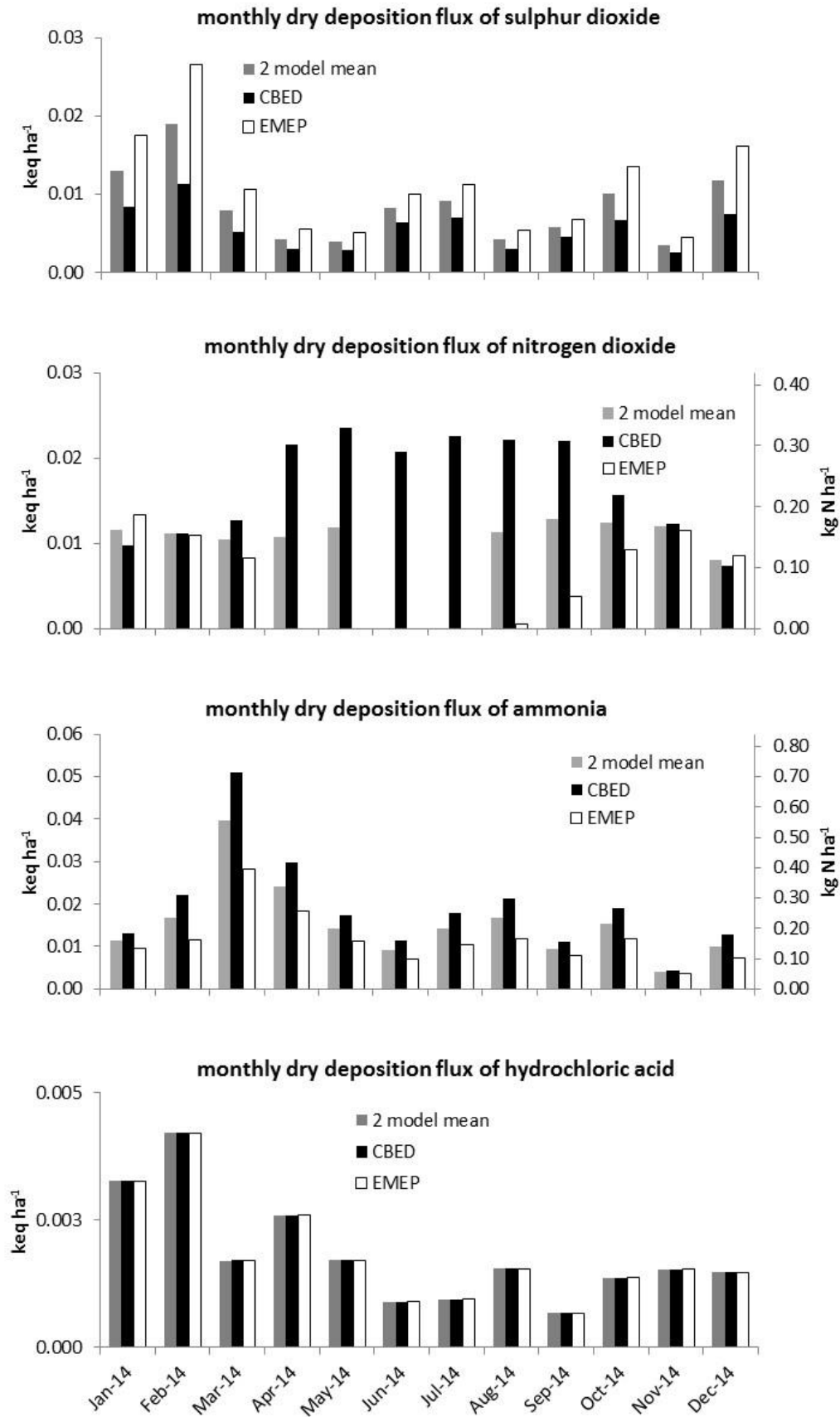
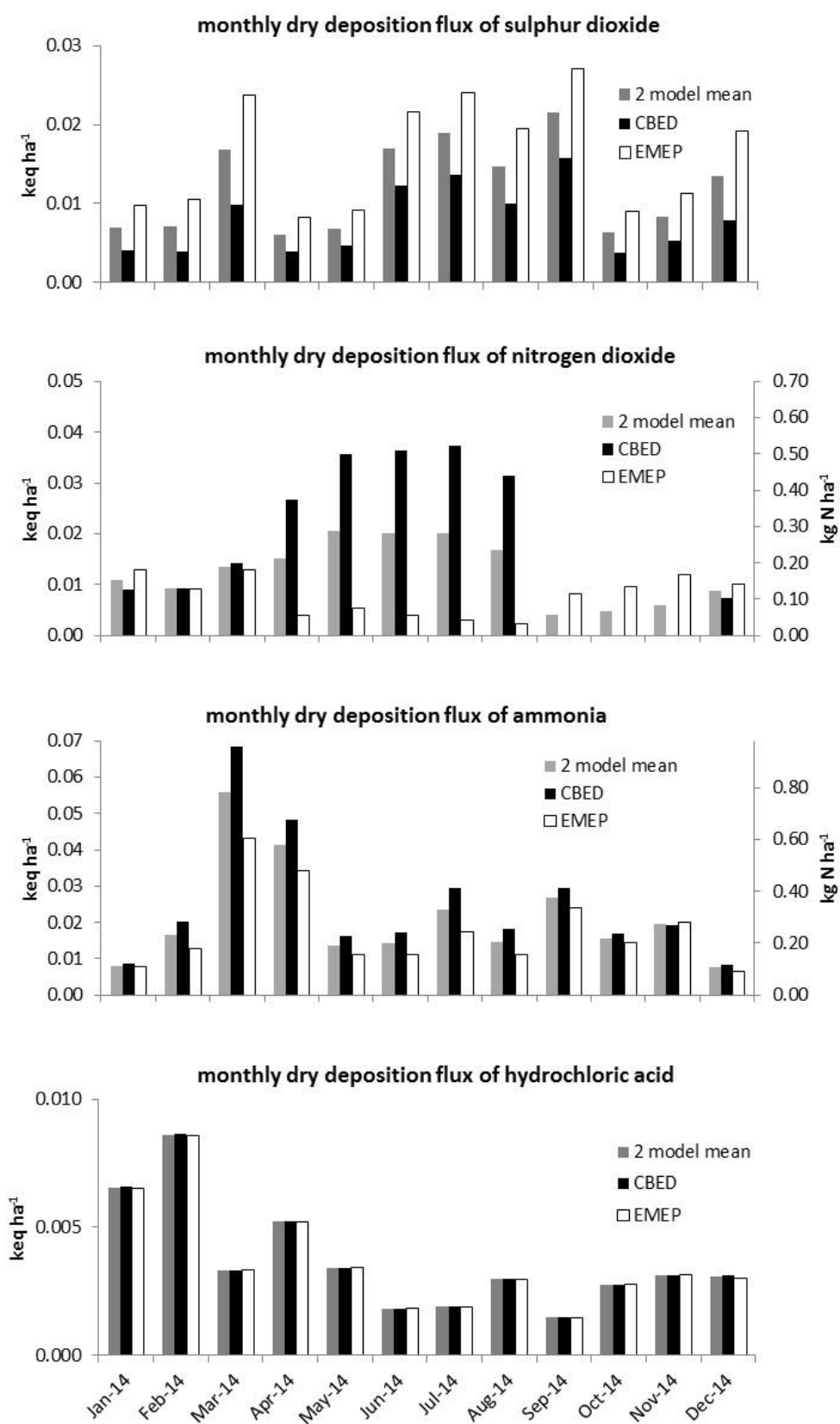


Figure 6.2.6 Monthly dry deposition estimates: Skipwith Common SAC

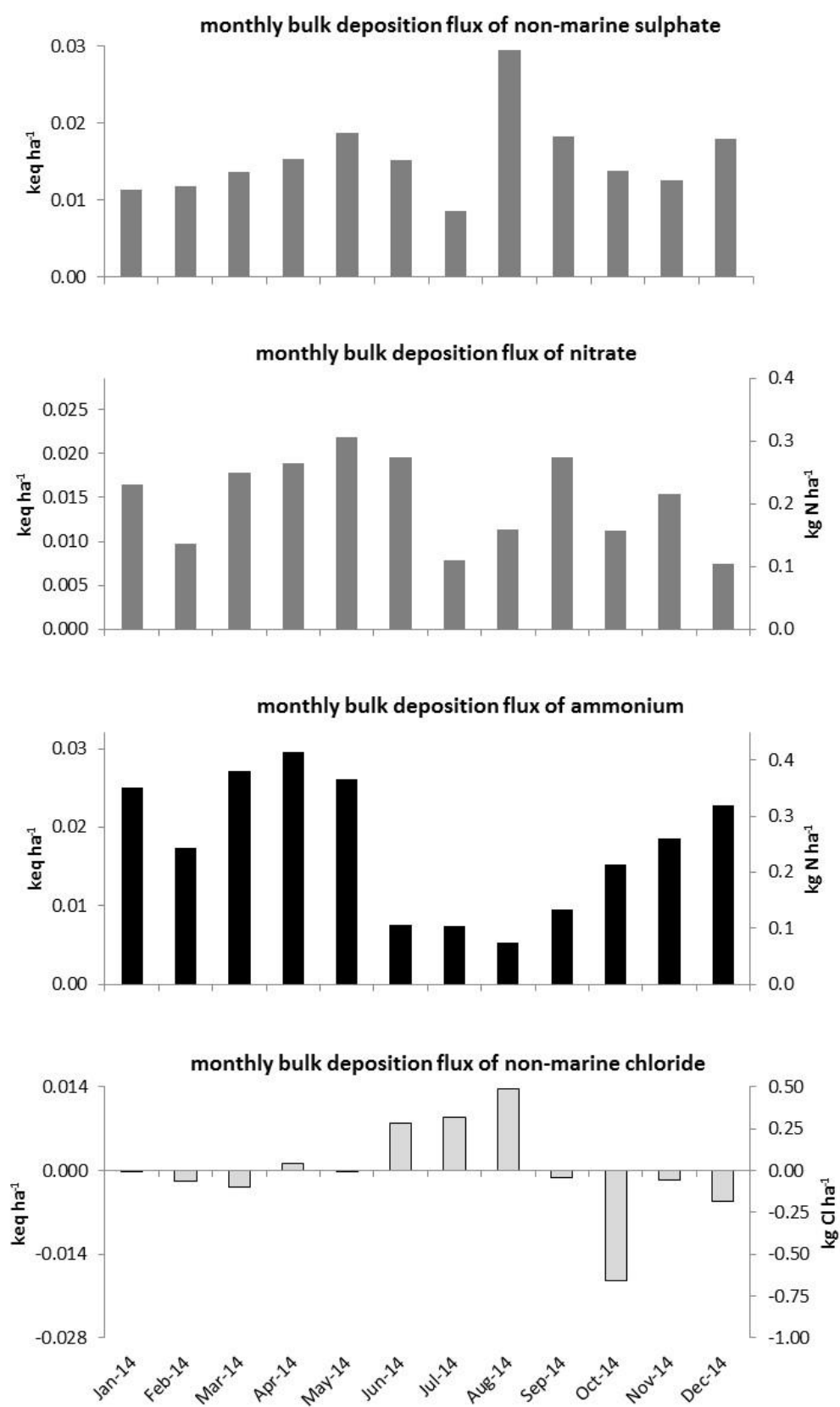


**Figure 6.2.7 Monthly dry deposition estimates: Thorne Moor SAC**

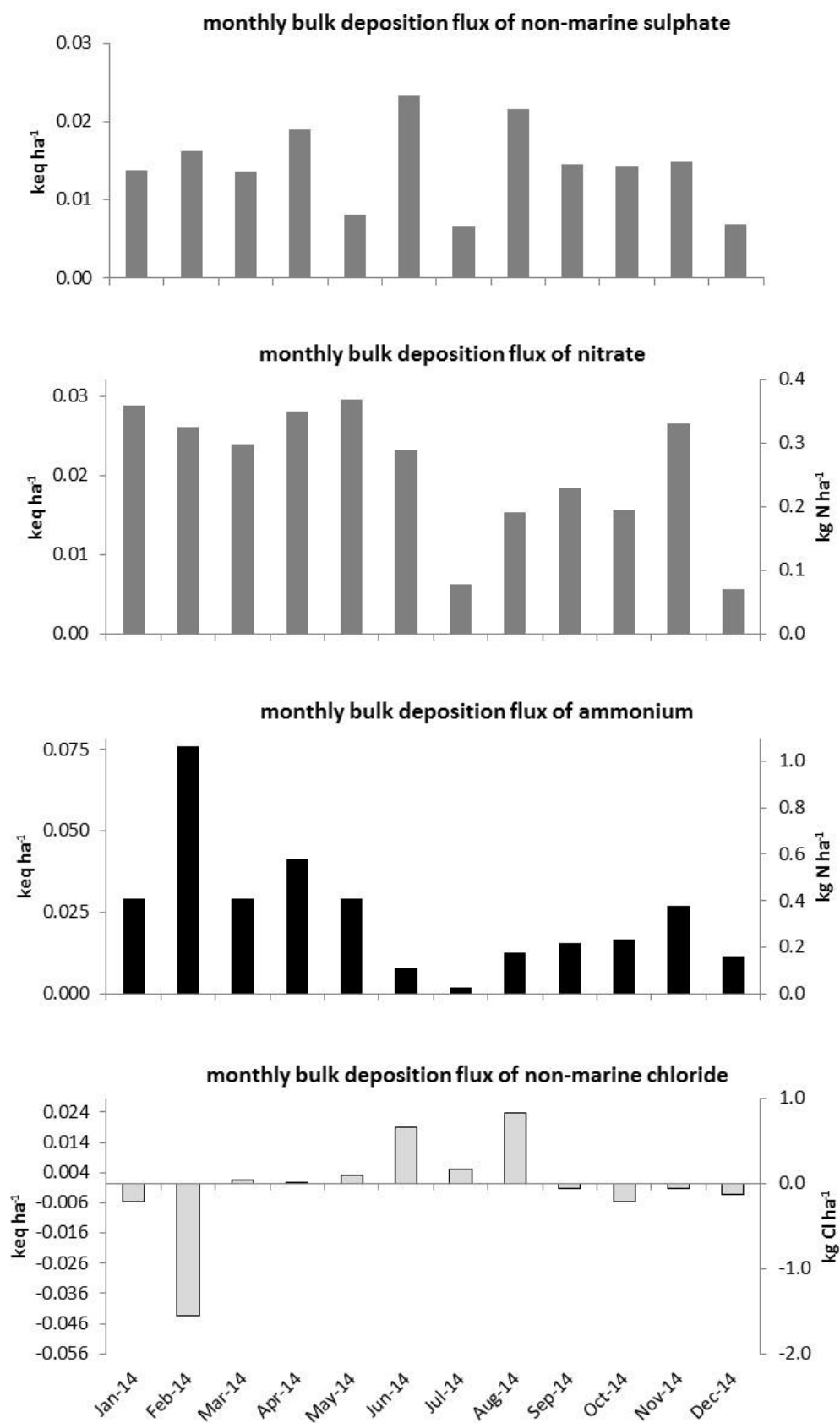


### 6.3 Bulk wet deposition concentrations

Figure 6.3.1 Monthly bulk wet deposition estimates: Manchester Mosses SAC



**Figure 6.3.2 Monthly bulk wet deposition estimates: Cannock Chase SAC**



**Figure 6.3.3 Monthly bulk wet deposition estimates: Cleddau Rivers SAC**

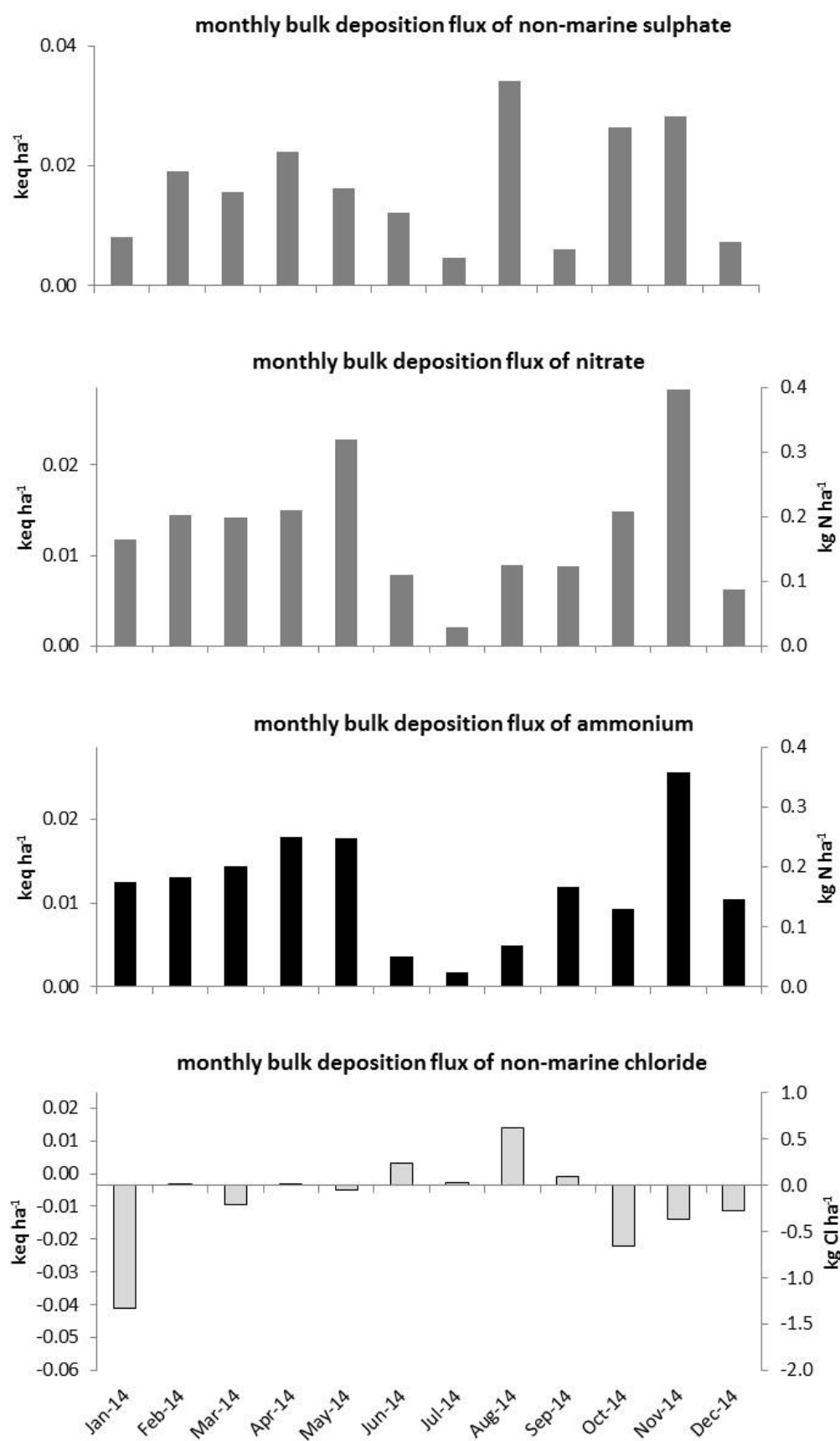
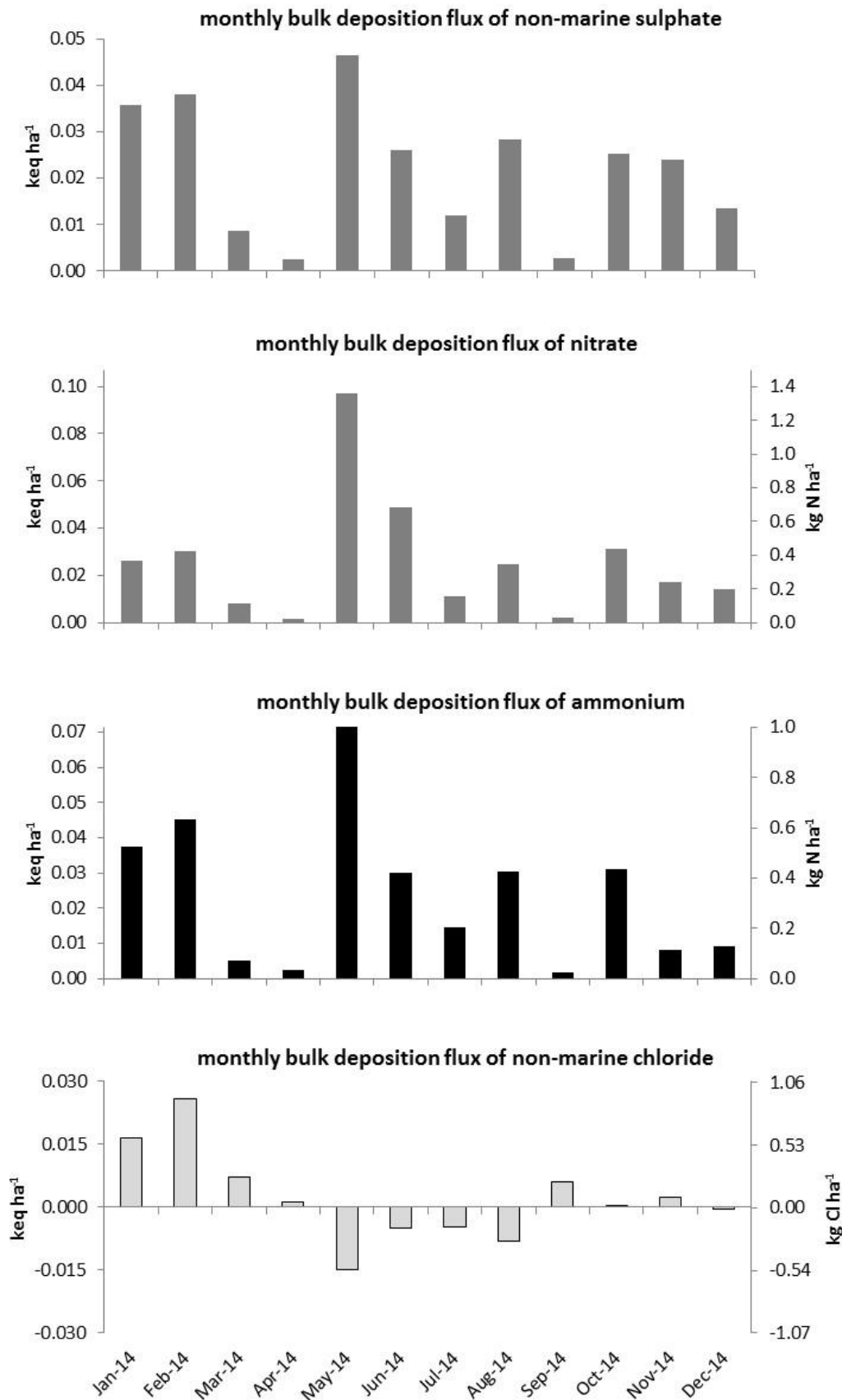
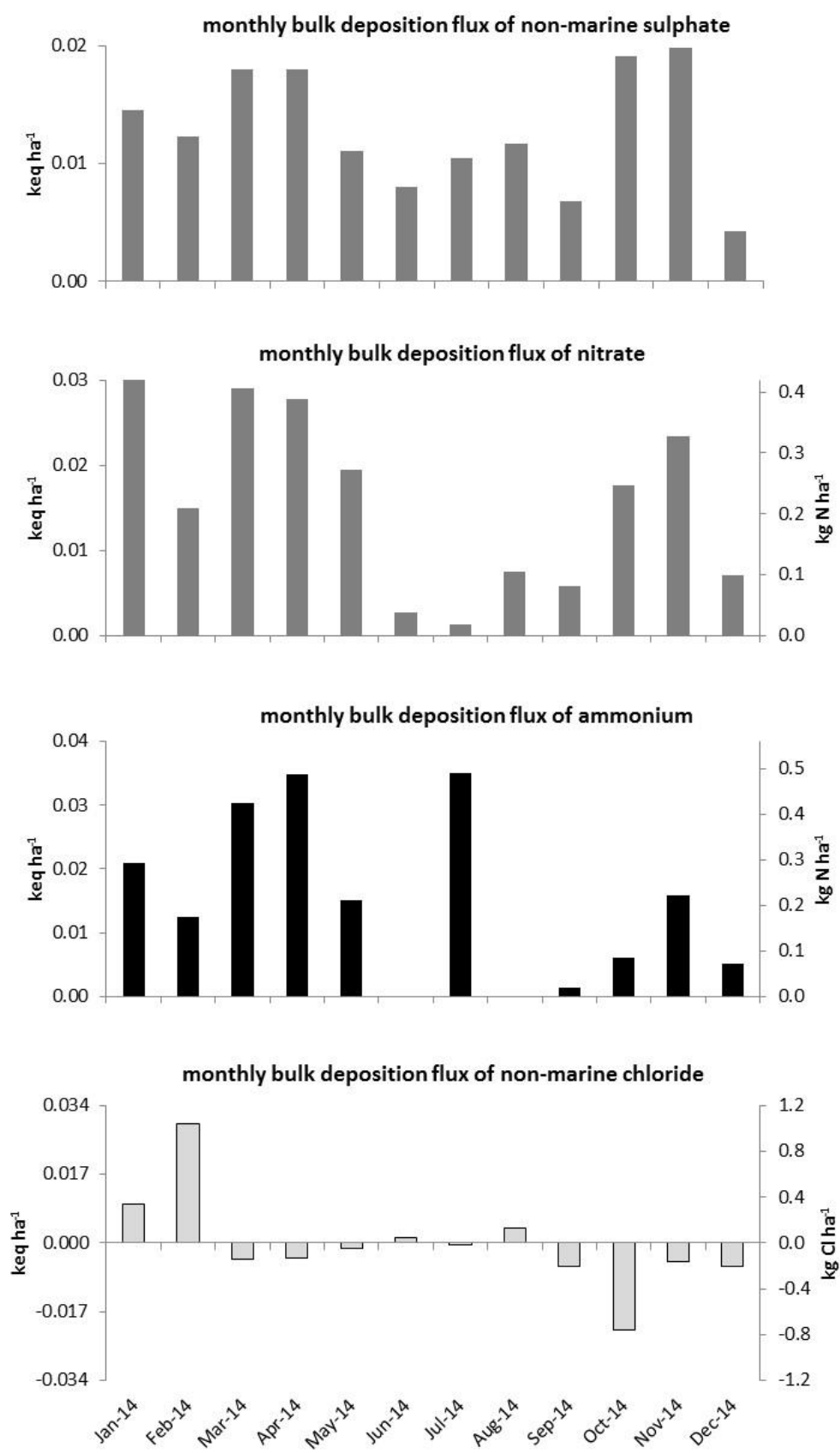


Figure 6.3.4 Monthly bulk wet deposition estimates: Usk Bats site SAC





**Figure 6.3.5 Monthly bulk wet deposition estimates: New Forest SAC**



**Figure 6.3.6 Monthly bulk wet deposition estimates: Skipwith Common SAC**

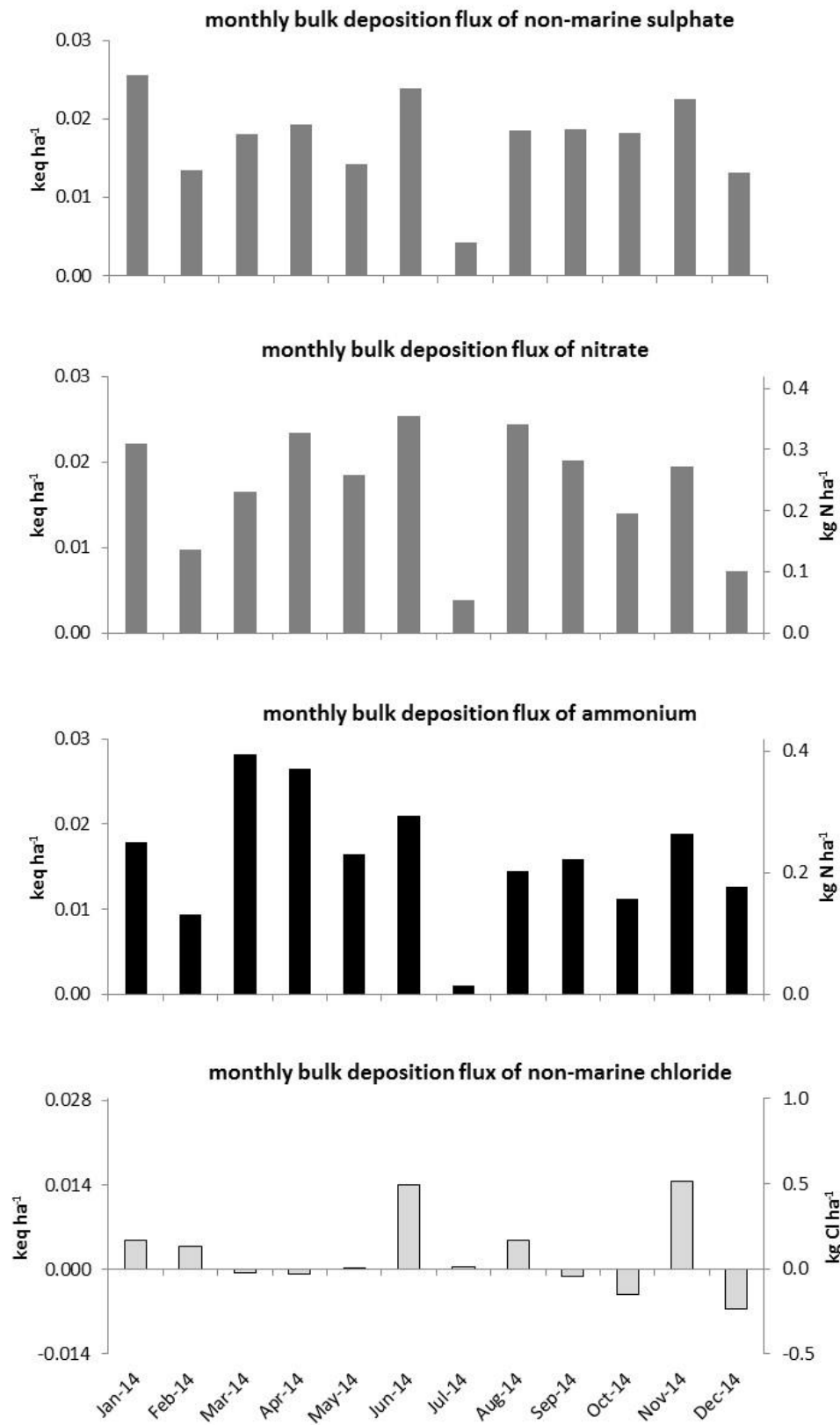
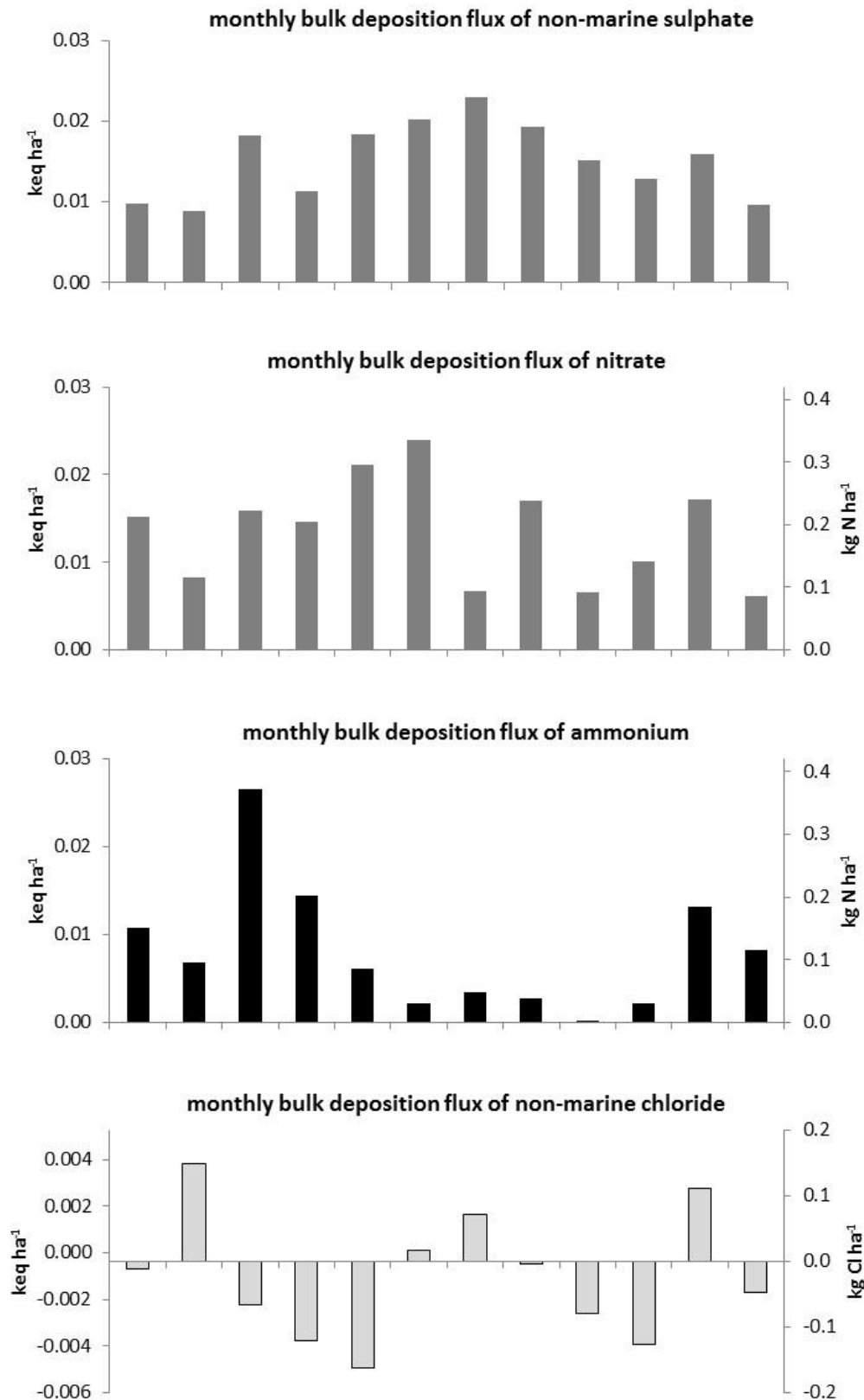


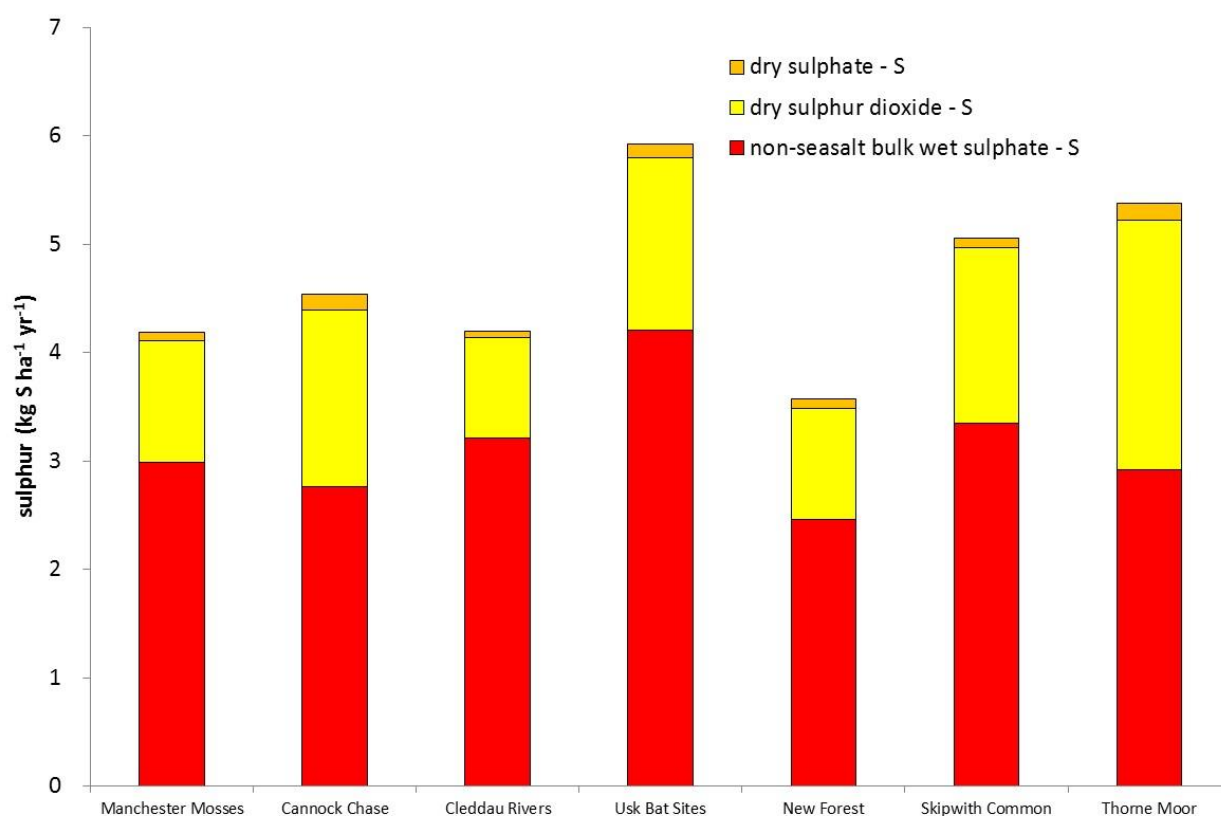
Figure 6.3.7 Monthly bulk wet deposition estimates: Thorne Moor SAC



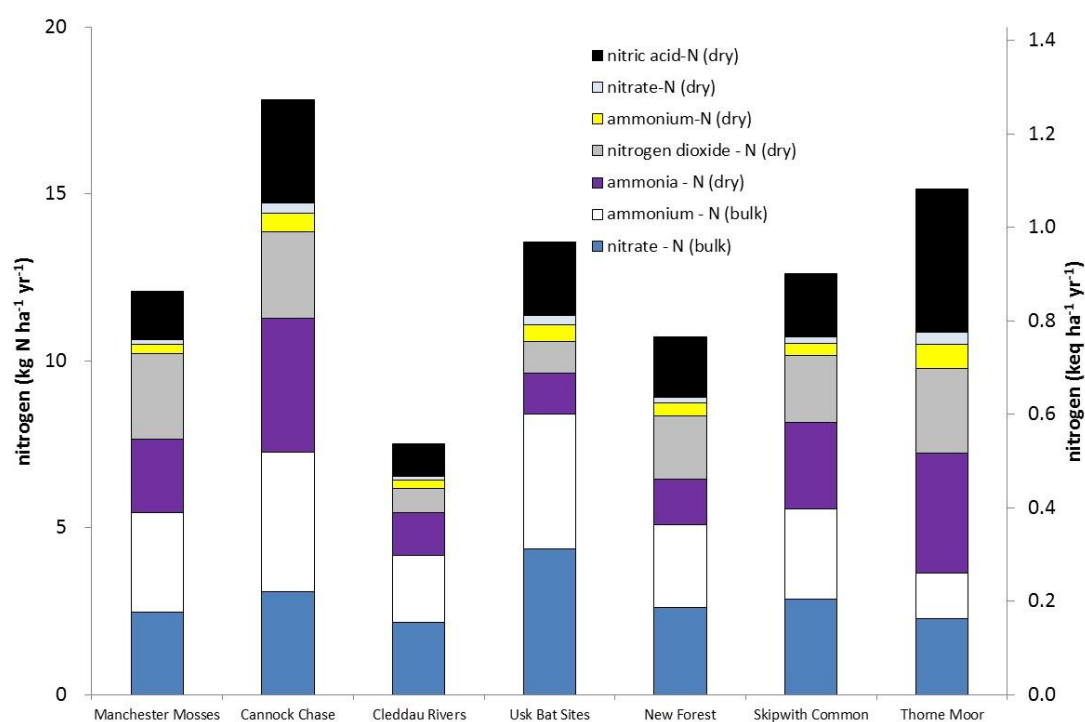
## 6.4 Annual deposition summaries for 2014

The plots in this section: a) summarise the measured monthly sulphur and nitrogen deposition data, (including modelled nitric acid and aerosol sulphate, nitrate and ammonium dry deposition data), in terms of annual fluxes to each site; b) illustrate the relative contributions of wet and dry deposition; and, c) provide a comparison of the relative contributions of sulphur and nitrogen deposition to total acidity.

**Figure 6.4.1 Estimated annual (2014) bulk wet and dry sulphur deposition. Dry sulphur dioxide contribution derived from original measured concentrations.**



**Figure 6.4.2. Estimated annual (2014) bulk wet and dry nitrogen deposition**



**Figure 6.4.3. Estimated total acidity contributed by bulk wet and dry non-seasalt sulphur (amalgamated) and bulk wet and dry nitrogen deposition (separated). Dry sulphur dioxide contribution derived from original measured concentrations.**

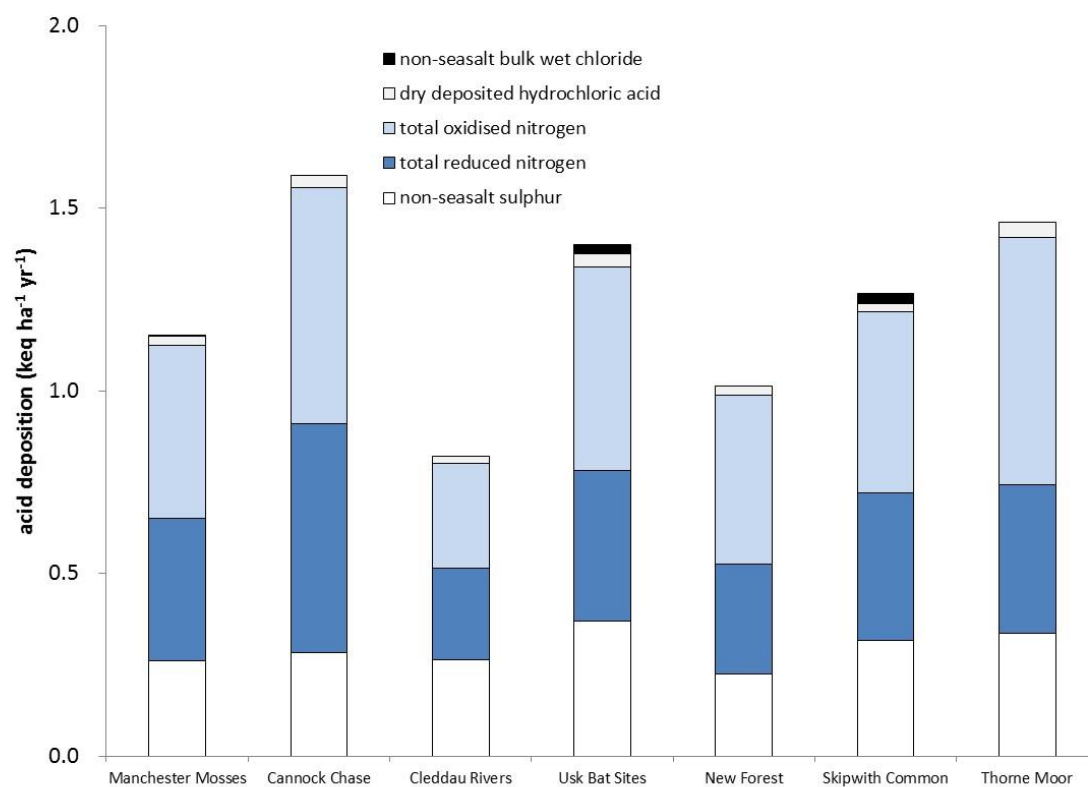


Table 6.4.1

Estimated annual wet and dry sulphur, nitrogen, chloride and total deposition as acidity. Dry sulphur dioxide contribution derived from original measured concentrations.

Species (keq ha <sup>-1</sup> yr <sup>-1</sup> )	Year	Man Mosses	Cannock Chase	Cleddau Rivers	Usk Bat Sites	New Forest	Skipwith Common	Thorne Moor
Dry SO <sub>4</sub> -S	2012	0.006	0.011	0.006	0.010	0.008	0.006	0.011
	2013	0.009	0.016	0.008	0.016	0.012	0.009	0.017
	2014	0.005	0.009	0.004	0.008	0.006	0.005	0.010
Dry SO <sub>2</sub> -S	2012	0.112	0.118	0.086	0.129	0.127	0.122	0.276
	2013	0.107	0.130	0.064	0.081	0.123	0.174	0.182
	2014	0.070	0.102	0.058	0.099	0.064	0.101	0.144
Non-seasalt bulk wet SO <sub>4</sub> -S	2012	0.219	0.157	0.175	0.222	0.164	0.268	0.225
	2013	0.132	0.133	0.159	0.192	0.121	0.188	0.184
	2014	0.187	0.172	0.201	0.263	0.154	0.209	0.183
Dry nitric acid-N	2012	0.115	0.234	0.083	0.153	0.162	0.127	0.269
	2013	0.207	0.347	0.163	0.293	0.253	0.198	0.420
	2014	0.103	0.220	0.069	0.159	0.128	0.135	0.308
Dry NO <sub>3</sub> -N	2012	0.026	0.050	0.023	0.046	0.042	0.030	0.059
	2013	0.014	0.024	0.012	0.027	0.021	0.014	0.027
	2014	0.010	0.022	0.008	0.019	0.013	0.013	0.025
Dry NH <sub>4</sub> -N	2012	0.010	0.020	0.009	0.020	0.017	0.012	0.023
	2013	0.027	0.049	0.022	0.047	0.041	0.029	0.057
	2014	0.019	0.041	0.018	0.036	0.028	0.026	0.052
Dry NH <sub>3</sub> -N	2012	0.132	0.243	0.085	0.073	0.077	0.170	0.226
	2013	0.201	0.344	0.112	0.086	0.106	0.161	0.208
	2014	0.158	0.288	0.091	0.087	0.097	0.186	0.258
Dry NO <sub>2</sub> -N	2012	0.184	0.176	0.024	0.059	0.116	0.121	0.185
	2013	0.173	0.184	0.028	0.056	0.122	0.124	0.167
	2014	0.183	0.184	0.052	0.068	0.136	0.143	0.181
Bulk wet NO <sub>3</sub> -N	2012	0.184	0.188	0.159	0.244	0.208	0.221	0.283
	2013	0.145	0.184	0.138	0.244	0.146	0.194	0.186
	2014	0.177	0.220	0.155	0.313	0.187	0.204	0.163
Bulk wet NH <sub>4</sub> -N	2012	0.198	0.186	0.170	0.208	0.143	0.254	0.229
	2013	0.184	0.224	0.131	0.230	0.101	0.194	0.175
	2014	0.212	0.298	0.143	0.288	0.177	0.193	0.097
Non-seasalt bulk wet chloride	2012	0.027	-0.037	-0.025	0.002	-0.134	0.017	-0.009
	2013	0.014	0.017	0.070	0.009	0.044	0.013	-0.003
	2014	0.001	-0.012	-0.053	0.026	-0.003	0.028	-0.008
Dry HCl	2012	0.032	0.054	0.023	0.042	0.038	0.032	0.067
	2013	0.039	0.039	0.025	0.041	0.032	0.030	0.060
	2014	0.025	0.034	0.020	0.034	0.024	0.022	0.044
TOTAL ACID DEPOSITION	2012	1.245	1.400	0.818	1.208	0.968	1.380	1.844
	2013	1.252	1.691	0.932	1.322	1.122	1.328	1.680
	2014	1.150	1.578	0.766	1.400	1.011	1.265	1.457



**Table 6.4.2 Estimated annual wet and dry nitrogen deposition 2012 - 2014.**

<b>species (kg N ha<sup>-1</sup> yr<sup>-1</sup>)</b>	<b>Year</b>	<b>Man Mosses</b>	<b>Cannock Chase</b>	<b>Cleddau Rivers</b>	<b>Usk Bat Sites</b>	<b>New Forest</b>	<b>Skipwith Common</b>	<b>Thorne Moor</b>
<b>Dry nitric acid_N</b>	2012	1.613	3.283	1.159	2.137	2.264	1.772	3.767
	2013	2.894	4.854	2.292	4.096	3.535	2.777	5.872
	2014	1.438	3.073	0.972	2.229	1.797	1.892	4.313
<b>Dry NO<sub>3</sub>-N</b>	2012	0.362	0.705	0.322	0.651	0.590	0.423	0.830
	2013	0.199	0.337	0.166	0.373	0.287	0.196	0.374
	2014	0.145	0.306	0.114	0.263	0.185	0.177	0.347
<b>Dry NH<sub>4</sub>-N</b>	2012	0.143	0.274	0.130	0.285	0.234	0.171	0.324
	2013	0.377	0.692	0.314	0.651	0.576	0.412	0.795
	2014	0.273	0.571	0.247	0.500	0.393	0.364	0.729
<b>Dry NH<sub>3</sub>-N</b>	2012	1.842	3.407	1.193	1.029	1.081	2.386	3.167
	2013	2.811	4.819	1.574	1.198	1.484	2.258	2.918
	2014	2.211	4.031	1.267	1.216	1.350	2.591	3.601
<b>Dry NO<sub>2</sub> N</b>	2012	2.573	2.460	0.338	0.821	1.627	1.688	2.596
	2013	2.415	2.580	0.398	0.782	1.713	1.742	2.341
	2014	2.564	2.574	0.727	0.957	1.903	2.005	2.532
<b>Bulk wet NO<sub>3</sub>-N</b>	2012	2.582	2.629	2.233	3.416	2.906	3.095	3.957
	2013	2.031	2.581	1.927	3.409	2.043	2.717	2.605
	2014	2.481	3.081	2.175	4.377	2.612	2.862	2.276
<b>Bulk wet NH<sub>4</sub>-N</b>	2012	2.777	2.599	2.373	2.916	2.000	3.559	3.200
	2013	2.573	3.131	1.833	3.219	1.419	2.720	2.452
	2014	2.962	4.175	2.001	4.032	2.475	2.703	1.356
<b>TOTAL N DEPOSITION</b>	2012	11.805	15.315	7.741	11.192	10.640	13.067	17.841
	2013	13.300	18.994	8.504	13.720	11.057	12.822	17.357
	2014	12.074	17.811	7.503	13.574	10.715	12.594	15.154

## 6.5 Soil solution chemistry (2014)

In this section annual mean concentrations of pH and solutes in soil water are provided together with time series plots of key chemical determinands. Bog habitats are monitored using 3 replicate dipwells that provide depth integrated samples. Heathland habitats are monitored using 3 replicate pairs of shallow and deep suction samplers.

**Table 6.5.1. Monthly (2014) mean concentrations of pH and solutes in monthly soil solution samples. All units, with exception of pH, in mg L<sup>-1</sup>. Cells denoted with an asterisk indicate an insufficient sample volume available for analysis.**

Site	date	sample	pH	Na	K	Ca	Mg	Al	PO4-P	NO3-N	NH4-N	Cl	SO4-S	DOC
Manchester Mosses	Jan-14	dipwell	4.30	5.15	1.63	0.90	0.62	0.25	0.016	0.022	0.116	9.94	0.044	44.60
Manchester Mosses	Feb-14	dipwell	4.38	5.27	1.69	0.87	0.62	0.24	0.010	0.032	0.215	10.21	0.055	36.53
Manchester Mosses	Mar-14	dipwell	4.28	5.25	1.30	0.84	0.60	0.20	0.000	0.047	0.189	8.03	0.188	35.80
Manchester Mosses	Apr-14	dipwell	4.28	5.16	1.18	0.90	0.65	0.17	0.000	0.027	0.092	10.07	0.044	32.23
Manchester Mosses	May-14	dipwell	4.24	5.09	0.48	1.00	0.72	0.19	0.023	0.024	0.050	9.38	0.101	36.43
Manchester Mosses	Jun-14	dipwell	4.30	4.96	0.21	1.03	0.70	0.18	0.063	0.031	0.311	10.05	0.135	32.87
Manchester Mosses	Jul-14	dipwell	4.25	5.24	0.30	1.11	0.79	0.23	0.015	0.003	0.446	9.58	0.174	41.80
Manchester Mosses	Aug-14	dipwell	4.48	4.86	0.30	1.10	0.75	0.19	0.048	0.055	0.484	10.46	0.175	40.07
Manchester Mosses	Sep-14	dipwell	4.26	5.62	0.34	1.16	0.73	0.19	0.041	0.056	0.399	10.13	0.279	35.90
Manchester Mosses	Oct-14	dipwell	4.07	5.57	0.24	0.90	0.72	0.16	0.002	0.031	0.065	11.13	0.282	29.83
Manchester Mosses	Nov-14	dipwell	4.19	5.04	0.18	0.91	0.64	0.16	0.002	0.040	0.068	9.04	0.200	29.57
Manchester Mosses	Dec-14	dipwell	4.18	5.42	0.20	0.91	0.72	0.17	0.006	0.033	0.082	10.05	0.146	27.07
Cannock Chase	Jan-14	deep	4.63	3.62	1.90	0.33	0.27	1.27	0.014	0.037	0.014	8.14	0.705	6.78
Cannock Chase	Jan-14	shallow	4.44	4.62	1.98	0.21	0.09	1.53	0.033	0.029	0.045	6.65	1.512	16.55
Cannock Chase	Feb-14	deep	4.71	3.43	1.82	0.24	0.14	1.35	0.000	0.040	0.029	6.69	1.520	6.00
Cannock Chase	Feb-14	shallow	4.38	3.66	1.84	0.06	0.07	1.47	0.000	0.040	0.000	5.41	1.870	11.90
Cannock Chase	Mar-14	deep	4.49	4.51	2.26	0.22	0.19	1.39	0.000	0.076	0.000	8.06	1.750	10.29
Cannock Chase	Mar-14	shallow	4.68	2.02	1.11	0.25	0.09	0.99	0.000	0.086	0.025	3.16	1.730	5.80
Cannock Chase	Apr-14	deep	4.65	4.12	1.83	0.29	0.20	1.15	0.018	0.027	0.017	7.53	1.555	7.60

Cannock Chase	Apr-14	shallow	4.38	4.14	2.07	0.09	0.08	1.53	0.006	0.036	0.044	6.98	1.244	14.65
Cannock Chase	May-14	deep	4.63	3.96	1.91	0.33	0.20	1.23	0.006	0.030	0.030	7.03	1.270	7.38
Cannock Chase	May-14	shallow	4.25	4.38	2.61	1.79	0.11	1.61	0.000	0.049	0.036	8.62	1.730	11.80
Cannock Chase	Jun-14	deep	4.79	3.38	1.49	0.26	0.13	1.04	0.041	0.031	0.000	5.75	1.290	8.99
Cannock Chase	Jun-14	shallow	4.23	3.83	2.30	0.08	0.06	1.42	0.044	0.114	0.000	8.40	1.600	12.70
Cannock Chase	Jul-14	deep	4.59	1.82	0.97	1.70	0.92	0.83	0.004	0.192	0.068	6.96	0.944	6.00
Cannock Chase	Jul-14	shallow	*	*	*	*	*	*	0.000	0.067	0.161	3.10	0.883	26.90
Cannock Chase	Aug-14	deep	No samples retrieved											
Cannock Chase	Aug-14	shallow	4.29	3.46	1.96	0.08	0.07	1.47	0.010	0.174	0.025	7.14	1.590	12.20
Cannock Chase	Sep-14	deep	5.25	*	*	*	*	*	0.000	0.119	0.014	4.38	1.185	10.80
Cannock Chase	Sep-14	shallow	5.03	3.35	1.91	0.00	0.04	1.41	0.015	0.068	0.063	3.76	1.284	16.20
Cannock Chase	Oct-14	deep	*	*	*	*	*	*	0.016	0.147	0.000	4.01	1.350	8.90
Cannock Chase	Oct-14	shallow	4.49	3.76	2.29	0.13	0.07	1.60	0.017	0.059	0.023	5.19	1.368	11.80
Cannock Chase	Nov-14	deep	4.70	2.11	0.73	0.29	0.10	0.85	0.000	0.059	0.041	2.59	1.440	6.55
Cannock Chase	Nov-14	shallow	4.42	4.69	2.42	0.00	0.05	1.71	0.000	0.055	0.063	7.48	1.234	18.75
Cannock Chase	Dec-14	deep	4.70	4.07	1.28	0.33	0.22	1.23	0.000	0.054	0.037	7.06	1.115	8.47
Cannock Chase	Dec-14	shallow	4.41	5.17	2.36	0.00	0.06	1.89	0.003	0.086	0.045	7.32	1.292	16.75
Cleddau Rivers	Jan-14	dipwell	4.24	7.28	0.46	0.50	0.80	0.06	0.018	0.019	0.063	13.67	0.441	18.63
Cleddau Rivers	Feb-14	dipwell	4.20	9.30	0.62	0.55	1.17	0.04	0.000	0.028	0.063	16.87	0.608	14.40
Cleddau Rivers	Mar-14	dipwell	4.76	8.77	0.86	1.38	0.83	0.06	0.006	0.030	0.771	13.87	0.288	22.87
Cleddau Rivers	Apr-14	dipwell	4.87	7.41	0.59	2.79	0.76	0.08	0.004	0.031	1.449	11.89	0.185	21.75
Cleddau Rivers	May-14	dipwell	4.93	6.75	0.42	2.66	0.73	0.11	0.212	0.028	0.545	9.40	0.107	30.23
Cleddau Rivers	Jun-14	dipwell	4.97	6.94	0.55	1.94	0.73	0.13	0.878	0.032	1.596	10.48	0.460	40.80
Cleddau Rivers	Jul-14	dipwell	5.01	8.53	2.18	3.31	1.19	0.15	0.507	0.007	6.642	9.10	1.487	31.23
Cleddau Rivers	Aug-14	dipwell	4.13	7.95	0.73	3.15	1.29	0.10	0.423	0.039	3.774	8.45	1.693	55.17
Cleddau Rivers	Sep-14	dipwell	5.33	8.16	0.13	3.13	1.17	0.16	0.619	0.028	0.918	8.39	0.981	53.27
Cleddau Rivers	Oct-14	dipwell	4.77	4.80	0.57	0.75	0.49	0.06	0.016	0.027	0.472	6.94	0.493	19.70
Cleddau Rivers	Nov-14	dipwell	4.76	5.30	0.37	1.39	0.63	0.11	0.003	0.035	0.608	6.56	0.275	29.03

Cleddau Rivers	Dec-14	dipwell	4.39	6.32	0.38	1.26	0.73	0.12	0.211	0.034	0.176	8.14	0.306	30.97
Usk Bat Sites	Jan-14	dipwell	4.27	5.01	0.17	0.67	0.49	0.06	0.015	0.028	0.319	10.58	0.687	8.10
Usk Bat Sites	Feb-14	dipwell	4.37	5.40	0.29	0.62	0.57	0.05	0.011	0.052	0.335	11.05	0.668	0.00
Usk Bat Sites	Mar-14	dipwell	4.27	4.71	0.28	0.50	0.43	0.07	0.000	0.077	0.324	9.19	0.586	12.70
Usk Bat Sites	Apr-14	dipwell	4.31	4.18	0.21	0.49	0.41	0.14	0.000	0.062	0.423	6.51	0.721	22.93
Usk Bat Sites	May-14	dipwell	4.26	3.72	0.11	0.54	0.42	0.17	0.002	0.035	0.419	5.22	0.615	27.33
Usk Bat Sites	Jun-14	dipwell	4.34	4.04	0.32	1.30	0.58	0.34	0.044	0.044	0.481	4.83	0.674	30.67
Usk Bat Sites	Jul-14	dipwell	4.46	3.34	0.25	0.58	0.50	0.12	0.003	0.033	0.424	4.28	1.323	23.27
Usk Bat Sites	Aug-14	dipwell	4.87	3.58	0.16	0.65	0.63	0.16	0.019	0.043	0.354	4.64	1.940	25.80
Usk Bat Sites	Sep-14	dipwell	4.39	3.61	0.46	0.64	0.51	0.13	0.002	0.441	0.667	4.85	1.048	21.10
Usk Bat Sites	Oct-14	dipwell	4.16	4.14	0.22	0.66	0.52	0.15	0.002	0.029	0.281	6.36	1.091	22.03
Usk Bat Sites	Nov-14	dipwell	4.29	4.07	0.45	0.71	0.65	0.16	0.000	0.053	0.498	6.54	0.500	30.80
Usk Bat Sites	Dec-14	dipwell	4.18	4.20	0.18	0.62	0.66	0.16	0.000	0.036	0.538	6.87	0.465	31.60
New Forest	Jan-14	deep	4.74	17.53	0.29	2.67	2.07	0.95	0.009	0.018	0.000	25.63	6.397	3.18
New Forest	Jan-14	shallow	4.50	14.35	0.38	0.96	1.39	2.68	0.023	0.026	0.064	18.13	3.853	38.53
New Forest	Feb-14	deep	4.98	16.87	0.21	2.41	2.04	0.93	0.000	0.033	0.008	23.73	6.627	2.97
New Forest	Feb-14	shallow	4.48	14.00	0.31	0.70	1.15	2.62	0.003	0.030	0.038	17.17	3.776	33.20
New Forest	Mar-14	deep	4.85	16.60	0.23	2.43	1.94	0.83	0.000	0.027	0.000	22.23	6.850	3.17
New Forest	Mar-14	shallow	4.46	14.35	0.35	0.67	1.03	2.24	0.000	0.024	0.040	17.20	3.819	45.05
New Forest	Apr-14	deep	4.89	16.30	0.22	2.22	1.82	0.77	0.000	0.021	0.000	21.17	7.017	3.54
New Forest	Apr-14	shallow	4.32	11.72	0.37	0.79	1.01	1.37	0.000	0.024	0.049	16.43	2.668	28.00
New Forest	May-14	deep	4.80	16.63	0.26	2.18	1.76	0.74	0.002	0.023	0.011	19.10	6.623	3.42
New Forest	May-14	shallow	4.42	13.70	0.36	0.67	0.99	1.43	0.018	0.022	0.039	17.63	2.492	19.30
New Forest	Jun-14	deep	4.77	15.60	0.23	1.91	1.60	0.68	0.007	0.019	0.000	20.23	6.840	4.01
New Forest	Jun-14	shallow	4.40	13.35	0.36	0.71	0.99	1.31	0.142	0.041	0.077	20.30	2.725	18.10
New Forest	Jul-14	deep	4.78	16.17	0.39	2.03	1.65	0.68	0.000	0.000	0.010	14.25	4.337	5.68
New Forest	Jul-14	shallow	4.39	13.60	0.28	0.74	1.00	1.13	0.000	0.000	0.014	18.45	3.410	19.90
New Forest	Aug-14	deep	4.75	15.30	0.33	1.92	1.59	0.68	0.010	0.040	0.022	21.03	6.260	4.01

New Forest	Aug-14	shallow	4.44	11.30	0.32	0.61	0.56	0.64	0.011	0.039	0.029	16.13	3.043	19.33
New Forest	Sep-14	deep	4.69	16.55	0.29	2.09	1.76	0.71	0.007	0.030	0.014	21.00	5.900	3.57
New Forest	Sep-14	shallow	4.24	15.30	0.29	0.89	0.89	0.76	0.000	0.024	0.000	17.70	3.740	20.60
New Forest	Oct-14	deep	4.68	18.33	0.26	2.30	1.88	0.71	0.002	0.017	0.000	20.03	6.477	3.25
New Forest	Oct-14	shallow	4.37	14.00	0.43	0.78	0.77	1.31	0.005	0.025	0.025	19.10	3.650	21.10
New Forest	Nov-14	deep	4.65	16.67	0.18	2.35	1.94	0.81	0.000	0.033	0.008	21.43	6.503	2.49
New Forest	Nov-14	shallow	4.37	15.70	0.26	0.85	1.37	2.02	0.000	0.027	0.025	20.60	3.750	32.70
New Forest	Dec-14	deep	4.80	17.90	0.16	2.80	2.29	0.97	0.000	0.021	0.030	21.80	6.427	2.94
New Forest	Dec-14	shallow	4.43	16.10	0.22	0.89	1.45	2.29	0.000	0.034	0.061	16.80	2.780	30.43
Skipwith Common	Jan-14	deep	4.48	6.12	1.71	0.55	0.56	5.54	0.005	0.018	0.376	17.43	1.460	24.60
Skipwith Common	Jan-14	shallow	4.03	5.49	2.69	0.78	0.90	5.47	0.022	0.017	1.792	13.31	1.770	75.20
Skipwith Common	Feb-14	deep	4.47	5.60	1.60	0.51	0.56	5.58	0.000	0.045	0.331	16.20	1.627	22.27
Skipwith Common	Feb-14	shallow	4.06	5.03	2.67	0.67	0.84	6.02	0.000	0.024	1.836	12.28	1.590	66.17
Skipwith Common	Mar-14	deep	4.41	5.86	1.60	0.54	0.55	5.38	0.000	0.050	0.302	8.96	7.350	24.13
Skipwith Common	Mar-14	shallow	4.03	4.85	2.66	0.67	0.74	5.75	0.000	0.028	1.875	7.24	4.860	77.70
Skipwith Common	Apr-14	deep	4.39	5.48	1.60	0.50	0.54	5.38	0.000	0.023	0.304	8.55	7.240	22.53
Skipwith Common	Apr-14	shallow	4.02	4.64	2.58	0.61	0.69	5.76	0.000	0.021	1.870	10.93	1.160	73.23
Skipwith Common	May-14	deep	4.29	5.58	1.73	0.59	0.55	5.47	0.013	0.018	0.282	8.07	7.013	22.07
Skipwith Common	May-14	shallow	4.05	4.63	2.73	0.64	0.63	6.01	0.002	0.017	1.767	7.30	3.533	71.70
Skipwith Common	Jun-14	deep	4.38	5.09	1.72	0.45	0.47	4.83	0.047	0.029	0.303	8.64	7.117	24.80
Skipwith Common	Jun-14	shallow	4.02	4.43	2.64	0.55	0.51	5.56	0.040	0.026	1.727	7.88	2.883	85.70
Skipwith Common	Jul-14	deep	4.39	5.09	1.78	0.54	0.50	5.12	0.003	0.022	0.240	7.84	6.343	27.10
Skipwith Common	Jul-14	shallow	4.02	4.44	2.82	0.57	0.53	5.75	0.003	0.000	1.583	12.82	4.473	88.50
Skipwith Common	Aug-14	deep	4.34	4.89	1.68	0.45	0.45	5.30	0.009	0.107	0.184	9.92	5.280	27.43
Skipwith Common	Aug-14	shallow	4.50	4.04	2.52	0.52	0.49	5.98	0.015	0.041	1.427	6.58	1.903	89.47
Skipwith Common	Sep-14	deep	4.37	4.78	1.70	0.40	0.38	5.08	0.000	0.042	0.255	6.61	6.173	26.30
Skipwith Common	Sep-14	shallow	4.04	4.35	2.65	0.53	0.47	6.07	0.002	0.031	1.423	5.70	1.690	86.47
Skipwith Common	Oct-14	deep	4.31	5.15	1.90	0.45	0.40	4.98	0.004	0.117	0.188	6.98	6.047	25.03

Skipwith Common	Oct-14	shallow	4.00	5.03	2.84	0.60	0.55	6.00	0.005	0.025	1.510	5.74	2.233	87.67
Skipwith Common	Nov-14	deep	4.35	4.73	1.58	0.35	0.36	5.59	0.000	0.049	0.404	6.85	7.775	27.65
Skipwith Common	Nov-14	shallow	4.10	4.78	2.38	0.58	0.53	5.92	0.000	0.031	1.560	4.63	2.423	114.47
Skipwith Common	Dec-14	deep	4.47	4.17	1.32	0.32	0.33	4.92	0.002	0.029	0.273	5.28	5.447	27.07
Skipwith Common	Dec-14	shallow	4.08	4.71	2.33	0.61	0.52	4.08	0.002	0.029	1.540	4.72	2.607	90.10
Thorne Moor	Jan-14	dipwell	3.81	6.17	1.05	2.32	0.97	1.00	0.029	0.022	0.752	10.54	0.802	106.80
Thorne Moor	Feb-14	dipwell	3.75	6.56	1.14	3.04	1.30	1.01	0.307	0.072	1.696	13.57	0.569	128.33
Thorne Moor	Mar-14	dipwell	3.69	8.29	0.49	3.71	1.47	1.89	0.064	0.094	0.807	13.43	0.388	148.33
Thorne Moor	Apr-14	dipwell	3.64	7.56	0.40	3.45	1.39	1.42	0.018	0.022	0.700	14.27	4.580	138.67
Thorne Moor	May-14	dipwell	3.69	6.57	0.93	3.13	1.18	1.37	0.022	0.023	0.506	10.06	0.234	131.33
Thorne Moor	Jun-14	dipwell	3.62	6.44	0.11	3.61	1.18	1.72	0.059	0.025	0.767	13.53	0.246	170.00
Thorne Moor	Jul-14	dipwell	3.57	7.23	0.39	4.45	1.47	2.05	0.024	0.006	0.562	12.33	0.543	190.67
Thorne Moor	Aug-14	dipwell	4.11	6.36	0.41	3.57	1.30	1.44	0.047	0.034	0.597	11.82	1.144	157.67
Thorne Moor	Sep-14	dipwell	3.71	7.46	0.28	4.89	1.43	1.84	0.016	0.023	1.771	13.77	0.125	178.00
Thorne Moor	Oct-14	dipwell	3.58	6.92	0.34	3.53	1.28	1.31	0.009	0.020	0.396	12.80	0.264	135.67
Thorne Moor	Nov-14	dipwell	3.69	6.53	0.89	3.18	1.20	1.14	0.040	0.045	0.415	11.93	0.500	132.33
Thorne Moor	Dec-14	dipwell	3.67	7.01	0.86	3.12	1.22	1.27	0.005	0.026	0.430	11.60	0.255	120.33



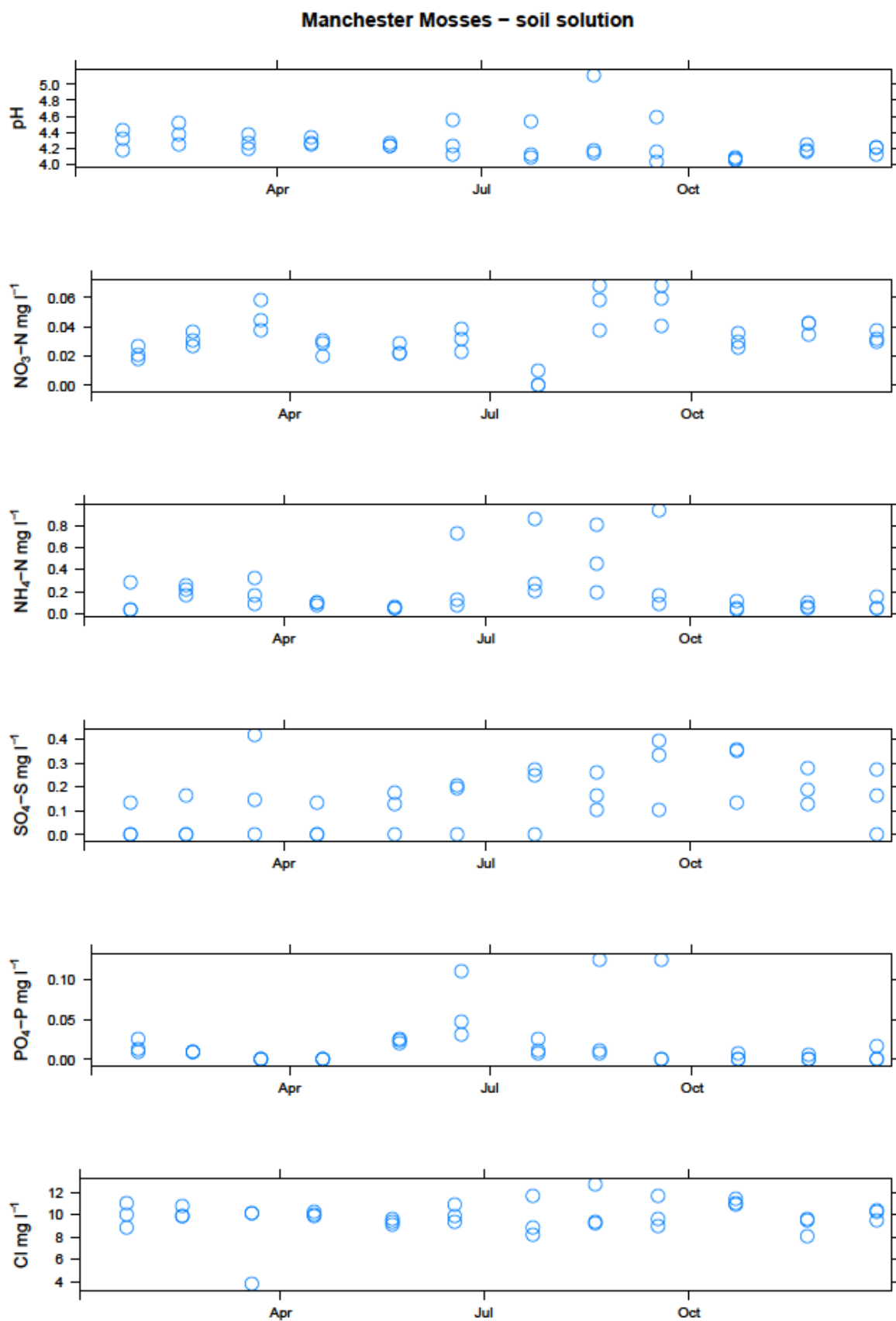
**Table 6.5.2. Annual (2012 - 2014) mean concentrations of pH and solutes in monthly soil solution samples.**

**Determined as means of monthly means. All units with exception of pH in mg L<sup>-1</sup>. Heathland soils, sampled at two depths, shaded.**

site	Year	pH	Na	K	Ca	Mg	Al	PO <sub>4</sub> -P	NO <sub>3</sub> -N	NH <sub>4</sub> -N	Cl	SO <sub>4</sub> -S	DOC
<b>Manchester Mosses</b>  (dipwell)	2012	4.33	4.50	0.28	1.31	0.61	0.20	0.021	0.031	0.319	9.07	0.117	41.04
	2013	4.34	4.67	1.06	1.03	0.61	0.26	0.026	0.027	0.157	9.05	0.150	40.26
	2014	4.27	5.22	0.67	0.97	0.69	0.19	0.019	0.033	0.210	9.84	0.152	35.23
<b>Cannock Chase</b>  (shallow)	2012	4.55	4.07	3.23	1.14	0.22	1.02	0.078	0.034	0.307	5.61	1.518	27.04
	2013	4.35	3.68	2.28	0.17	0.09	1.24	0.006	0.057	0.043	5.78	1.693	15.50
	2014	4.45	3.92	2.08	0.24	0.07	1.51	0.011	0.072	0.044	6.10	1.445	14.67
<b>Cannock Chase</b>  (deep)	2012	5.38	3.39	1.87	1.24	0.28	0.60	0.034	0.048	0.298	5.74	2.082	12.56
	2013	4.63	2.67	1.80	0.42	0.17	0.97	0.003	0.068	0.038	5.18	1.562	6.92
	2014	4.71	3.45	1.58	0.44	0.26	1.15	0.009	0.074	0.023	6.20	1.284	7.98
<b>Cleddau Rivers</b>  (dipwell)	2012	5.61	5.27	0.94	3.69	0.72	0.19	0.408	0.032	3.417	7.73	0.610	34.39
	2013	5.55	6.28	1.02	4.22	0.88	0.09	1.388	0.025	7.964	9.13	0.746	31.07
	2014	4.70	7.29	0.65	1.90	0.88	0.10	0.241	0.028	1.423	10.31	0.610	30.67
<b>Usk Bats Site</b>  (dipwell)	2012	4.76	3.72	0.37	1.99	0.55	0.21	0.054	0.087	0.825	6.36	0.779	28.87
	2013	4.38	4.31	0.37	0.96	0.75	0.19	0.025	0.173	0.614	6.83	1.703	15.86
	2014	4.35	4.17	0.26	0.66	0.53	0.14	0.008	0.078	0.422	6.74	0.860	21.36
<b>New Forest</b>  (shallow)	2012	4.35	14.54	0.28	0.82	1.09	2.03	0.009	0.025	0.093	20.97	2.64	37.06
	2013	4.40	13.92	0.31	0.85	1.08	1.60	0.005	0.023	0.042	17.47	3.922	30.62
	2014	4.40	13.96	0.33	0.77	1.05	1.65	0.017	0.026	0.038	17.97	3.309	27.19
<b>New Forest</b>  (deep)	2012	4.63	18.35	0.24	2.50	2.07	1.00	0.003	0.018	0.052	27.00	6.551	5.03
	2013	4.50	17.39	0.21	2.27	1.87	0.80	0.004	0.019	0.025	25.94	6.881	3.19
	2014	4.78	16.70	0.25	2.27	1.86	0.79	0.003	0.024	0.009	20.97	6.355	3.52

<b>Skipwith Common</b> <b>(shallow)</b>	2012	3.98	5.34	2.11	0.75	0.67	5.91	0.003	0.055	0.835	8.43	4.196	76.05
	2013	3.97	4.69	2.30	0.67	0.61	5.99	0.005	0.028	1.132	7.29	3.133	78.61
	2014	4.08	4.70	2.62	0.61	0.61	5.70	0.008	0.024	1.659	8.26	2.594	83.86
<b>Skipwith Common</b> <b>(deep)</b>	2012	4.40	5.34	1.37	0.58	0.50	5.26	0.004	0.144	0.148	7.72	7.577	34.82
	2013	4.36	5.05	1.31	0.40	0.43	5.13	0.003	0.112	0.212	7.89	5.674	25.21
	2014	4.39	5.21	1.66	0.47	0.47	5.26	0.007	0.046	0.287	9.28	5.739	25.08
<b>Thorne Moor</b> <b>(dipwell)</b>	2012	3.71	6.68	0.93	3.62	1.33	1.37	0.016	0.025	0.448	10.74	1.670	131.81
	2013	3.73	6.84	0.53	3.77	1.20	1.36	0.054	0.026	0.832	11.75	0.787	111.02
	2014	3.71	6.93	0.61	3.50	1.28	1.45	0.053	0.034	0.783	12.47	0.804	144.84

Figure 6.5.1 Soil solution chemistry (2014): Manchester Mosses SAC



# Manchester Mosses – soil solution cont.

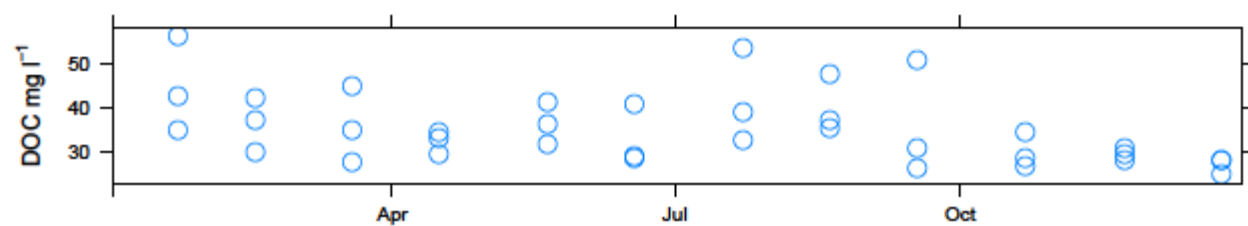
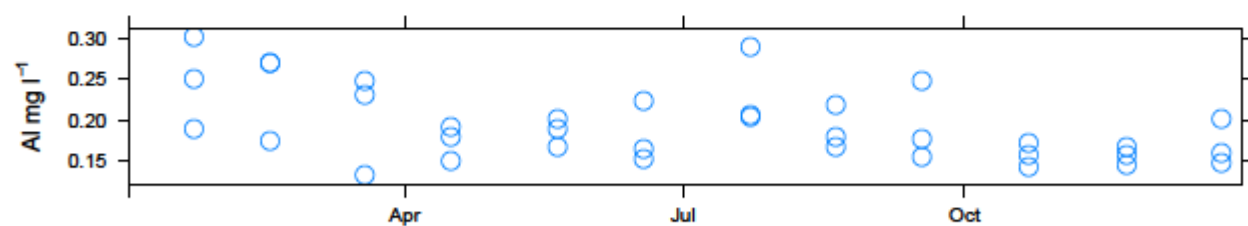
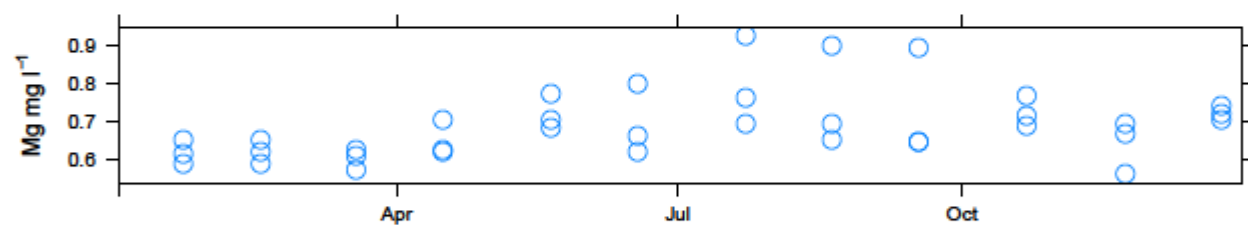
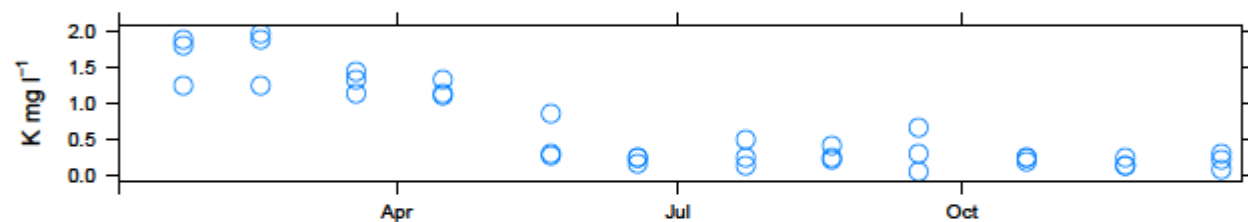
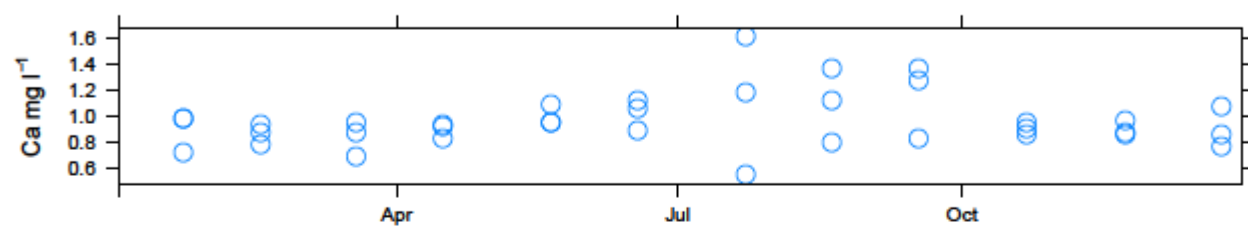
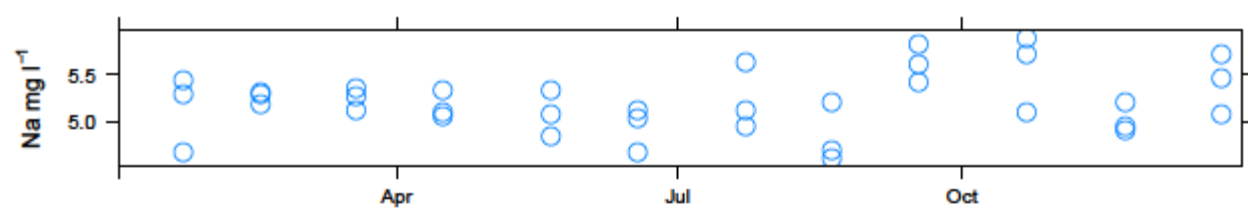
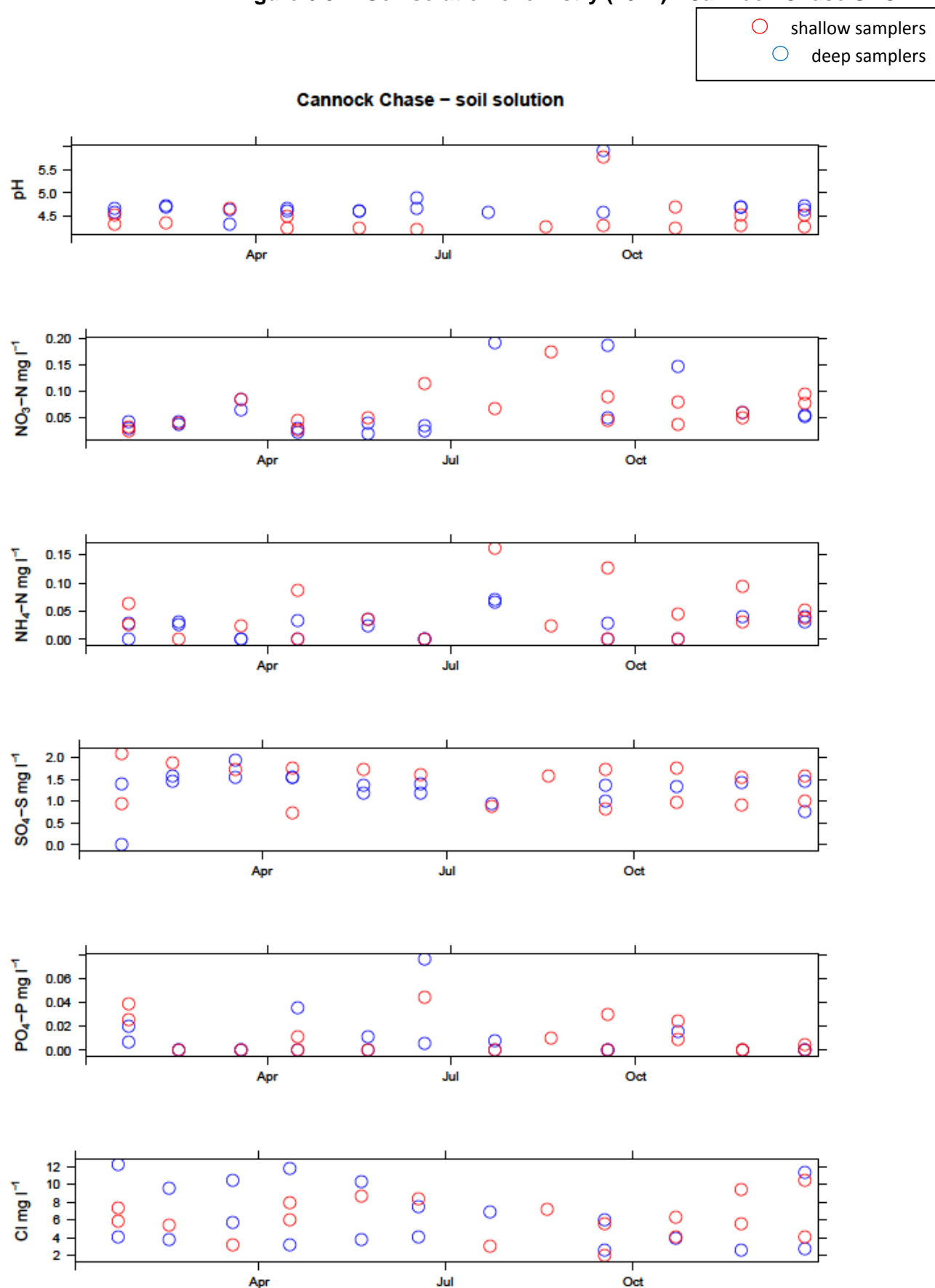


Figure 6.5.2 Soil solution chemistry (2014): Cannock Chase SAC



# Cannock Chase – soil solution cont.

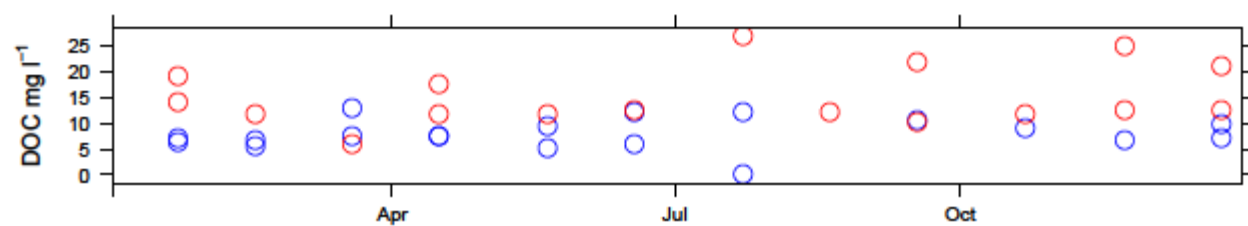
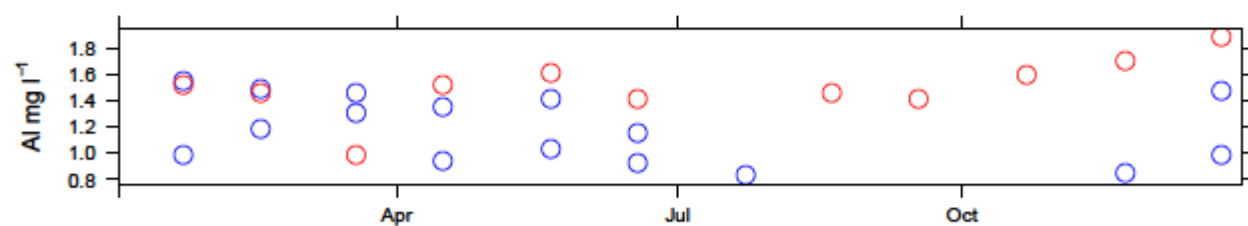
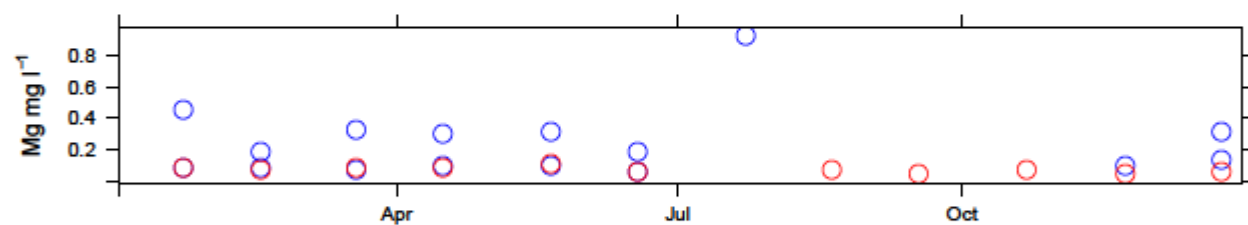
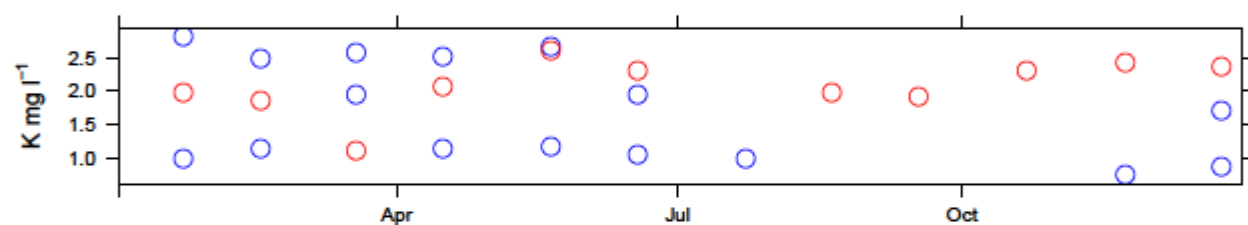
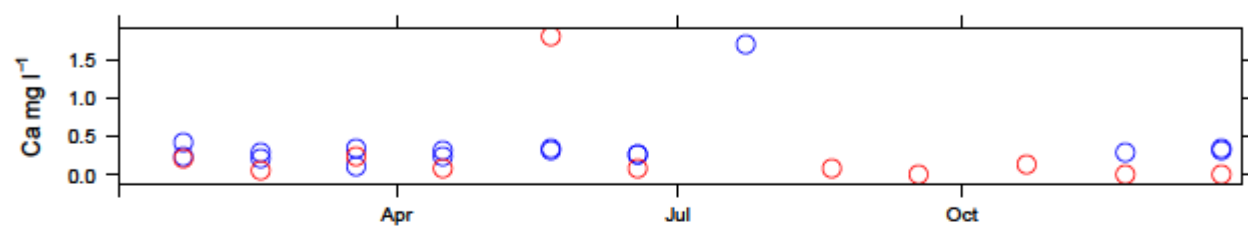
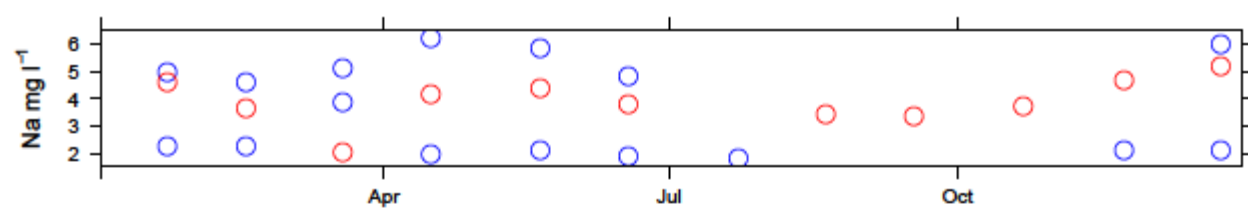
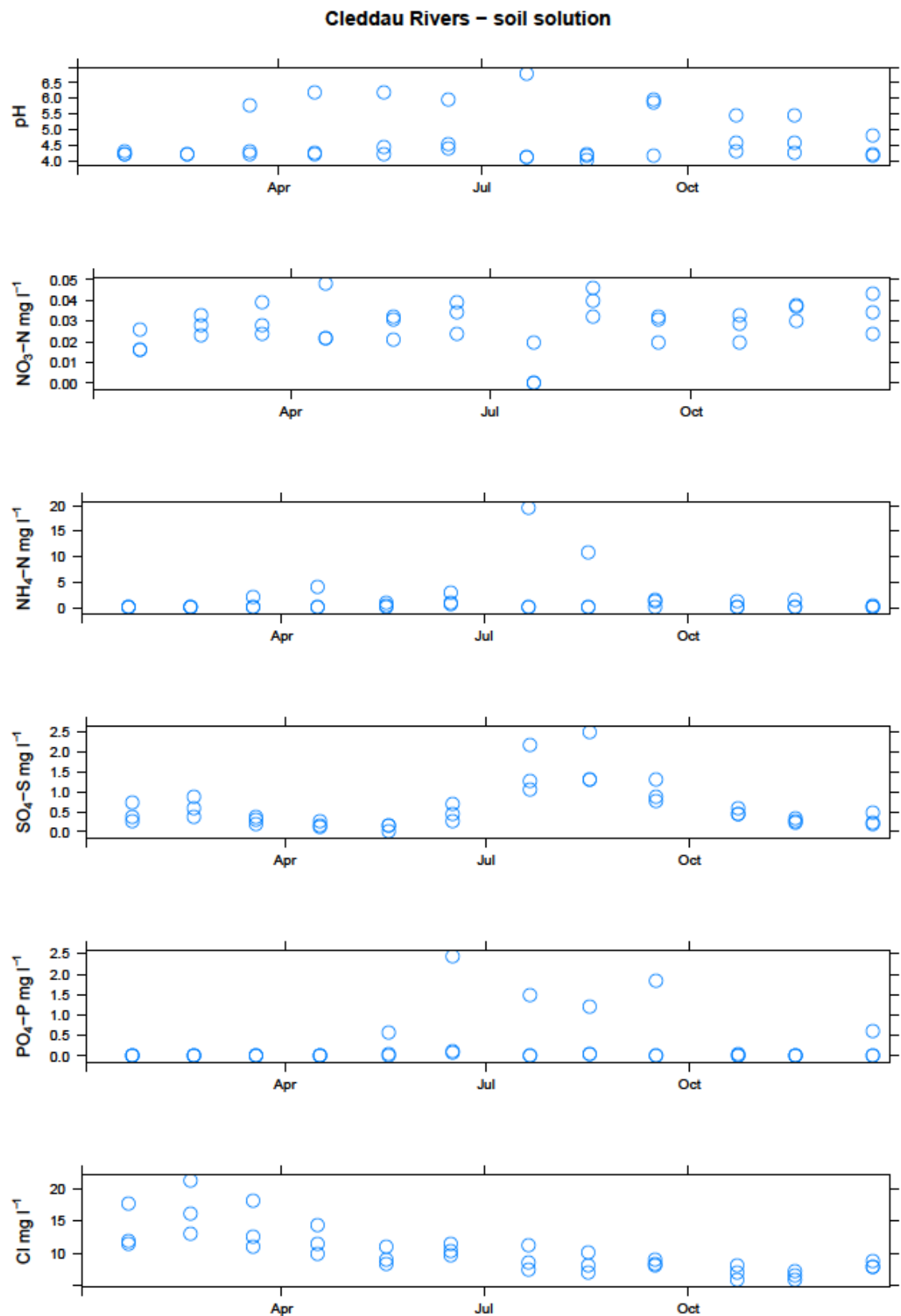




Figure 6.5.3 Soil solution chemistry (2014): Cleddau Rivers SAC



### Cleddau Rivers – soil solution – cont.

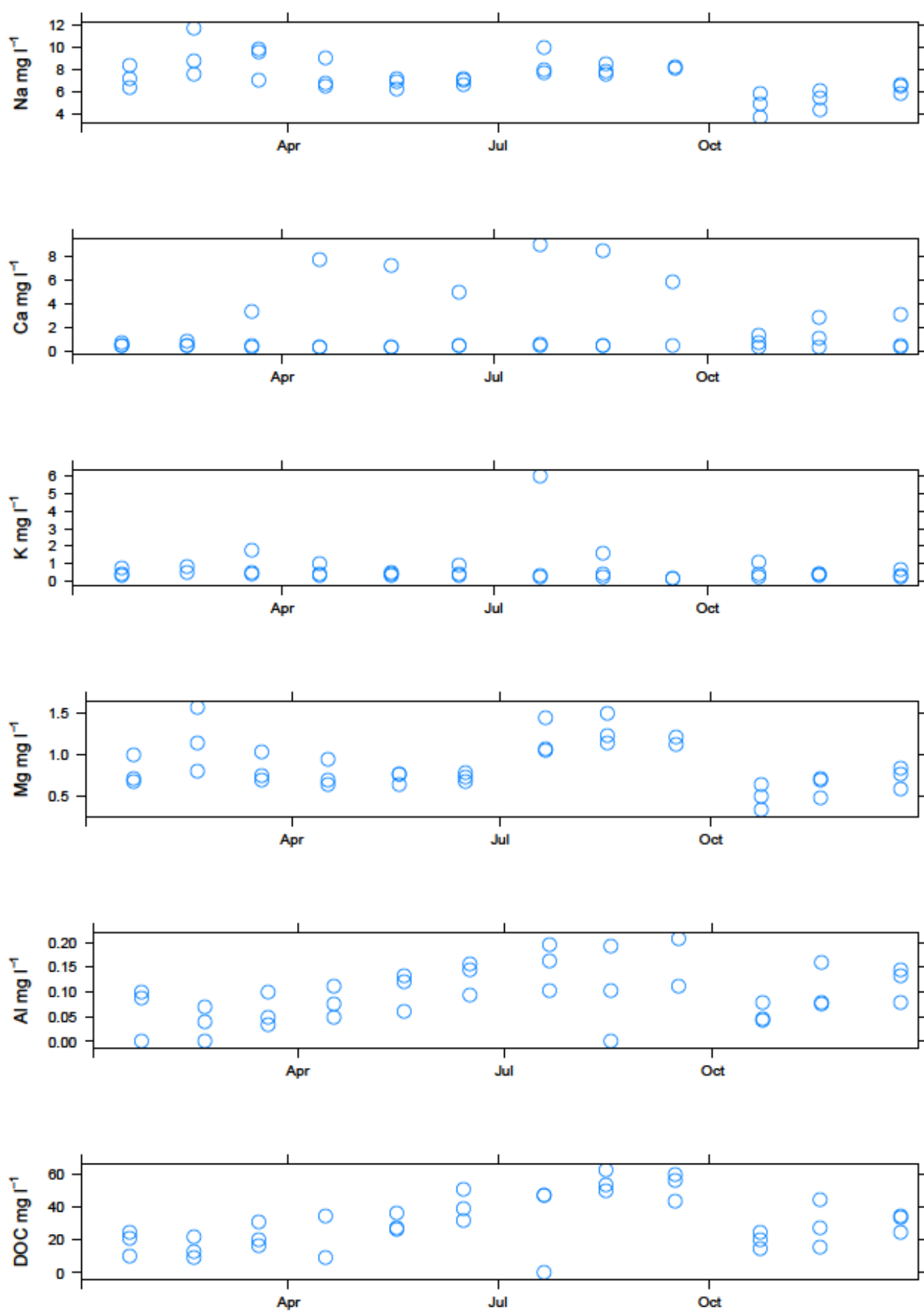
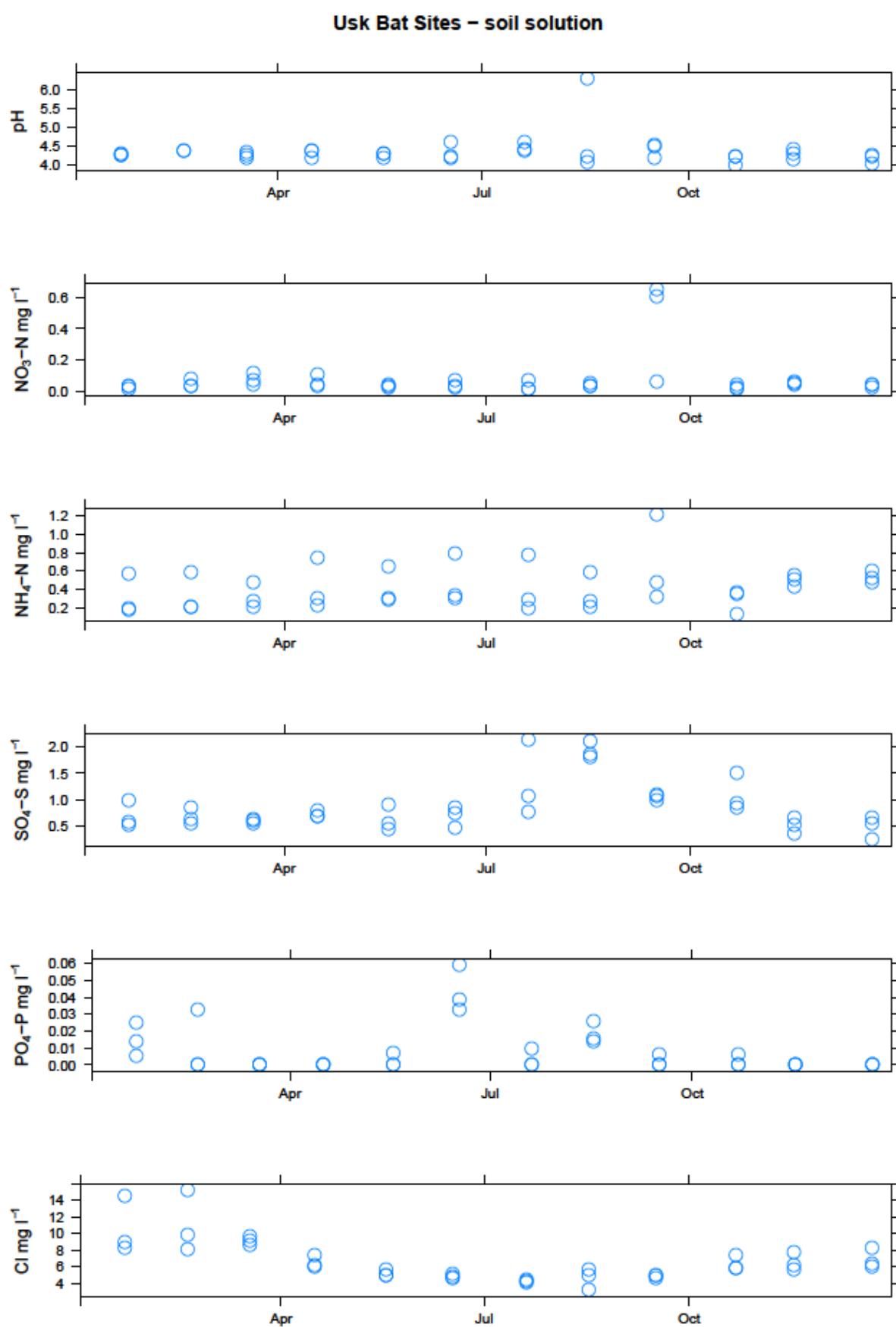


Figure 6.5.4 Soil solution chemistry (2014): Usk Bat Sites SAC



# Usk Bat Sites – soil solution – cont.

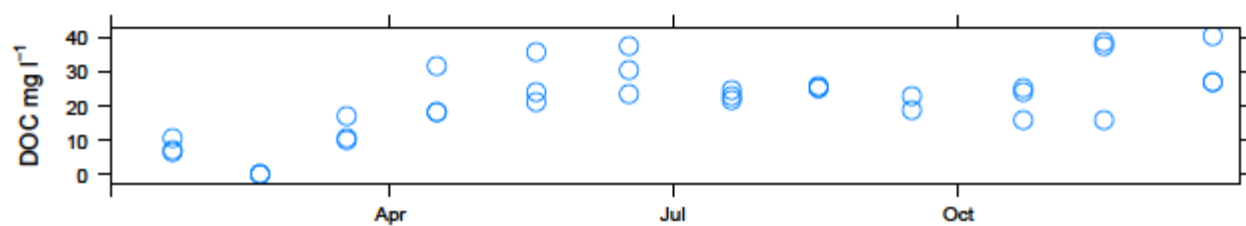
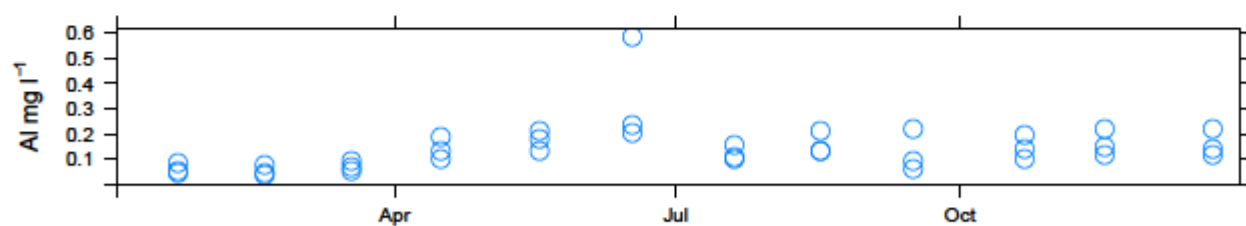
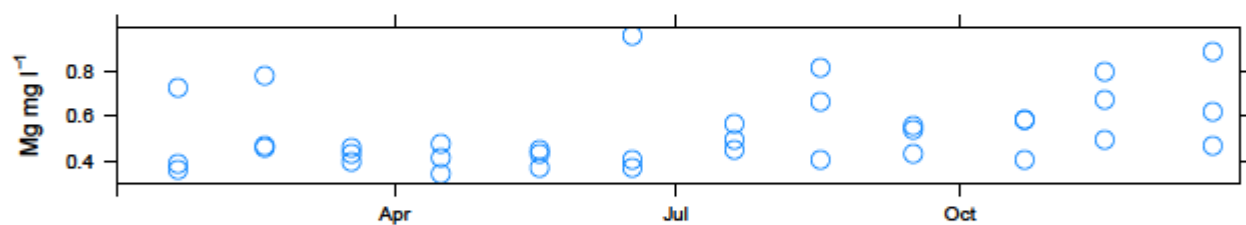
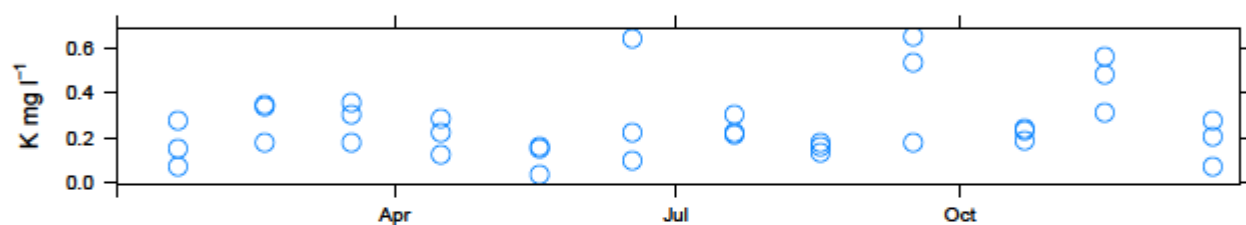
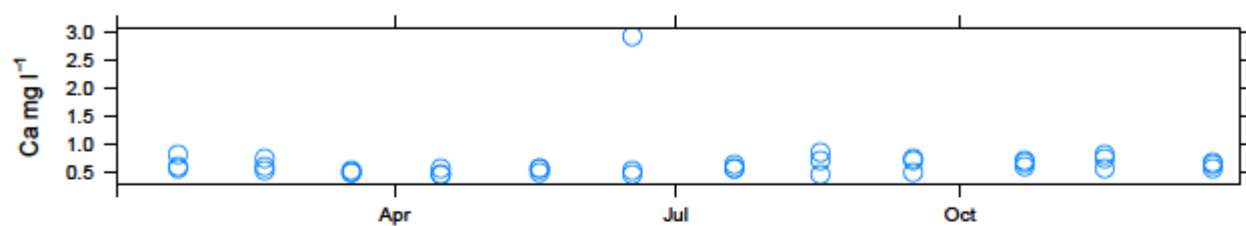
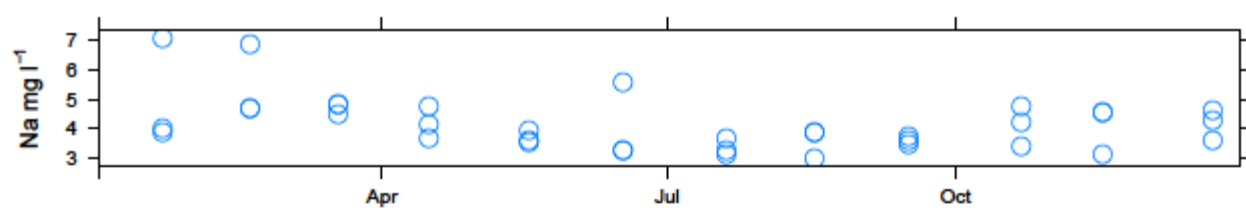
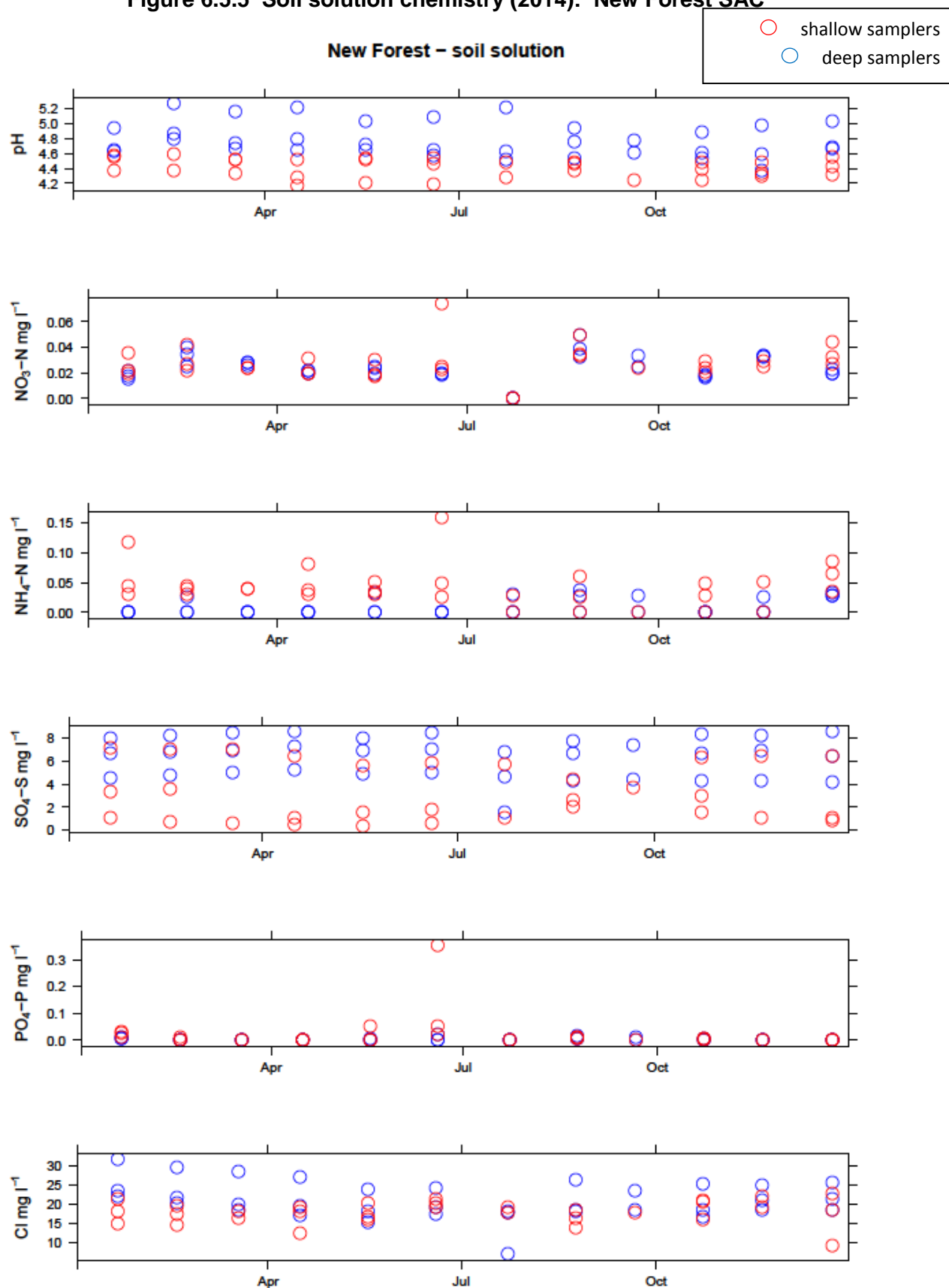


Figure 6.5.5 Soil solution chemistry (2014): New Forest SAC



# New Forest – soil solution – cont.

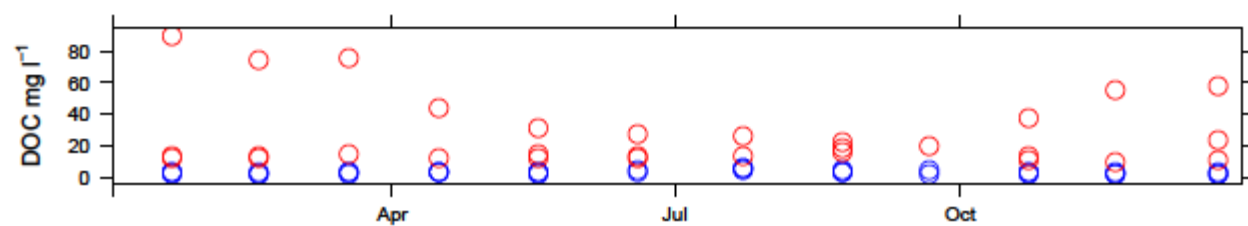
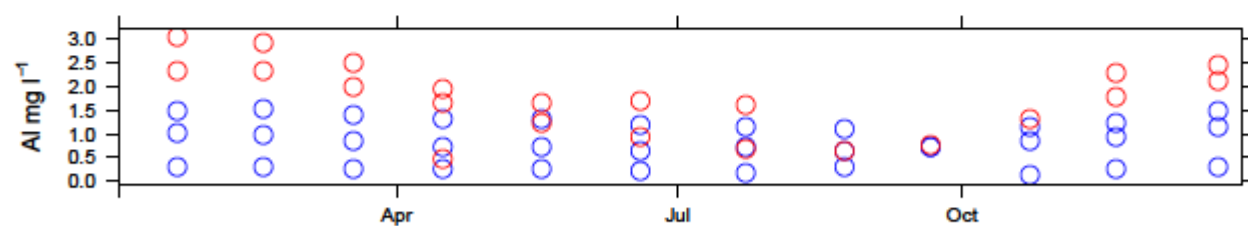
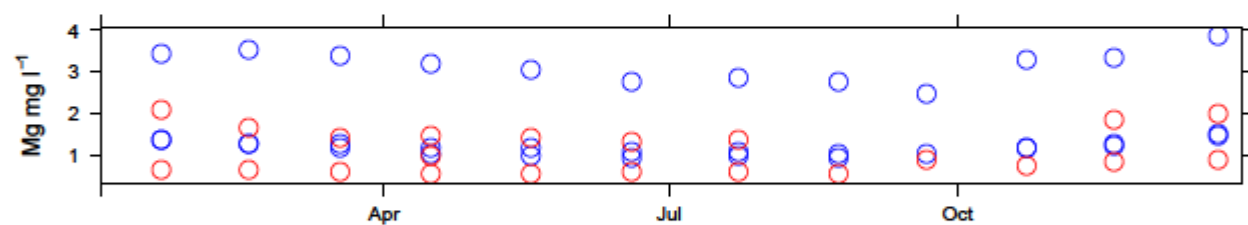
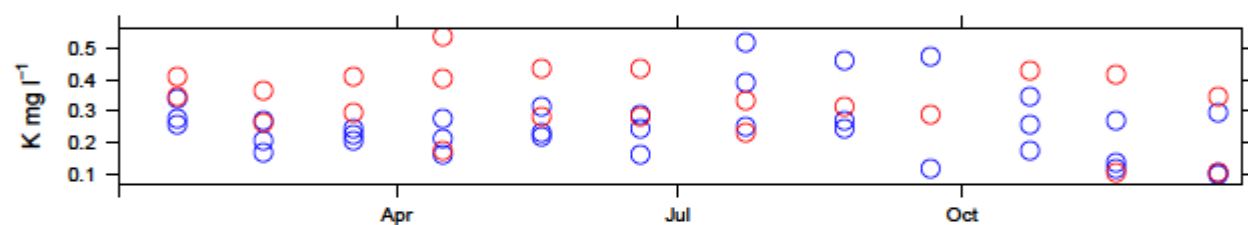
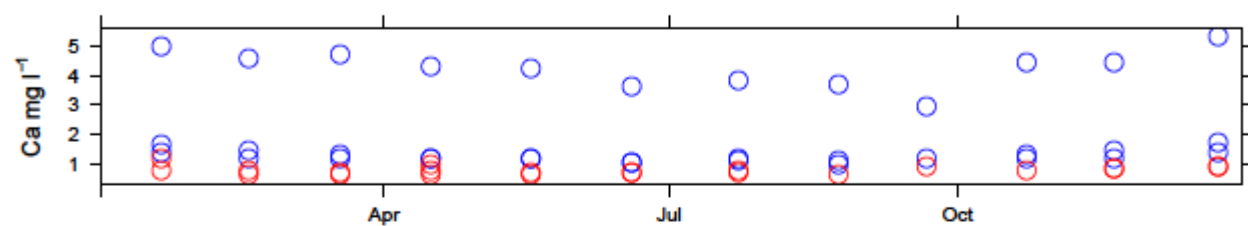
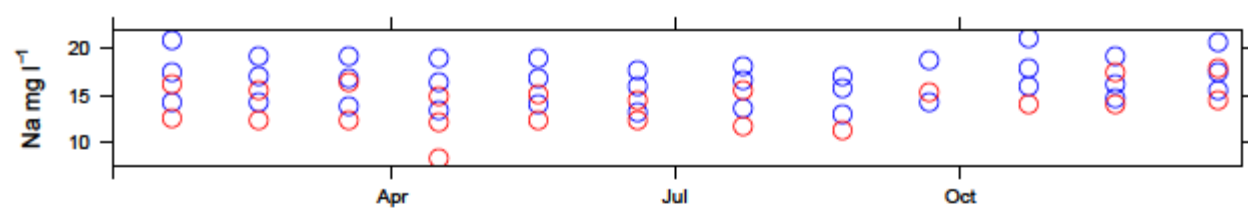
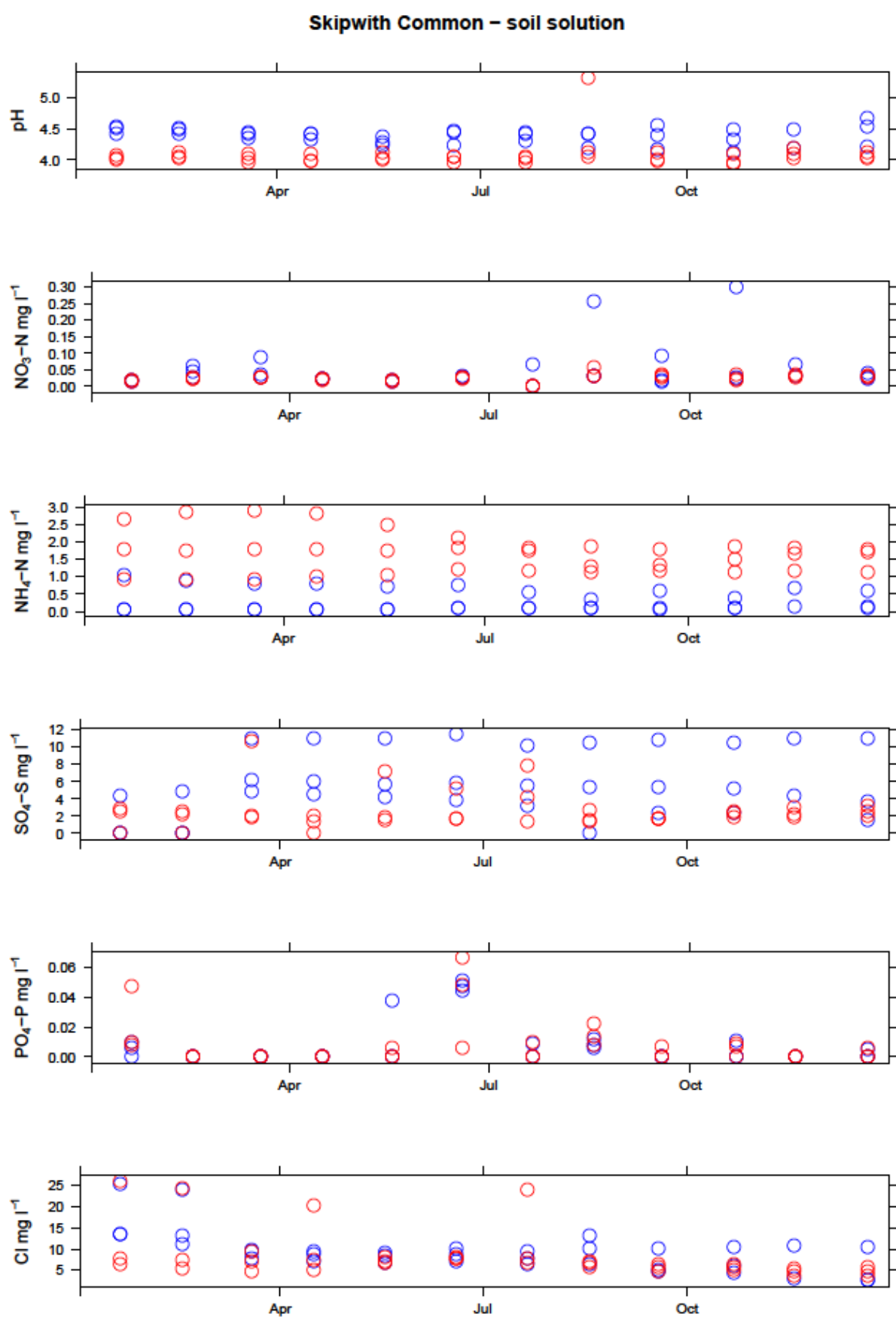




Figure 6.5.6 Soil solution chemistry (2014): Skipwith Common SAC



# Skipwith Common – soil solution – cont.

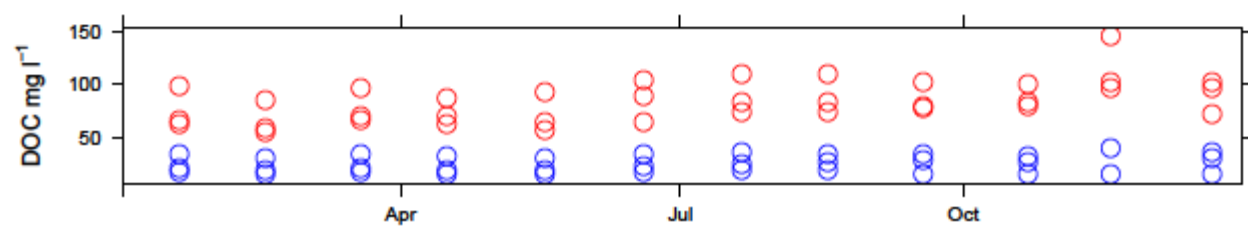
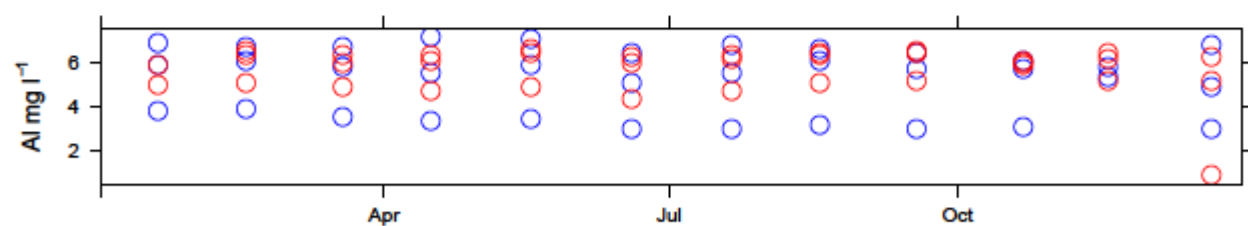
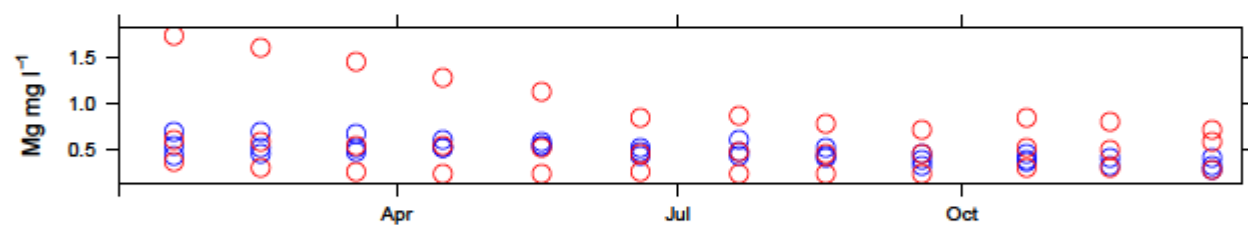
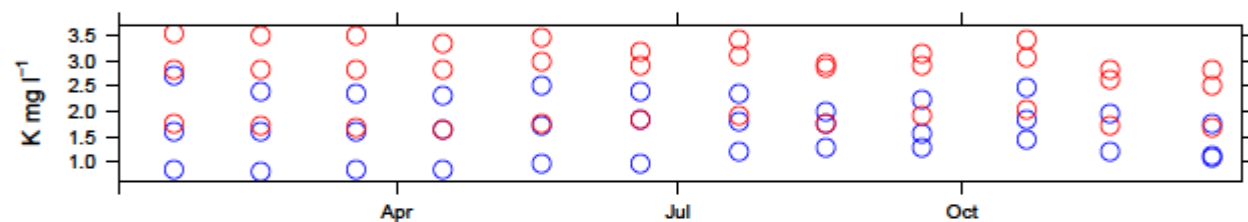
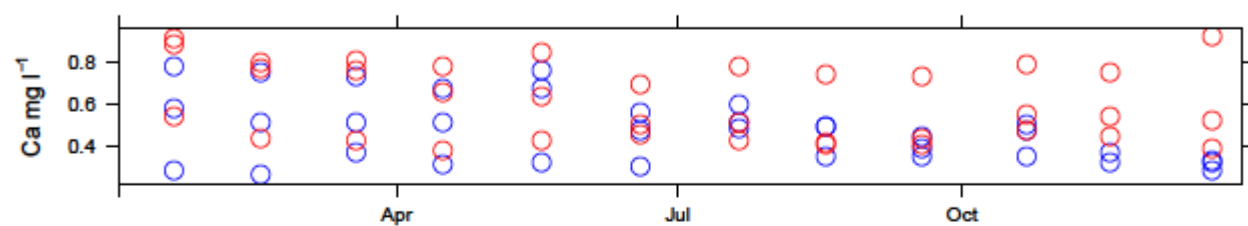
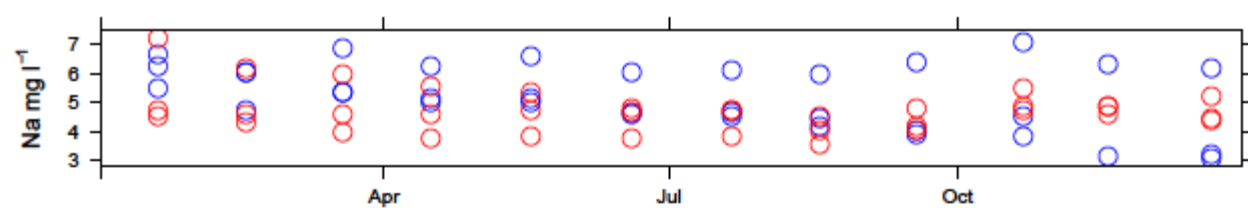
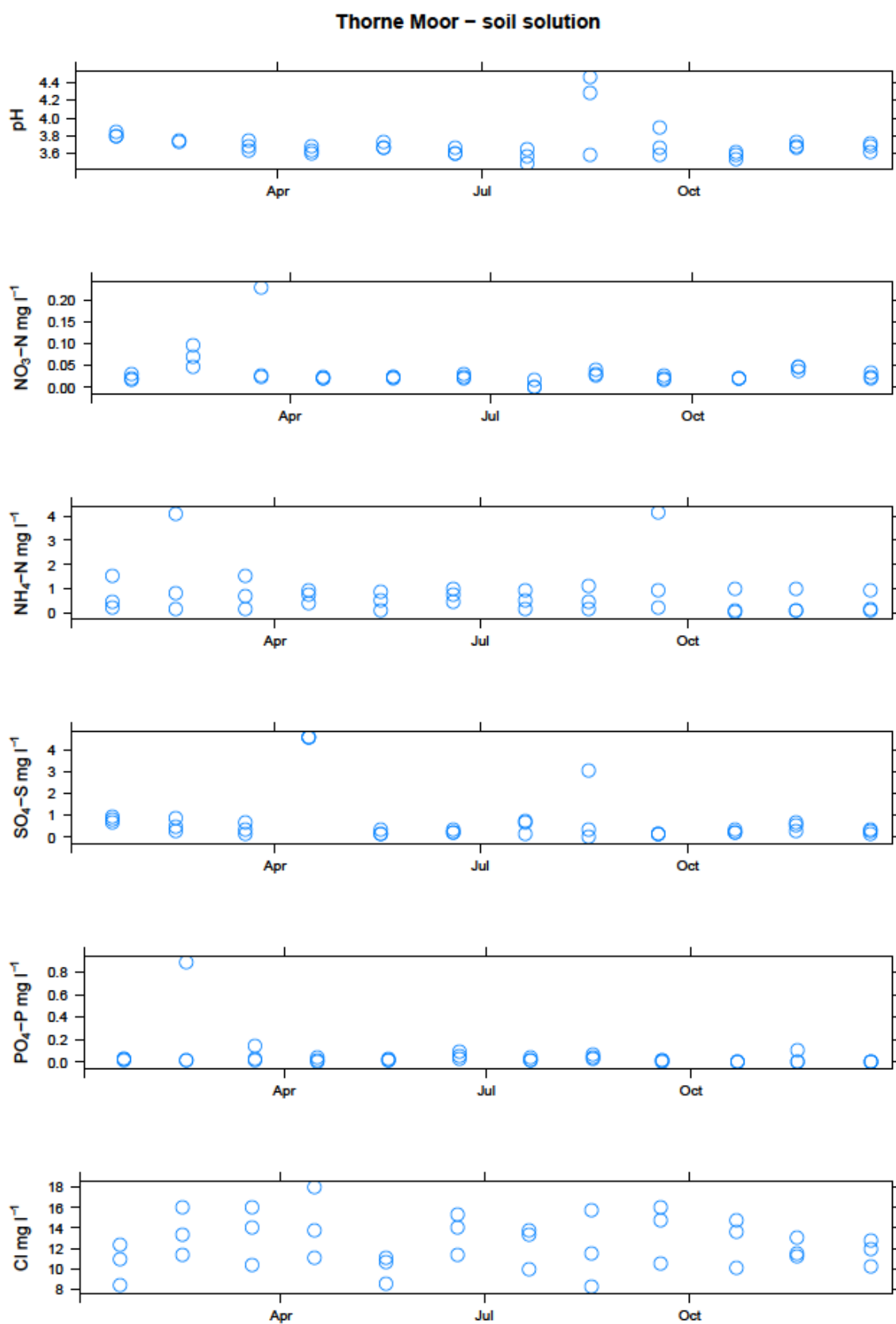
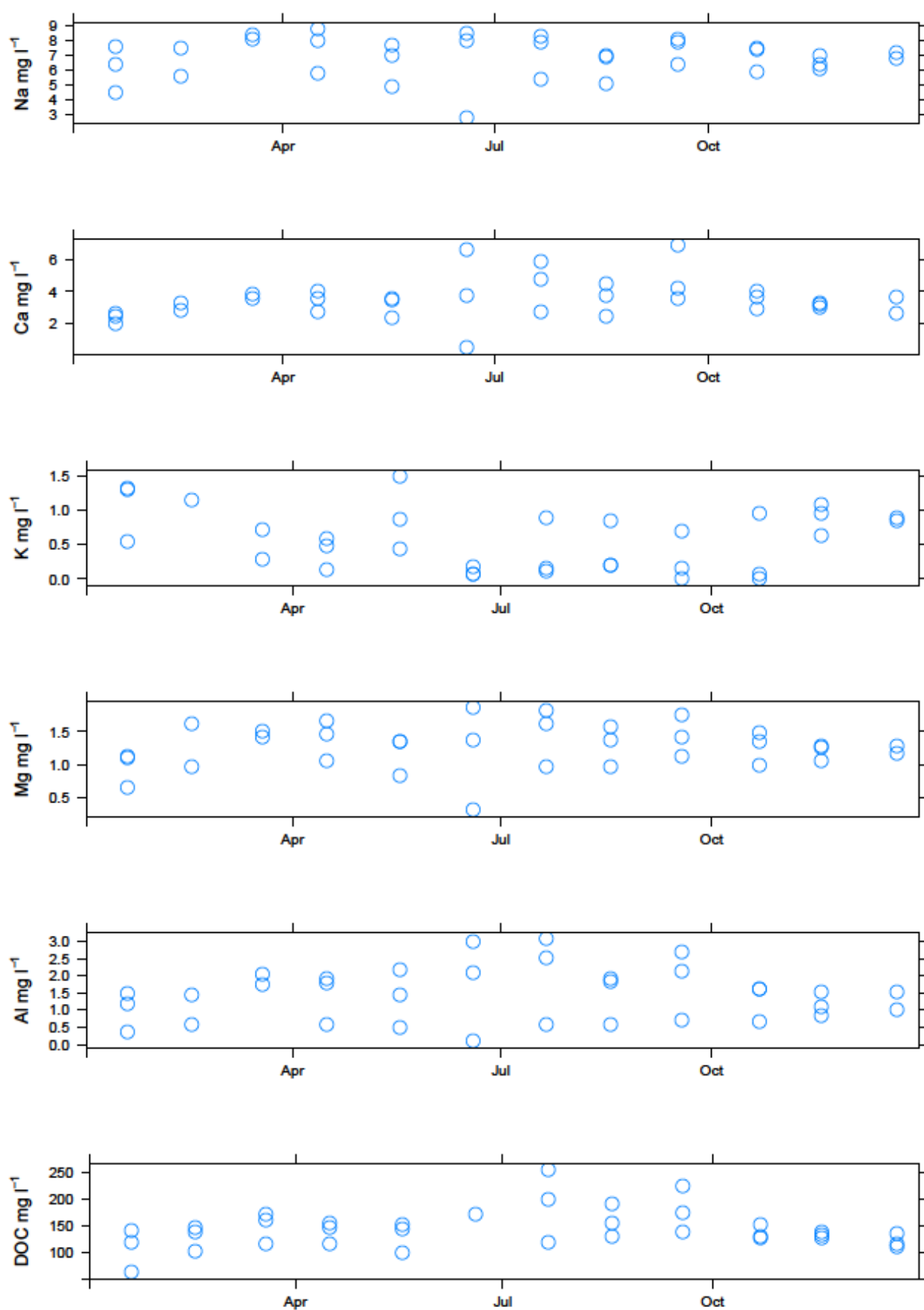


Figure 6.5.7 Soil solution chemistry (2014): Thorne Moor SAC



### Thorne Moor – soil solution – cont.



## 6.6 Comparison of annual summary data for 2012-14

### 6.6.1 Deposition measurements

Overall, the magnitude of deposition estimates for individual sites has remained highly consistent over the 2012-14 monitoring period. Thorne Moor, which showed the highest levels of total acid deposition in all three years also provided an indication of a possible downward trend in this deposition metric, but elsewhere there was no clear evidence for reductions over the three years of monitoring. Total acid deposition increased slightly at Usk Bat Sites and in 2014 was at a similar level to both Thorne Moor and Cannock Chase. Cleddau Rivers received consistently the lowest amounts of total acid deposition, followed by New Forest. It is likely that this reflects the influence of relatively clean Atlantic air masses at these near coastal locations, as indicated by elevated concentrations of seasalt-derived chloride in bulk wet deposition. At most sites, nitrogen species dominated the acid load throughout the three years. With the exception of Cleddau Rivers, N species represented between 65 and 81% of total acid deposition in 2014, as opposed to 16 to 34% for sulphur species.

Spatially, bulk wet non-seasalt  $\text{SO}_4$  deposition has been highest at Thorne Moor, Skipwith Common and Usk Bat Sites while estimated dry deposition of  $\text{SO}_2$  has been substantially higher at Thorne Moor than all other sites. In contrast to  $\text{SO}_4$ , levels of wet deposited  $\text{NO}_3$  at Thorne Moor were at a similar level to most other sites, while Usk Bat sites consistently showed the highest fluxes of this species. Bulk wet deposition of  $\text{NH}_4$  has also tended to be highest at Usk Bat sites, with the exception of 2012 when levels at Thorne Moor were higher. Conversely, in 2014 bulk wet deposition of  $\text{NH}_4$  at Thorne Moor was the lowest of all sites on the network. Dry  $\text{NO}_2$  deposition was substantially higher at Thorne Moor, Manchester Mosses and Cannock Chase than other sites, while deposition of  $\text{NH}_3$  was highest at Cannock Chase, followed by Thorne Moor.

Patterns of interannual variability in deposition estimates for individual S and N species and wet and dry forms varied between sites. Generally, bulk wet  $\text{SO}_4$  was lowest in 2013 – possibly reflecting relatively low total annual rainfall in this year compared to 2012 and 2014, but there was not such a consistent pattern in inter-annual variation in bulk wet  $\text{NO}_3$  or  $\text{NH}_4$ , or in dry  $\text{SO}_2$ ,  $\text{NO}_2$  or  $\text{NH}_3$  deposition. Overall annual deposition estimates of dry  $\text{NO}_2$  at individual sites were the most consistent between years of all species estimated.

### 6.6.2 Soil chemistry measurements

The pH of soil solution collected in the bog dipwells of Manchester Mosses, Cleddau Rivers, Usk Bat Sites and Thorne Moor, differed markedly between sites. The lowest pH occurred at Thorne Moor. Mean annual pH at this site was particularly stable – ranging from 3.71 to 3.73. Mean annual pH of Manchester Mosses and Usk Bat Sites soil water fell mostly between pH 4.3 and 4.4 and provided little evidence of any directional trend. Soil water chemistry of the Cleddau Rivers site appears to have been strongly influenced by fluctuating hydrology. The apparent drop in mean pH in 2014, relative to the two previous years, followed re-positioning of one sampler in 2013 which was becoming routinely blocked. The new location of this sampler appears less influenced by groundwater, as indicated by a large reduction in base cation concentration.

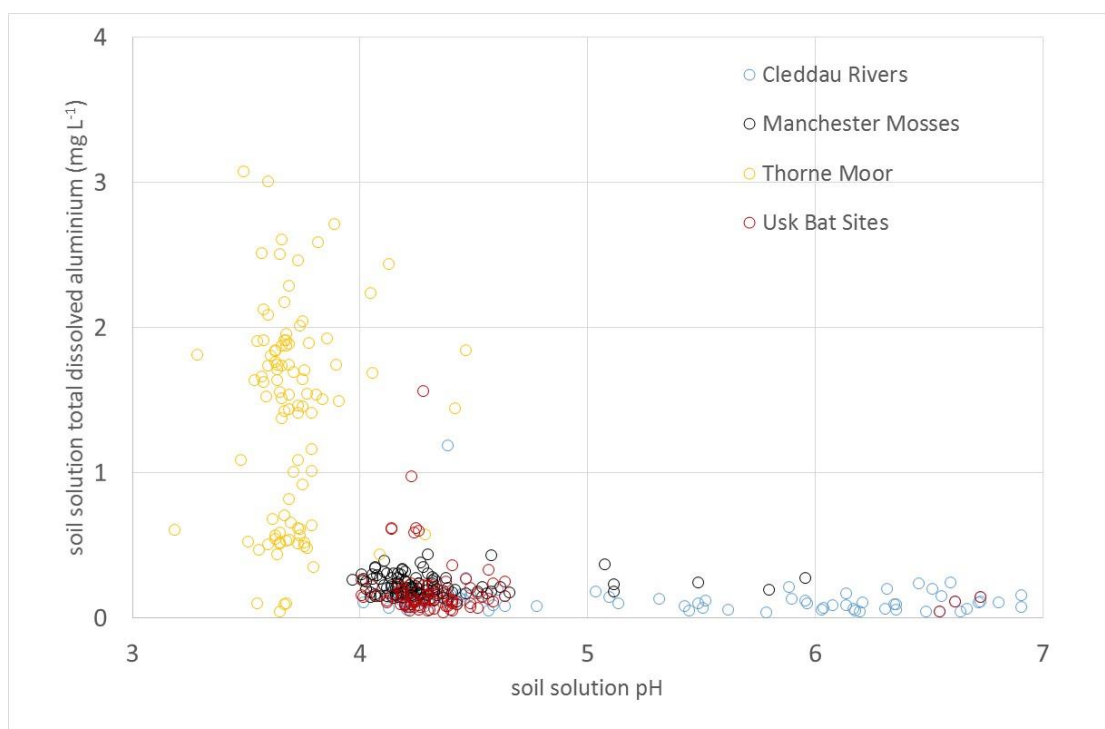
Soil solution pH of shallow and deep soil suction samplers at the heathland sites, Skipwith Common, Cannock Chase and New Forest was also very stable between years and showed no clear evidence of change with time. The most acidic shallow soil water occurred at Skipwith Common with all three samplers regularly registering a pH of around 4.0. Shallow soil solution pH at Cannock Chase and

New Forest generally oscillated around pH 4.5. Deep soil solution pH tended to be higher than shallow pH at these three sites, reflecting less influence from organic acids and greater buffering by the mineral soil horizons. An apparent drop in deep soil pH at Cannock Chase after 2012 is most likely due to variation in the sampling efficiency of some samplers over time in what is normally a very well drained soil.

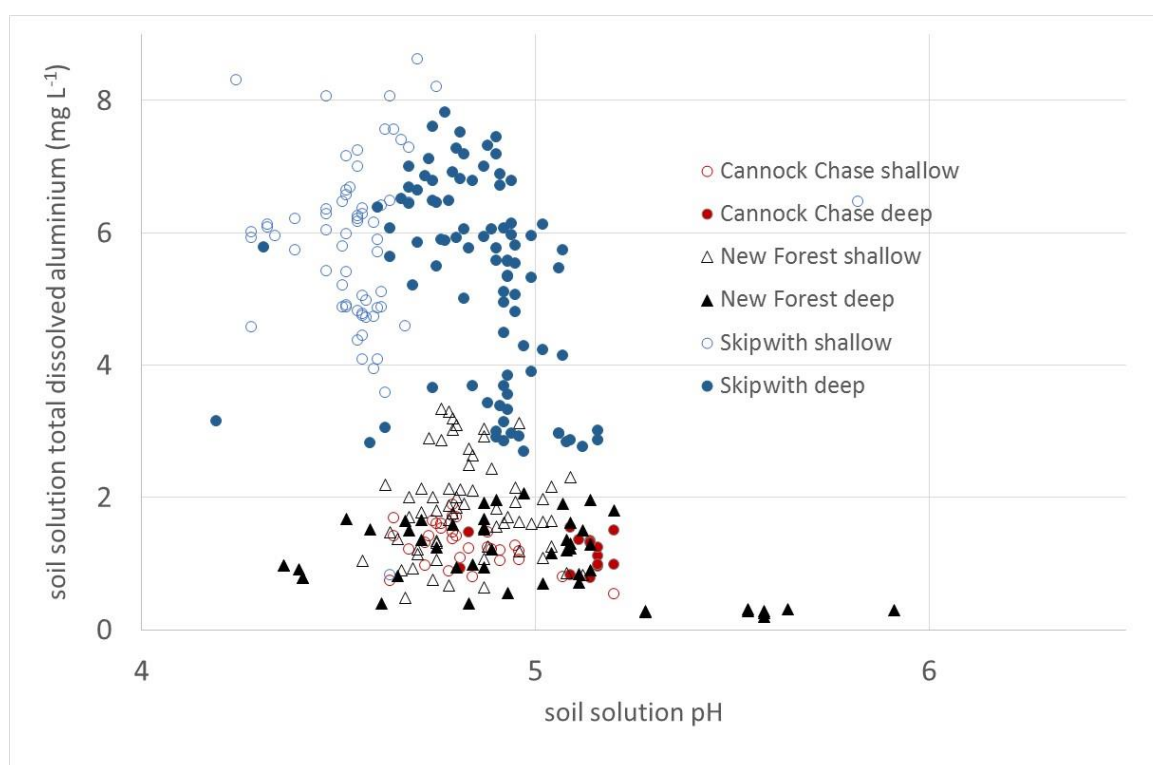
Figure 6.6.2a-b illustrates the relationship between total dissolved aluminium and soil water pH in the soil water of all samples in peatland and heathland sites respectively. This shows that aluminium levels were consistently low in samples with pH>5 – mostly from the relatively lightly impacted Cleddau Rivers site, but maximum concentrations increase sharply as pH falls below 5.0. In this lower pH range most aluminium is likely to occur in ionic form (i.e.  $\text{Al}^{3+}$ ) that is toxic to various plant species. Soil water aluminium concentrations in Cleddau Rivers were consistently low, reflecting relatively high pH, whereas soil water at Thorne Moor was characterised by low pH and particularly high aluminium levels. The highest soil water aluminium concentrations across the network were recorded at Skipwith Common, but shallow soil pH at all three heathland sites fell frequently below 5.0 with associated elevated aluminium concentrations.

**Figure 6.6.2 Relationship between soil solution total aluminium concentration and pH in individual samples from Habitats Monitoring Network bog sites (a) and heathland sites (b)**

a)



b)



Concentrations of  $\text{SO}_4$  in the suction samplers of the three heathland soils tended to be consistently much higher than in the dipwells of the bog sites. This is likely to reflect differences in soil redox conditions associated with waterlogging. Sulphur in anaerobic soils tends to be held in an immobile reduced state (in the form of sulphide) but is oxidised to  $\text{SO}_4$  and released to soil water following dry periods when water tables are temporarily lowered, for example during drought. Both shallow and deep samplers at Skipwith Common showed progressive declines in  $\text{SO}_4$ , in addition to  $\text{NO}_3$ , concentration over the three years, and a similar downward trend in  $\text{SO}_4$  was also observed in the deep samplers at Cannock Chase. There was no clear evidence of changes in these acid anion concentrations in either depths of the New Forest soil, nor in the peats of the three bog sites.

Nitrate concentrations were very stable from year to year in the peat soil solutions of all the bog sites. However, most N in solution in these soils is in the reduced form of  $\text{NH}_4$  which varied markedly between years. The only clear directional trend in  $\text{NH}_4$  in the bog sites was a year to year reduction at Usk Bat Sites. Ammonium concentrations also tended to be higher than  $\text{NO}_3$  in the heathland soils at both depths. The only clear directional trend in N species in the heathland soils was a reduction in  $\text{NH}_4$  and increase in  $\text{NO}_3$  in both shallow and deep samplers at Cannock Chase, indicating an increased rate of nitrification. Three years is, however, too short a period to draw clear inferences regarding the likely longer-term direction of changes in soil chemistry that might be expected in response to long-term changes in S and N deposition.



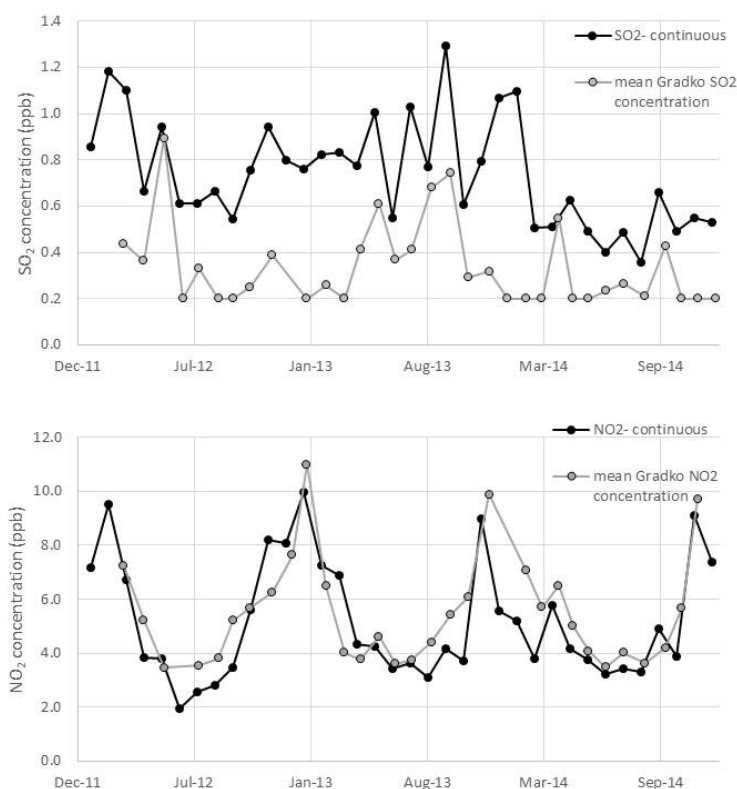
## 6.7 Considerations of uncertainty in deposition estimates with respect to sulphur dioxide concentration and diurnal variation in concentrations

### 6.7.1 Comparison of diffusion tube and gas analyser $\text{SO}_2$ measurements

Sulphur dioxide concentrations determined by Gradko diffusion tubes have fallen below limits of detection over several months and at several sites over the past two years. A standard procedure for calculation and reporting of deposition fluxes has been followed whereby all data falling below the detection limit (of circa 0.4 ppb) are substituted for half this value (i.e. 0.2 ppb). No such issue has arisen with respect to  $\text{NO}_2$  concentrations as these have invariably been recorded substantially above the limit of detection.

Over the monitoring period, additional  $\text{SO}_2$  and  $\text{NO}_2$  Gradko diffusion tubes have been deployed alongside a gas analyser at a test site, Bottesford in the East Midlands. For the purpose of this study, hourly mean values have been obtained from the one minute frequency gas analyser data. These, in turn, have been used to compare monthly mean concentrations obtained by the two methods. After replacement of below detection values recorded by the  $\text{SO}_2$  diffusion tubes with a standard value of 0.2 ppb, mean monthly diffusion tube estimated concentrations of  $\text{SO}_2$  at Bottesford were, on average, about half the monthly mean hourly concentrations measured by gas analyser (Figure 6.7.1). In contrast, mean monthly diffusion tube concentrations of  $\text{NO}_2$  compared well with monthly mean hourly gas analyser based measurements at the Bottesford co-location test site.

**Figure 6.7.1 Comparison of monthly mean concentrations of  $\text{SO}_2$  and  $\text{NO}_2$  at Bottesford measured using a gas analyser (calendar month means), and mean concentrations of triplicate  $\text{SO}_2$  and  $\text{NO}_2$  estimated using Gradko tubes deployed on an approximately monthly schedule.**



It also apparent that mean  $\text{SO}_2$  concentrations determined by diffusion tube for the monitoring period at the seven Habitats Monitoring Network sites are similarly consistently lower than 2010-13  $\text{SO}_2$

concentration estimates provided by the Air Pollution Information System (APIS) at the monitoring site locations (extracted using the 'Search by location tool'). The APIS SO<sub>2</sub> concentrations are derived on the basis of spatial extrapolation of CEH DELTA (DEnuder for Long Term Atmospheric sampling) gas sampler measurements provided by the Acid Gas and Aerosol Network. It is currently unclear to what extent these discrepancies may result from any inherent bias towards under-estimation of SO<sub>2</sub> concentrations using diffusion tubes. Gradko technical representatives have been consulted but have been unable to provide information on performance of their tubes at the relatively low ambient levels of SO<sub>2</sub> that now occur throughout much of the UK.

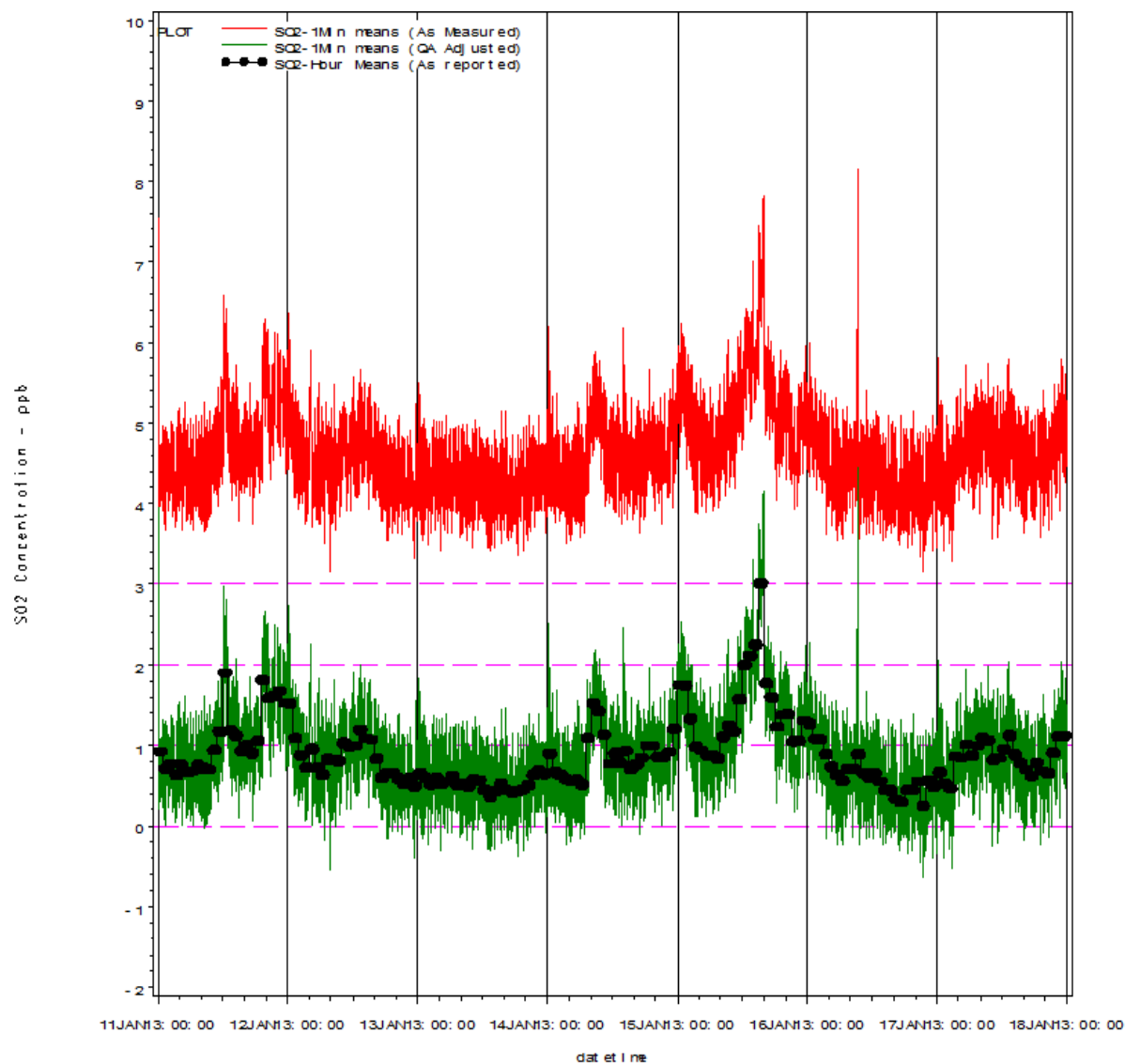
Most automatic monitoring of SO<sub>2</sub> in the UK is undertaken within UK Air Quality Strategy and EU Air Quality Directive guidelines. Analysers are typically configured to measure SO<sub>2</sub> concentration up to and above the limit values of 350 µg/m<sup>3</sup> averaged over one hour (not to be exceeded more than 24 times in a calendar year). The directive requires that SO<sub>2</sub> monitoring using UV fluorescence should be made with a measurement uncertainty of less than 15%. Uncertainty in SO<sub>2</sub> concentrations reported from the DEFRA Automatic Urban and Rural Network (AURN) has been proved to be within this uncertainty limit (Stevenson *et al.*, 2009). The SO<sub>2</sub> analyser at Bottesford is not part of the AURN, but it is installed/maintained and operated on a broadly equivalent basis, as agreed with the Environment Agency (JEP & EA, 2003), and similar uncertainty would, therefore, be expected for SO<sub>2</sub> data reported for this site.

The stated 15% uncertainty relates to measurements at high concentration for comparison with the hourly 350ug/m<sup>3</sup> air quality objective concentration, however ambient concentrations tend to be considerably lower than this. The uncertainty associated with a continuous ambient monitoring system's ability to respond to extremely low concentrations is considered in the DEFRA AURN Local Site Operators manual (Yardley *et al.*, 2012). A typical DEFRA specification for an SO<sub>2</sub> analyser is that it should operate with a zero repeatability of less than 2.5ug/m<sup>3</sup>. (approximately 1ppb). Consequently any reported SO<sub>2</sub> concentrations from automatic UV fluorescence are likely to have this uncertainty associated with the response around zero ppb (and very low concentrations).

To visualise the uncertainty associated with SO<sub>2</sub> measurements used to derive the monthly concentrations, Figure 6.7.2 shows an example of the variability associated with the 1-minute sample data at very low SO<sub>2</sub> concentrations. The majority of the raw (1 minute interval) data (red line) fall between 3.5 ppb and 6 ppb with minute by minute variations around 1 ppb (attributable to measurement uncertainty). The data have then been adjusted on the basis of a daily zero check, resulting in the final reported values black dots (see also QA adjusted minute values shown as green-lines).

Whilst the actual short-term variability of the Bottesford analyser response (around 1 ppb "noise") will be less important when averaging over monthly timescales, the apparent systematic under-reading by the SO<sub>2</sub> diffusion tubes should be considered within the context of the SO<sub>2</sub> analyser's core specification for zero repeatability (1ppb). This does not reject the possibility of systematic bias in the reporting of low SO<sub>2</sub> concentrations by the diffusion tubes, but does suggest that the diffusion tube measurements are within the uncertainty bounds of the Botteford gas analyser measurements.

Figure 6.7.2. Sulphur dioxide (1 minute) data recorded by gas analyser at Bottesford between 11<sup>th</sup>-18<sup>th</sup> January 2013. The red line represents raw data, while the green line represents the corrected data following routine zero checks. Black dots represent hourly means.



6.7.2 Revised sulphur and acidity flux estimates on the basis of potential under-estimate of sulphur dioxide concentrations measured by diffusion tube

The plots and table in this Section mimic Figures 6.4.1 and 6.4.3, and Table 6.4.1, with the exception that SO<sub>2</sub> dry deposition estimates have been multiplied by 2.0 to allow for a potential 50% underestimation of SO<sub>2</sub> concentrations arising from the use of diffusion tubes. The adjustments result in relatively slight increases in estimates of total acid deposition (since this is dominated by nitrogen species), but more marked increases in estimates of total sulphur deposition across the network.

Figure 6.7.2 Estimated annual (2014) bulk wet and dry sulphur deposition. Original sulphur dioxide dry deposition estimate multiplied by 2.0.

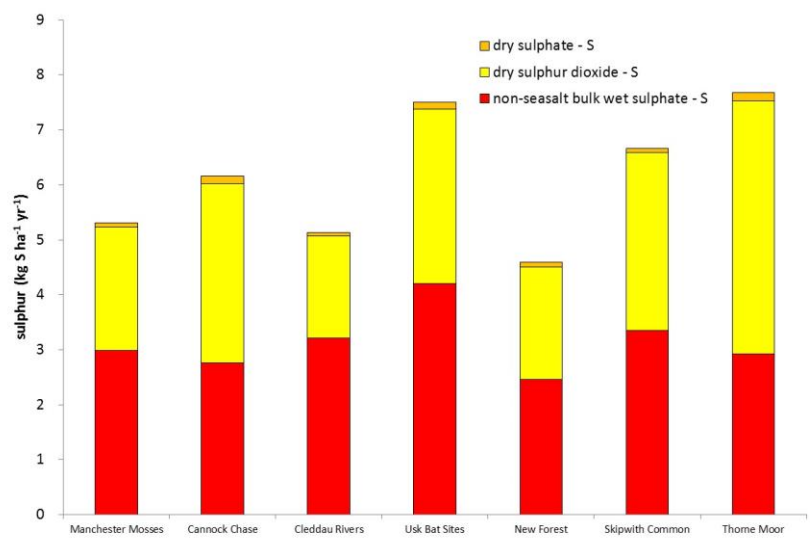


Figure 6.7.3 Estimated total acidity contributed by bulk wet and dry non-seasalt sulphur (amalgamated) and bulk wet and dry nitrogen deposition (separated). Original sulphur dioxide dry deposition estimate multiplied by 2.0.

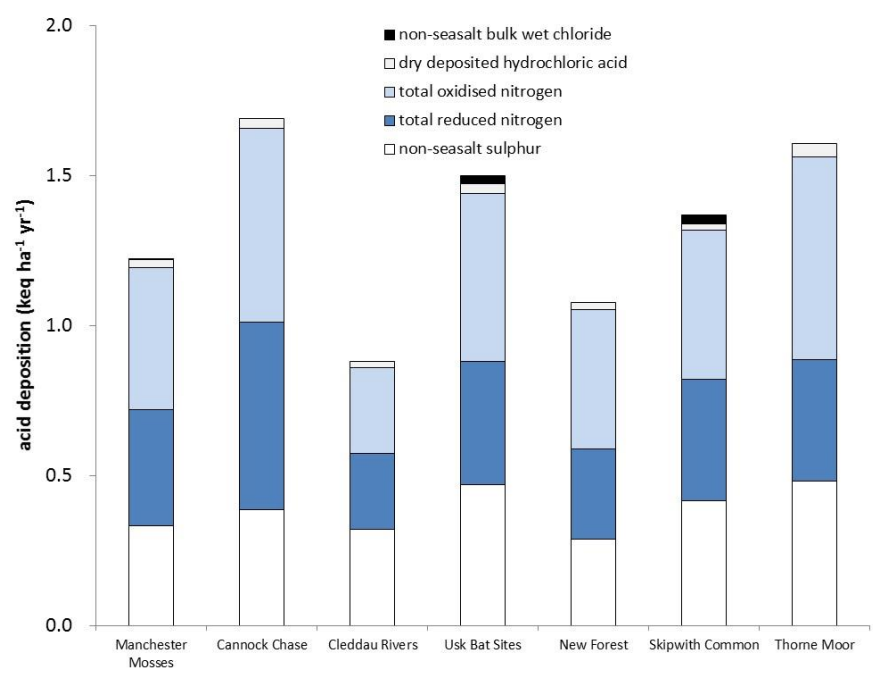


Table 6.7.1

**Adjusted estimated annual wet and dry sulphur, nitrogen, chloride and total deposition as acidity.  
Original sulphur dioxide dry deposition estimate multiplied by 2.0.**

Species (keq ha <sup>-1</sup> yr <sup>-1</sup> )	Year	Man Mosses	Cannock Chase	Cleddau Rivers	Usk Bat Sites	New Forest	Skipwith Common	Thorne Moor
Dry SO <sub>4</sub> -S	2012	0.006	0.011	0.006	0.010	0.008	0.006	0.011
	2013	0.009	0.016	0.008	0.016	0.012	0.009	0.017
	2014	0.005	0.009	0.004	0.008	0.006	0.005	0.010
Dry SO <sub>2</sub> -S	2012	0.224	0.236	0.172	0.258	0.254	0.244	0.552
	2013	0.214	0.260	0.128	0.162	0.246	0.348	0.364
	2014	0.140	0.204	0.116	0.198	0.128	0.202	0.288
Non-seasalt bulk wet SO <sub>4</sub> -S	2012	0.219	0.157	0.175	0.222	0.164	0.268	0.225
	2013	0.132	0.133	0.159	0.192	0.121	0.188	0.184
	2014	0.187	0.172	0.201	0.263	0.154	0.209	0.183
Dry nitric acid-N	2012	0.115	0.234	0.083	0.153	0.162	0.127	0.269
	2013	0.207	0.347	0.163	0.293	0.253	0.198	0.420
	2014	0.103	0.220	0.069	0.159	0.128	0.135	0.308
Dry NO <sub>3</sub> -N	2012	0.026	0.050	0.023	0.046	0.042	0.030	0.059
	2013	0.014	0.024	0.012	0.027	0.021	0.014	0.027
	2014	0.010	0.022	0.008	0.019	0.013	0.013	0.025
Dry NH <sub>4</sub> -N	2012	0.010	0.020	0.009	0.020	0.017	0.012	0.023
	2013	0.027	0.049	0.022	0.047	0.041	0.029	0.057
	2014	0.019	0.041	0.018	0.036	0.028	0.026	0.052
Dry NH <sub>3</sub> -N	2012	0.132	0.243	0.085	0.073	0.077	0.170	0.226
	2013	0.201	0.344	0.112	0.086	0.106	0.161	0.208
	2014	0.158	0.288	0.091	0.087	0.097	0.186	0.258
Dry NO <sub>2</sub> -N	2012	0.184	0.176	0.024	0.059	0.116	0.121	0.185
	2013	0.173	0.184	0.028	0.056	0.122	0.124	0.167
	2014	0.183	0.184	0.052	0.068	0.136	0.143	0.181
Bulk wet NO <sub>3</sub> -N	2012	0.184	0.188	0.159	0.244	0.208	0.221	0.283
	2013	0.145	0.184	0.138	0.244	0.146	0.194	0.186
	2014	0.177	0.220	0.155	0.313	0.187	0.204	0.163
Bulk wet NH <sub>4</sub> -N	2012	0.198	0.186	0.170	0.208	0.143	0.254	0.229
	2013	0.184	0.224	0.131	0.230	0.101	0.194	0.175
	2014	0.212	0.298	0.143	0.288	0.177	0.193	0.097
Non-seasalt bulk wet chloride	2012	0.027	-0.037	-0.025	0.002	-0.134	0.017	-0.009
	2013	0.014	0.017	0.070	0.009	0.044	0.013	-0.003
	2014	0.001	-0.012	-0.053	0.026	-0.003	0.028	-0.008
Dry HCl	2012	0.032	0.054	0.023	0.042	0.038	0.032	0.067
	2013	0.039	0.039	0.025	0.041	0.032	0.030	0.060
	2014	0.025	0.034	0.020	0.034	0.024	0.022	0.044
TOTAL ACID DEPOSITION	2012	1.357	1.518	0.904	1.337	1.095	1.502	2.120
	2013	1.359	1.821	0.996	1.403	1.245	1.502	1.862
	2014	1.220	1.680	0.824	1.499	1.075	1.366	1.601

### 6.7.3 Assessment of potential discrepancies associated with the use of either hourly or monthly averaged SO<sub>2</sub> and NO<sub>2</sub> concentrations to estimate monthly and annual fluxes

Both CBED and EMEP modelled dry deposition estimates of SO<sub>2</sub> and NO<sub>2</sub> derived for this project were based on the application of half hourly meteorological data to monthly “average” SO<sub>2</sub> and NO<sub>2</sub> concentrations determined by monthly diffusion tube measurements.

However, concentrations of these gasses are highly dynamic and show significant diurnal variation. It is feasible, therefore, that biases in the calculation of fluxes might arise as a consequence of assuming a static monthly concentration as opposed to a continually varying one. The cost of deploying continuous gas analysers precluded their use at the Habitats Monitoring Network sites. However, as explained in the previous section, hourly SO<sub>2</sub> and NO<sub>2</sub> concentration data were available from the Bottesford test site, at which Gradko SO<sub>2</sub> and NO<sub>2</sub> diffusion tubes were also deployed. The continuous data were applied, therefore, to test for evidence of an effect of using monthly averaged concentrations on the SO<sub>2</sub> and NO<sub>2</sub> deposition estimates.

CBED and EMEP monthly estimates of SO<sub>2</sub> and NO<sub>2</sub> dry deposition at Bottesford were generated using half hour meteorological data collated at the Thorne Moor monitoring site which lies approximately 50 miles to the north (as local meteorological data were not available), and either hourly or monthly averaged concentrations determined by the gas analyser.

Figure 6.7.4 illustrates a comparison of SO<sub>2</sub> dry deposition fluxes at Bottesford (determined from the mean of CBED and EMEP estimates) using monthly averaged and hourly gas analyser data. This demonstrates a consistent difference in monthly estimates with the former, on average, 8.7 % higher than those estimated using the hourly gas data.

**Figure 6.7.4 Comparison of SO<sub>2</sub> dry deposition fluxes (mean of CBED and EMEP estimates) at Bottesford using monthly averaged and hourly SO<sub>2</sub> concentration data**

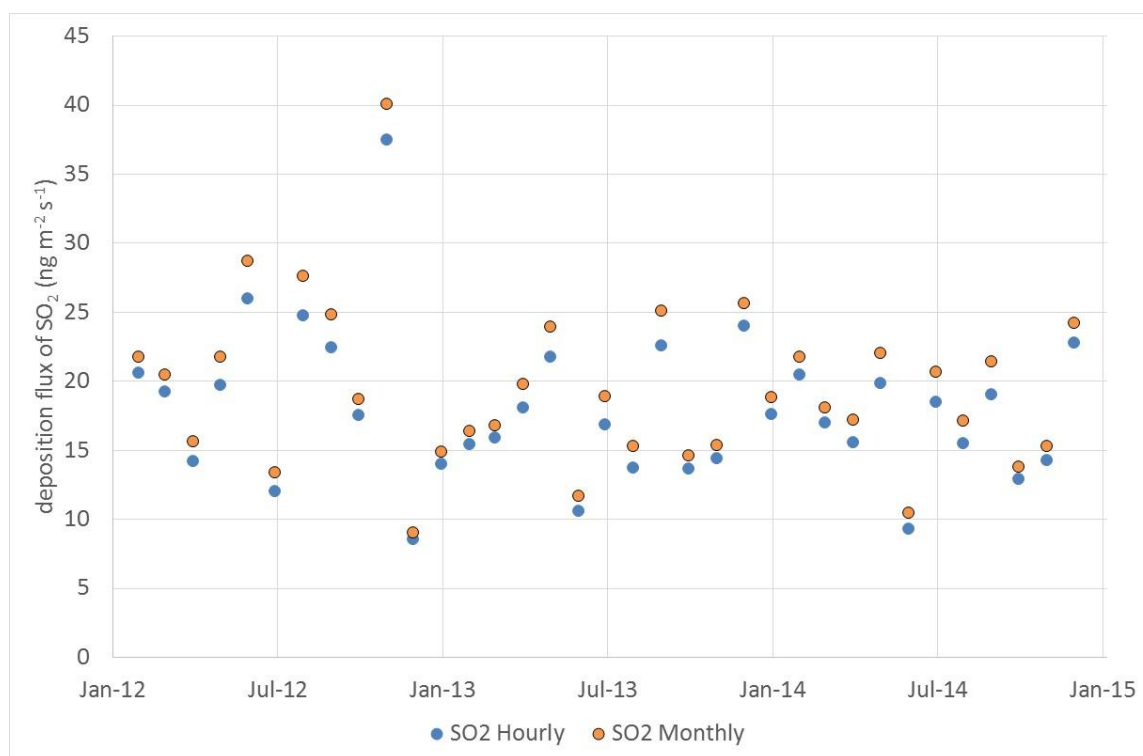


Figure 6.7.5 provides a comparable plot for NO<sub>2</sub> dry deposition. This shows less consistency in the direction of deviation, with monthly deposition estimates based on hourly gas concentrations higher than those based on monthly averages in some months and lower in others. On average, monthly estimates based on the monthly averaged concentration data were 7.8 % higher than those based on hourly gas data.

**Figure 6.7.5 Comparison of NO<sub>2</sub> dry deposition fluxes at Bottesford (mean of CBED and EMEP estimates) using monthly averaged and hourly SO<sub>2</sub> concentration data**

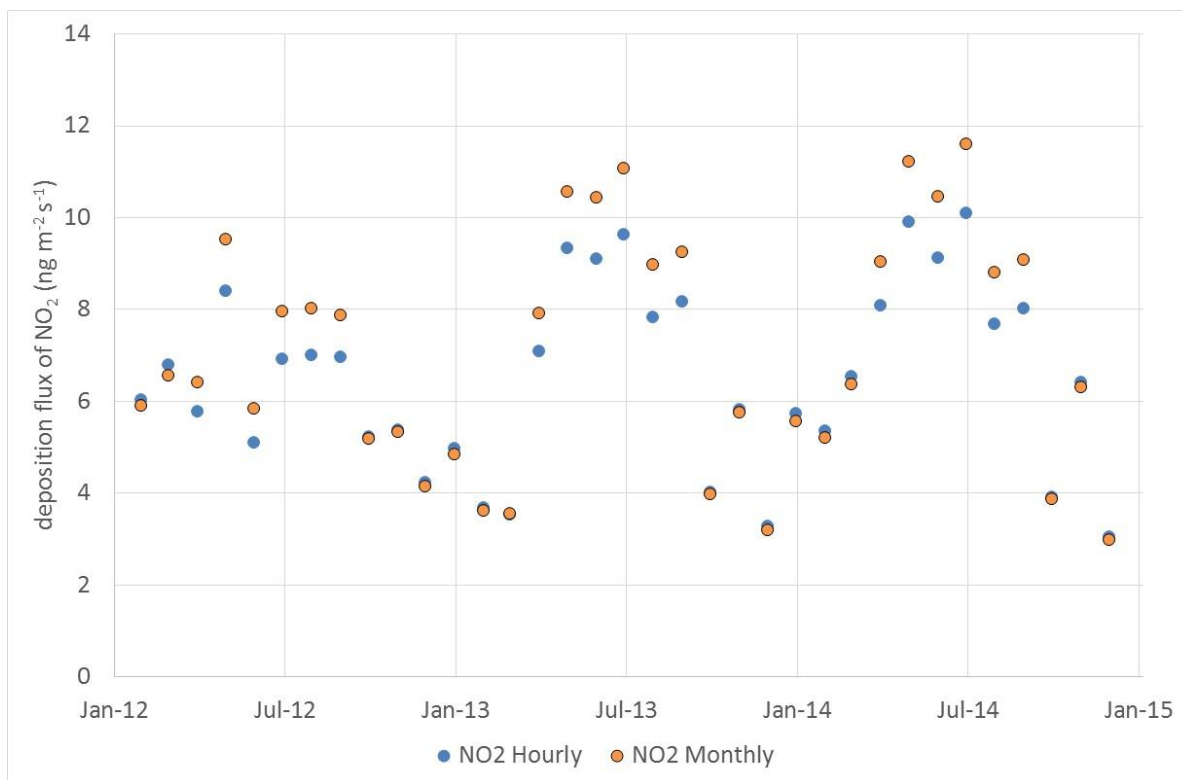


Table 6.7.2 summarises deposition flux estimates at an annual scale. This shows that annual SO<sub>2</sub> dry deposition estimates using averaged monthly data were between 8.5 and 8.9 % higher than those based on hourly data, while NO<sub>2</sub> dry deposition estimates using averaged monthly data were between 6.7 and 8.8 % higher than those based on hourly data.

**Table 6.7.2 Annual estimates of SO<sub>2</sub> and NO<sub>2</sub> dry deposition fluxes for Bottesford (average of CBED and EMEP estimates) based on hourly and monthly gas analyser concentration data and monthly diffusion tube data.**

Method or comparator	species	kg ha <sup>-1</sup> yr <sup>-1</sup> (sulphur or nitrogen) or % difference between approaches		
		2012	2013	2014
Hourly gas analyser	SO <sub>2</sub>	6.32	5.28	5.34
	NO <sub>2</sub>	1.89	2.01	2.21
Monthly gas analyser	SO <sub>2</sub>	6.86	5.74	5.81
	NO <sub>2</sub>	2.02	2.19	2.38
<b>% difference monthly/ hourly</b>	<b>SO<sub>2</sub></b>	<b>8.54</b>	<b>8.67</b>	<b>8.90</b>
	<b>NO<sub>2</sub></b>	<b>6.74</b>	<b>8.76</b>	<b>7.91</b>

A comparison of dry deposition estimates based on separate CBED and EMEP output (Table 6.7.3) demonstrates that most of the difference in the estimate of SO<sub>2</sub> dry deposition flux when using hourly or monthly concentration data is due to differences in EMEP estimates which range from 12.6 to 13.5 %. In contrast, the CBED dry SO<sub>2</sub> deposition estimate based on monthly concentration data ranged from -1.3 to 1.2 % relative to that based on hourly data.

**Table 6.7.3 Annual estimates of SO<sub>2</sub> and NO<sub>2</sub> dry deposition fluxes using either hourly or monthly averaged gas concentration data (gas analyser only) determined by CBED and EMEP models separately.**

	<b>kg ha<sup>-1</sup> yr<sup>-1</sup> (sulphur or nitrogen) or % difference between approaches</b>		
	<b>2012</b>	<b>2013</b>	<b>2014</b>
CBED SO <sub>2</sub> hourly	10.03	10.70	10.68
CBED SO <sub>2</sub> monthly	9.91	10.81	10.81
<b>% difference monthly/hourly</b>	<b>-1.26</b>	<b>1.01</b>	<b>1.20</b>
EMEP SO <sub>2</sub> hourly	23.83	25.24	25.53
EMEP SO <sub>2</sub> monthly	27.04	28.42	28.96
<b>% difference monthly/hourly</b>	<b>13.48</b>	<b>12.57</b>	<b>13.43</b>
CBED NO <sub>2</sub> hourly	6.34	6.83	7.75
CBED NO <sub>2</sub> monthly	7.24	8.24	9.02
<b>% difference monthly/hourly</b>	<b>14.32</b>	<b>20.54</b>	<b>16.43</b>
EMEP NO <sub>2</sub> hourly	1.71	1.76	2.04
EMEP NO <sub>2</sub> monthly	1.41	1.14	1.34
<b>% difference monthly/hourly</b>	<b>-17.39</b>	<b>-35.16</b>	<b>-34.16</b>

Larger differences between dry deposition estimates based on hourly and monthly concentrations were apparent with respect to NO<sub>2</sub>. For this species, CBED estimates based on monthly concentration data were between 14.3 and 20.5 % higher than those based on hourly concentration whereas EMEP estimates based on monthly concentration data were between 17.4 and 35.2 % lower than those based on hourly concentration data. In the case of NO<sub>2</sub>, therefore, a much closer agreement between dry deposition estimates using hourly or monthly averaged concentration data is reached when EMEP and CBED output is combined.

The effect of using hourly concentrations relative to monthly concentrations will depend on a combination of the size and shape of the diurnal variation in the concentration and the size and shape of the diurnal variation in the modelled dry deposition velocity. The concentration and meteorological inputs are the same for both the EMEP and CBED models; hence it is primarily the differences in the dry deposition velocity calculations, and the way in which these incorporate the input data, that drive the differences between the output from the two models. Examples of relevant differences in the model approaches include:

- Surface wetness, which determines non-stomatal uptake, is determined by relative humidity data in the EMEP routine, and wetness sensor data in the CBED routine;



- Canopy resistance ( $R_c$ ) (see Section 5.2.1) determined by EMEP takes into account the influence of  $\text{NH}_3$  in changing the pH of the surface film and its consequent effect on the rate of  $\text{SO}_2$  uptake by the film, resulting in enhanced rates of deposition relative to CBED;
- In the EMEP routine, dry deposition of  $\text{NO}_2$  falls to zero when ambient concentrations fall below 4 ppb.

In summary, relatively small differences in dry deposition estimates of both  $\text{SO}_2$  and  $\text{NO}_2$  were identified when comparing methods based on hourly and monthly averaged concentration data and these are likely to be within the wider uncertainty of the CBED and EMEP models overall. In general, estimates of annual  $\text{SO}_2$  dry deposition (based on the average of CBED and EMEP estimates) using monthly data were less than 10 % higher than when using hourly data, with the differences mostly due to discrepancies in the output from the EMEP model. Differences in estimates of dry  $\text{NO}_2$  deposition (based on the average of CBED and EMEP estimates) were even smaller, reflecting a partial cancelling out of the opposing differences between the monthly and hourly concentration based  $\text{NO}_2$  deposition predictions by the CBED and EMEP routines.

## 7. Summary

An environmental monitoring network of seven terrestrial sites, representing potentially pollutant-sensitive Natura 2000 Special Areas of Conservation has now been operating for over three years. Regular monthly measurements, covering meteorology, sulphur and nitrogen gaseous concentrations, bulk wet deposition chemistry and soil solution chemistry have been made at all sites since the onset of 2012 or earlier and are continuing. All samples are returned to the Environmental Change Network Coordination Unit (ECN CCU) at CEH offices in the Lancaster Environment Centre. Most samples are analysed by the CEH chemistry laboratories, while Gradko tubes, for the measurement of SO<sub>2</sub> and oxides of nitrogen, are processed by the UK Gradko laboratory. With the exception of the meteorological data, managed by E.ON, all data are compiled in a relational database at the ECN CCU, and raw data for both the initial surveys and the consequent non-meteorological monitoring have been presented in this report.

Initial problems concerning the over-estimation of precipitation and supply of power have been overcome but some stations have continued to be affected by other problems – mostly tipping bucket rainfall, but also relative humidity (RH) and temperature (T) sensor, failures. This report includes explanations of how rainfall volumes derived from bulk wet deposition monitoring, and wider meteorological data obtained from the web-based Skylink network, have been used to fill in the resulting gaps in the project's meteorological records.

Two dry deposition modelling routines, CBED and EMEP, have been applied to generate monthly and annual dry deposition estimates of SO<sub>2</sub>, NO<sub>2</sub> and NH<sub>3</sub> for each site. There is generally reasonable agreement between models for most species and sites; differences between these are currently considered to provide an indication of the uncertainties associated with the “Big-Leaf” approach. Monthly fluxes of HNO<sub>3</sub>, HCl, and aerosol SO<sub>4</sub>, NO<sub>3</sub> and NH<sub>4</sub> dry deposition at the network sites have been derived by application of modelling routines similar to CBED and EMEP to interpolated concentration measurements collected across the UK Acid Gases and Aerosols Monitoring Network AGANET.

Comparison of monthly SO<sub>2</sub> and NO<sub>2</sub> concentrations determined using diffusion tubes and mean monthly concentrations measured by gas analyser at the test site, Bottesford, demonstrate good agreement with respect to NO<sub>2</sub> measurements, but SO<sub>2</sub> concentrations measured by diffusion tube have been approximately 50% of those measured by gas analyser. Similar discrepancies have also been observed between diffusion tube-based SO<sub>2</sub> measurements at the seven network sites and levels interpolated from DELTA sampler data from the UK Acid Gases and Aerosols Monitoring Network. An assessment of the Bottesford gas analyser performance criteria concludes that while there may be a systematic bias to reporting of lower SO<sub>2</sub> concentrations by the diffusion tubes, the diffusion tube measurements are within the uncertainty bounds of the Bottesford gas analyser measurements. To allow for a possible 50% underestimation of SO<sub>2</sub> concentrations by the diffusion tubes, however, adjusted sulphur and acidity deposition estimates are provided in a section discussing uncertainty.

While there are marked differences between sites in levels of S, N and acidity deposition and S, N and acidity levels in soil waters, there is no indication of systematic directional changes in these parameters over the first three years of monitoring that might be indicative of effects of reduced S

and N emissions. However, inter-sample variability resulting from seasonal variation and effects of weather and other more random variation is considered too great for trends to be identified over a three year period of measurement.

## 8. References

- Ferm, M.: Method for determination of atmospheric ammonia. *Atmospheric Environment*, 13, 1385-1493, 1979.
- Flechar, C. R., Nemitz, E., Smith, R. I., Fowler, D., Vermeulen, A. T., Bleeker, A., Erisman, J. W., Simpson, D., Zhang, L., Tang, Y. S., and Sutton, M. A.: Dry deposition of reactive nitrogen to European ecosystems: a comparison of inferential models across the NitroEurope network, *Atmos. Chem. Phys.*, 11, 2703-2728, doi:10.5194/acp-11-2703-2011, 2011.
- JEP & EA: Joint Environmental Programme, Monitoring To Assess Power Station Compliance With AQS Objectives Technical Methodology. EA agreed methodology. Issue 6, February 2003
- Monteith, D.T., Sherrin, L., Halford, A. and Nemitz, E.: Monitoring of acidifying and eutrophifying deposition and ecological parameters at seven potentially vulnerable Natura 2000 sites in England and Wales. Second Report to the Power Station and Refinery Operators. NERC Centre for Ecology & Hydrology, 2013.
- Simpson, D., Fagerli, H., Hellsten, S., Knulst, J. C., and Westling, O.: Comparison of modelled and monitored deposition fluxes of sulphur and nitrogen to ICP-forest sites in Europe, *Biogeosciences*, 3, 337–355, doi:10.5194/bg-3-337-2006, 2006.
- Smith, R. I., Fowler, D., Sutton, M. A., Flechar, C., and Coyle, M.: Regional estimation of pollutant gas deposition in the UK: model description, sensitivity analyses and outputs, *Atmos. Environ.*, 34, 3757–3777, 2000.
- Stevenson, K., Yardley, R., Stacey, B. and Maggs, R.: QA/QC Procedures for the UK Automatic Urban and Rural Air Quality Monitoring Network (AURN). Report to Defra and the Devolved Administrations. AEA Technology plc. Ref. AEAT/ENV/R/2837. Sept 2009
- Targa, J. and Loader, A.: Diffusion Tubes for Ambient NO<sub>2</sub> Monitoring: Practical Guidance. Report to Defra and the Devolved Administrations by the the Defra Working Group on Harmonisation of Diffusion Tubes. AEA Energy & Environment. Ref. ED48673043, 2008.
- Vieno, M.: The use of an Atmospheric Chemistry-Transport Model (FRAME) over the UK and the development of its numerical and physical schemes, PhD thesis, University of Edinburgh, 2005.
- Watkins, S.: Response to reports submitted with respect to the monitoring programme to assess changes in acidification and eutrophication deposition and ecological effects at appropriate Natura 2000 sites. Environment Agency, 2014.
- Yardley, R. et al.: Automatic Urban and Rural Network: Site Operator's Manual. Report to Defra and the Devolved Administrations. Ricardo-AEA Ltd. Ref. AEAT/ENV/R/3303 Issue 1. July 2012