

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

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

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## 1. Introduction

Operators of power stations and refineries in England and Wales who had “opted in” to the Large Plant Combustion Directive (LCPD) were 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 issued in relation to their Pollution Prevention and Control (PPC) permit applications in 2006. 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. Following confirmation from the Environment Agency that the monitoring programme could be terminated at the end of 2015, a contract extension was subsequently granted to enable measurements of deposition and soil water chemistry to continue to the end of 2015, providing four complete calendar years of data – and for the results to be reported in 2016.

The monitoring programme was 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 continued to be 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 focussed 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 provided 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 is the seventh report to the power station and refinery operators. It provides a summary of all deposition and soil water chemistry data collected over the four year monitoring period, and also includes details of monthly measurements of wet deposition chemistry, gaseous concentrations and soil solution chemistry collated over 2015 particularly. Monthly data for previous years is provided in respective reports (see Monteith et al., 2013; Monteith et al., 2014 and Monteith et al., 2015).

Two dry deposition models that combine meteorological observations with gaseous concentration measurements were used to produce monthly estimates of dry deposition.

Two dry deposition models that combine meteorological observations with gaseous concentration measurements were 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<sub>4</sub>), nitrate (NO<sub>3</sub>) and ammonium (NH<sub>4</sub>) dry deposition) for the three years.

An error was identified in the calculation of bulk wet deposition of non-seasalt sulphate, nitrate, ammonium and non-seasalt bulk wet chloride for the Usk Bat Sites in 2014 only. This has been corrected in the tables summarising annual deposition estimates in Section 6.4.

Also, following a recent review of measurements made by DELTA samplers across the UKEAP network that highlighted a systematic overestimation in nitric acid concentrations, a correction factor has been introduced for all pre-2015 nitric acid estimates. This has been incorporated into summary tables provided in Section 6.

## 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 Uniper staff. These included 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; \*\*Rugeley Power Station closed in June 2016;

\*\*\* Ferrybridge Power Station closed in March 2016

### 3. Field Measurements and sample analysis

Monitoring protocols followed 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 were deployed from the Autumn of 2011 until the end of 2015 at each site by Uniper. 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 were deployed and replaced on a monthly basis. Weighed prior to deployment, retrieved bottles were 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 were determined by reweighing before samples were analysed chemically. The following species were 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

### 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>) were 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 followed Gradko protocols. Retrieved Gradko tubes were placed in the sample crate and returned to the CEH laboratory along with the other water samples where they were logged before being sent in monthly batches to Gradko for analysis. Concentrations of NH<sub>3</sub> were measured using Adapted Low-cost Passive High Absorption (ALPHA) samplers and analysed at the CEH Lancaster laboratory.

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 were 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 were used to monitor potential contamination problems only and were not 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 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 was used to empty the tubes into polyethylene sample bottles which were then treated as above.

When received by the CEH laboratory, individual sample bottles were first assessed to determine the volume collected. Samples were filtered through a 0.45  $\mu\text{m}$  filter. Where sufficient volumes were collected, as was normally case for dip well samples, the following measurements were 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 were collected to allow all the analyses, as was sometimes the case for the heathland sites, upper and lower samples are bulked, and if the bulked samples were 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 were 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 Uniper 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.

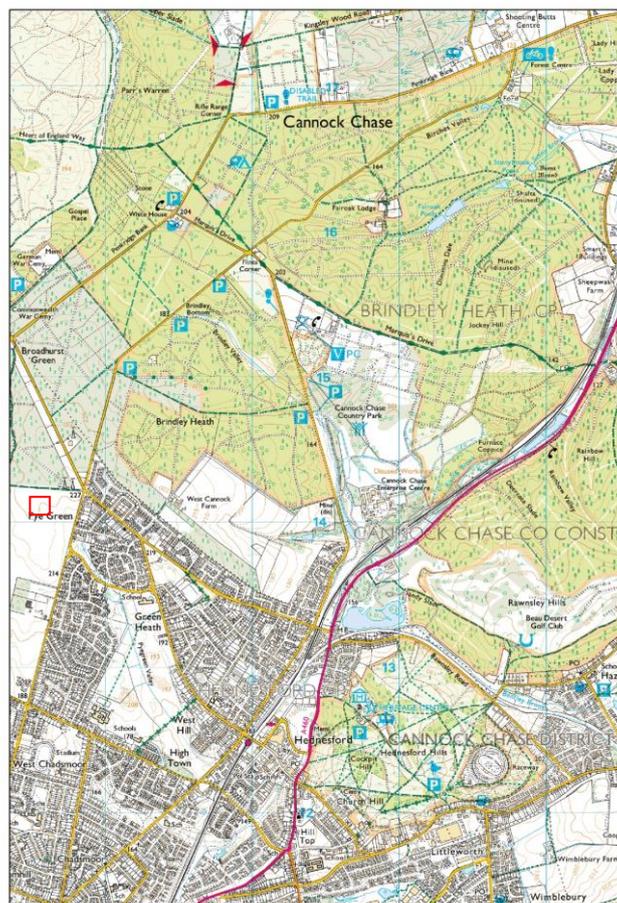


## 4.2 Cannock Chase SAC

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)



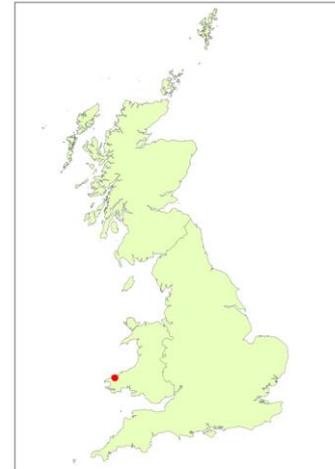
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Figure 4.2.2 Aerial photograph (Google Earth) of Cannock Chase site. Locations for the Meteorological/Deposition, and soil water monitoring sites indicated by blue and red symbols respectively.



### 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.



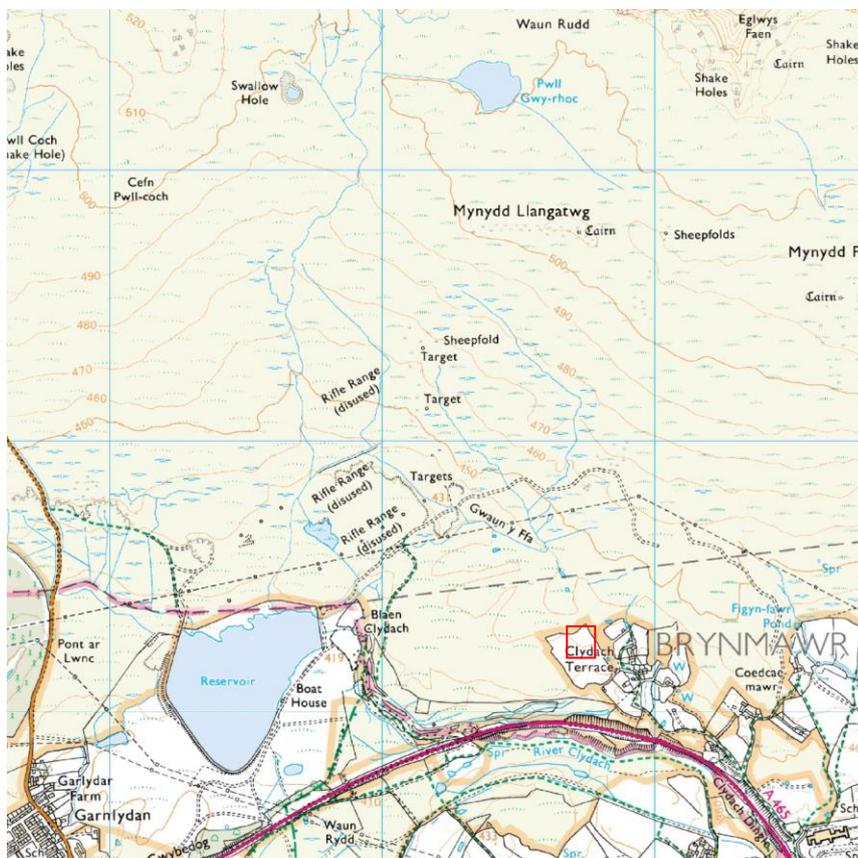
#### 4.4 Usk Bat Sites SAC - Mynydd Llangatwyg

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. Given the uncertainty, no adjustment has 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.

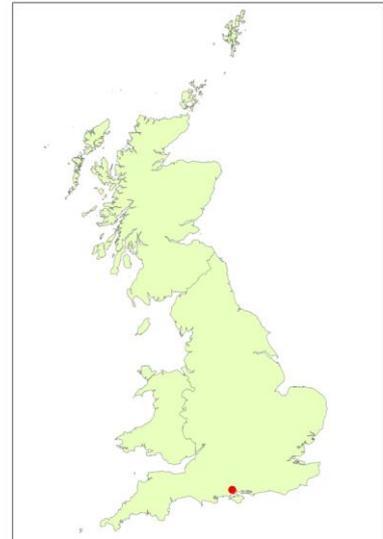
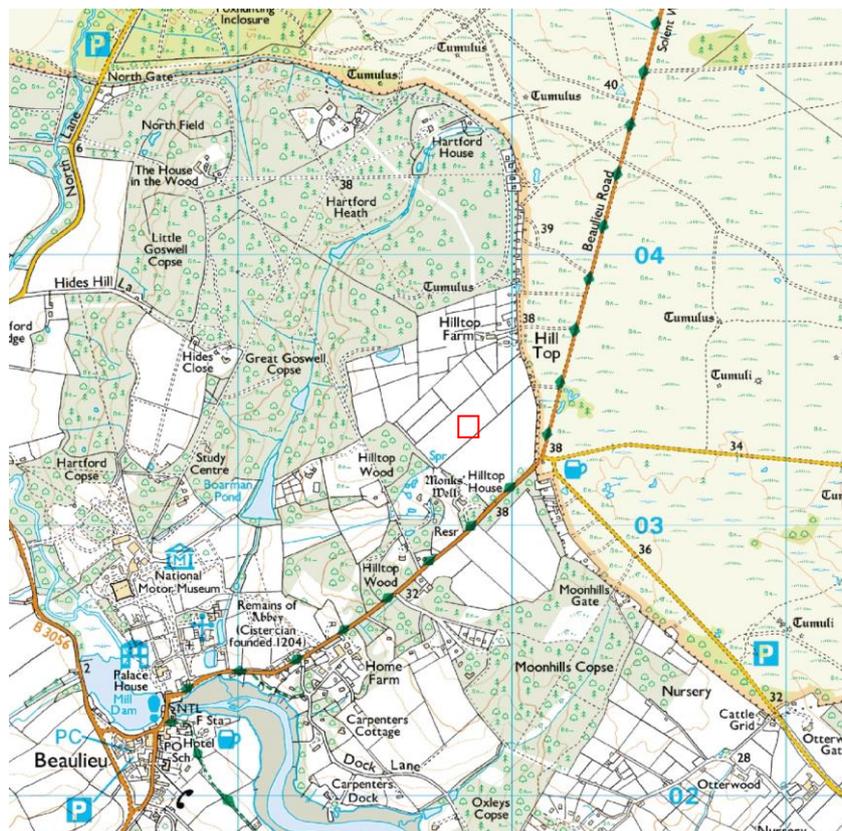


Figure 4.5.1 New Forest, Beaulieu site and location of the Met/deposition station (red box)



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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.





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

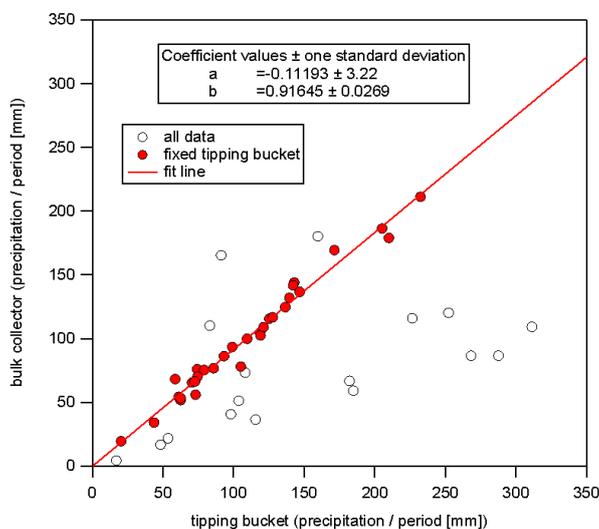
### 5.1 Bulk wet deposition

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 were 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, and the primary objective was to determine the total acid deposition flux, it was considered appropriate to treat both positive and negative non-seasalt chloride values as “real”. Thus, where present, small negative annual wet chloride deposition estimates were deducted from the total acidity estimate for the site rather than re-setting this value to zero.

An error in a spreadsheet used to calculate bulk wet deposition flux for the 2014 deposition report (Monteith et al., 2015) resulted in an overestimate of bulk wet deposited sulphate, nitrate and ammonium to the Usk Bat Sites collectors at Clydach Terrace for that year only. Corrections to the 2014 data have therefore been made in Tables 6.4.1 and 6.4.2.

## 5.2 Dry deposition

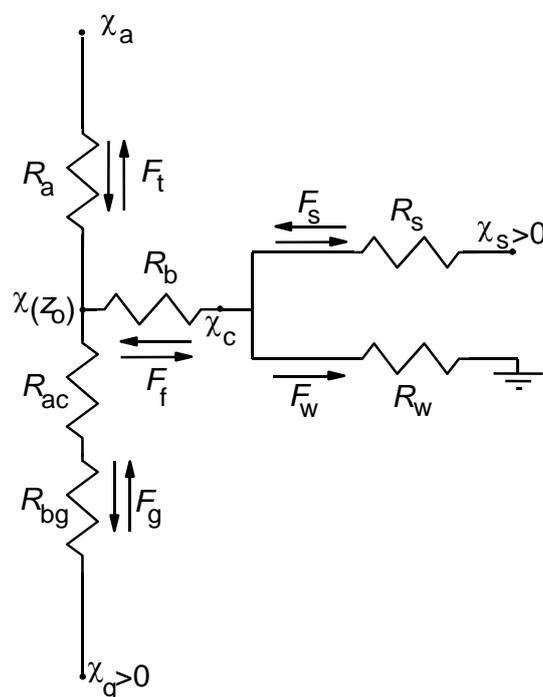
### 5.2.1 Dry deposition models

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  $\text{NH}_3$ , Alpha samplers, were 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  $\text{NH}_3$  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  $\text{NO}$  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, any missing concentration data 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 2015 some stations experienced periods of battery power failure and some sensor failures - mostly relative humidity (RH) and temperature (T) sensors, but also, intermittently, wind speed and direction.

With respect to the parameters listed in Table 5.2.2, we have adopted a similar approach to gap filling to that outlined in the previous 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 2015 data collection only**

Project Site	Start	End	Parameter	Corresponding Skylink Network Site
Cleddau Rivers SAC	01/01/2015	07/01/2015	temperature and Humidity Sensor faulty	Milford Haven
Cleddau Rivers SAC	16/01/2015	22/01/2015	Failure of replacement battery at site	Milford Haven

Cannock Chase	28/01/2015	30/01/2015	failure of battery power supply at site	Walsall
All Sites	31/03/2015	31/03/2015	No data download from server	Various
Usk Bat Sites SAC	02/12/2015	08/12/2015	premature failure of battery power supply at site	No Skylink data available 2 – 7/12/2015
Cleddau Rivers SAC	22/12/2015	31/12/2015	failure of battery power supply at site	Various, Skylink data archive at Uniper technologies was incomplete for the period 27/12/2015 – 03/01/2016
Skipwith Common	24/12/2015	31/12/2015	failure of battery power supply at site	
New Forest	26/12/2015	31/12/2015	failure of battery power supply at site	
Manchester Mosses SAC	28/12/2015	31/12/2015	failure of battery power supply at site	
Thorne Moor	28/12/2015	31/12/2015	failure of battery power supply at site	
Cannock Chase	28/12/2015	31/12/2015	failure of battery power supply at site	
All Sites	Throughout year		Various short term data anomalies	Various

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 2015 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 SO<sub>2</sub>, NH<sub>3</sub> and NO<sub>2</sub> deposition were generated for both models, from which single monthly mean fluxes were calculated in units of ng m<sup>-2</sup> s<sup>-1</sup>. For the monthly dry deposition calculations presented in Section 6.2, estimates were then scaled up to provide monthly deposition estimates in units of kg ha<sup>-1</sup> and keq ha<sup>-1</sup>. 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 previous years there was reasonably good agreement between CBED and EMEP models for SO<sub>2</sub> and NH<sub>3</sub> deposition, with CBED deriving larger deposition for NH<sub>3</sub>, but considerably smaller deposition for SO<sub>2</sub> 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 SO<sub>2</sub>, and also for NH<sub>3</sub>, depends on the annual average air concentration ratio of SO<sub>2</sub> / NH<sub>3</sub> and therefore differs between sites. This effect on the chemical climate of the site reflects the potential of deposited SO<sub>2</sub> to be neutralised by NH<sub>3</sub> (and *vice versa*) which counteracts the tendency for deposition to be self-limiting by reducing (or increasing) the leaf water pH. The SO<sub>2</sub>/NH<sub>3</sub> ratio ranged from 0.5 at Cannock Chase to 1.9 at the New Forest site, where the EMEP model predicted the SO<sub>2</sub> deposition that was most similar to the CBED routine.

Estimates for NO<sub>2</sub> 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 NO<sub>2</sub> deposition which would reduce uptake of NO<sub>2</sub> by the plant. In addition, NO emitted from the soil can be converted chemically to NO<sub>2</sub> by reaction with ozone (O<sub>3</sub>), resulting in a non-zero concentration of NO<sub>2</sub> in the canopy, which reduces transport of atmospheric NO<sub>2</sub> towards the plant. To account for these effects the EMEP parameterisation sets the deposition to zero for NO<sub>2</sub> 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 NO<sub>2</sub> deposition.

Comparisons of monthly mean SO<sub>2</sub> concentrations determined by Gradko diffusion tubes with mean monthly hourly SO<sub>2</sub> gas analyser measurements at the Bottesford air quality monitoring site have shown that, throughout their deployment, diffusion tube measurements and associated model-derived fluxes have been consistently lower than those based on the analyser. In the previous deposition report (Monteith et al., 2015) we stated that the difference was of an order of circa 50%. Over the last year of monitoring (2015), AURN SO<sub>2</sub> monthly estimates were generally considerably lower than for previous months, while Gradko measurements were below limits of detection (and consequently adjusted to 0.2 ppb) for all but two months. Gradko SO<sub>2</sub> measurements were also below the detection limit in five out of twelve months in 2014.

The data show that the ratio of AURN to Gradko mean monthly concentrations has increased as the Gradko measurements have approached or reached the detection limit. We attribute this tendency to our procedure of transforming all values that fall beneath a fixed detection limit to half that value, since this will result in an underestimate if the true atmospheric concentration lies anywhere between the two levels. The ratio, to 1 significant figure, of Bottesford SO<sub>2</sub> annual deposition fluxes calculated from the AURN analyser and Gradko concentration data, was 2.0 for the years 2012 and 2013, 3.1 in 2014 and 2.7 in 2015.

It was also noted in the previous deposition report that similar differences were observed when Gradko-based SO<sub>2</sub> 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 SO<sub>2</sub> deposition at HMN sites resulting from the use of diffusion tubes, and taking into account an apparent higher differential as Gradko measurements have increasingly fallen below the limit of detection, Section 6.7 of this report provides alternative estimates of total sulphur deposition and total acid deposition, incorporating an upward adjustment of the annual SO<sub>2</sub> dry deposition estimates. First, a sample adjustment factor of either 2.0 or 3.0 was allocated to each Gradko SO<sub>2</sub> measurement depending on whether the measurement was above or below the detection limit respectively. A site- and year-specific adjustment factor was then determined from the weighted average of the sample adjustment factors. Hence, for sites and years where most measurements were above the detection limit the adjustment approximated to 2.0, whereas the adjustment was closer to 3.0 at sites and years where most measurements fell below the limit.

### **5.3 Annual deposition calculation**

Annual (2012-2015) 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 2.8 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, HNO<sub>3</sub> and HCl species are obtained by driving a similar dry deposition model as used for NH<sub>3</sub>, NO<sub>2</sub> and SO<sub>2</sub> 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 NH<sub>3</sub>, NO<sub>2</sub> and SO<sub>2</sub> to take into account different deposition mechanisms. Rates of deposition of NH<sub>3</sub>, SO<sub>2</sub> and NO<sub>2</sub> to leaf surfaces and through leaf stomata depend on species-specific solubility, reactivity and molecular diffusivity. HNO<sub>3</sub> 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). HCl is modelled

analogously to  $\text{HNO}_3$  using a very low  $R_c$  value. The  $R_b$  term for HCl is adjusted to account for the difference in the molecular diffusivities of HCl and  $\text{HNO}_3$ .

Recently, CBED model results from 2004 to 2013 have been updated following a quality control study by NERC CEH and Defra (report under review). The CBED model uses chemical concentration data measured on monthly or fortnightly periods at UKEAP sites across the UK. The study assessed the DELTA sampler configuration's specificity for  $\text{HNO}_3$  measurement and showed additional sampling of other atmospheric oxidised nitrogen species ( $\text{HONO}$ ,  $\text{N}_2\text{O}_5$ , and  $\text{ClNO}_2$ ) i.e. the tests highlighted a systematic overestimation in  $\text{HNO}_3$  concentrations by the original UKEAP measurements. As a result the method is being changed. For data using the original method, a correction factor of 0.45 has been calculated and applied to revise previous  $\text{HNO}_3$  concentrations used in the CBED mapping, and also in the APIS data. This correction factor was considered and approved during a meeting of end users (modellers) and the research team. It is noted that the deposition of other atmospheric oxidised nitrogen species (e.g.  $\text{HONO}$ ,  $\text{N}_2\text{O}_5$  and  $\text{ClNO}_2$ ) are not assessed in UKEAP or CBED. The correction factor has therefore been applied to the  $\text{HNO}_3$  dry deposition data in Section 6.4 and Section 6.7 for all four years (2012-2015).

## 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 2015 are presented for sulphur and nitrogen species in addition to soil solution chemistry parameters. These include:

Section 6.1. Monthly gaseous concentration measurements for 2015 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 2015 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 2015 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 (2015 only) and tabulated (2012-2015) 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 2015 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 four years of complete data, and considers possible reasons for any clear differences and trends over the four years.

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, were considered in detail in the previous deposition report covering the data collected from 2012 to 2014 (Monteith et al., 2015). Section 6.7 assesses the 2015 monitoring data in the context of the conclusions from this previous review.

## 6.1 Gaseous concentrations

**Table 6.1.1 Monthly mean concentrations of gaseous concentrations for 2015**

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-15	9.73	14.90	5.17	0.200	0.608
Manchester Mosses	Feb-15	9.26	11.00	1.75	0.200	0.825
Manchester Mosses	Mar-15	8.59	12.29	3.69	0.200	1.193
Manchester Mosses	Apr-15	7.23	10.02	2.79	0.200	1.206
Manchester Mosses	May-15	4.35	8.06	3.71	0.200	0.597
Manchester Mosses	Jun-15	5.33	9.16	3.83	0.200	1.042
Manchester Mosses	Jul-15	5.03	8.73	3.70	0.200	0.836
Manchester Mosses	Aug-15	5.30	10.71	5.42	0.200	1.123
Manchester Mosses	Sep-15	7.36	13.11	5.75	0.200	1.071
Manchester Mosses	Oct-15	10.58	16.19	5.61	0.200	0.820
Manchester Mosses	Nov-15	8.63	9.58	0.96	0.200	0.527
Manchester Mosses	Dec-15	9.41	12.20	2.79	0.200	0.778
Cannock Chase	Jan-15	11.03	13.05	2.02	0.200	0.895
Cannock Chase	Feb-15	9.27	10.45	1.17	0.200	0.979
Cannock Chase	Mar-15	8.74	11.25	2.51	0.200	1.740
Cannock Chase	Apr-15	5.53	8.62	3.09	0.200	2.163
Cannock Chase	May-15	4.37	8.01	3.63	0.200	1.478
Cannock Chase	Jun-15	4.64	7.58	2.94	0.200	2.089
Cannock Chase	Jul-15	5.12	8.66	3.54	0.200	1.586
Cannock Chase	Aug-15	6.04	10.28	4.25	0.200	1.686
Cannock Chase	Sep-15	6.42	9.97	3.55	0.233	0.624
Cannock Chase	Oct-15	12.06	15.49	3.42	0.380	1.356
Cannock Chase	Nov-15	8.98	12.17	3.19	0.200	0.842
Cannock Chase	Dec-15	10.19	11.35	1.17	0.347	0.600
Cleddau Rivers	Jan-15	1.37	4.82	3.45	0.200	0.318
Cleddau Rivers	Feb-15	1.50	3.58	2.08	0.200	0.450
Cleddau Rivers	Mar-15	1.50	3.91	2.41	0.200	0.749
Cleddau Rivers	Apr-15	1.41	3.36	1.94	0.200	1.156
Cleddau Rivers	May-15	1.14	5.15	4.01	0.200	0.695
Cleddau Rivers	Jun-15	1.15	4.65	3.50	0.200	0.858
Cleddau Rivers	Jul-15	0.97	4.79	3.82	0.200	0.438
Cleddau Rivers	Aug-15	0.96	5.40	4.44	0.337	0.432
Cleddau Rivers	Sep-15	1.41	4.38	2.98	0.233	0.734
Cleddau Rivers	Oct-15	1.94	5.21	3.27	0.257	0.559
Cleddau Rivers	Nov-15	0.82	2.02	1.20	0.200	0.363
Cleddau Rivers	Dec-15	1.11	2.56	1.45	0.577	0.362
Usk Bat Sites	Jan-15	4.25	6.84	2.59	0.200	0.090
Usk Bat Sites	Feb-15	4.57	5.50	0.92	0.200	0.113
Usk Bat Sites	Mar-15	3.86	6.72	2.86	0.200	0.518
Usk Bat Sites	Apr-15	3.07	5.55	2.49	0.200	0.751
Usk Bat Sites	May-15	2.34	6.55	4.21	0.200	0.250
Usk Bat Sites	Jun-15	2.46	5.60	3.14	0.200	0.631
Usk Bat Sites	Jul-15	2.80	6.28	3.47	0.200	0.279
Usk Bat Sites	Aug-15	3.10	6.63	3.52	0.200	0.358
Usk Bat Sites	Sep-15	2.46	6.36	3.91	0.200	0.427
Usk Bat Sites	Oct-15	4.74	6.87	2.13	0.200	0.249
Usk Bat Sites	Nov-15	3.42	5.18	1.58	0.690	0.071

Usk Bat Sites	Dec-15	3.51	6.27	2.77	1.283	0.243
New Forest	Jan-15	6.07	8.98	2.91	0.200	0.274
New Forest	Feb-15	6.14	8.64	2.50	0.200	0.241
New Forest	Mar-15	6.64	9.26	2.62	0.200	1.349
New Forest	Apr-15	5.07	7.10	2.03	0.200	0.816
New Forest	May-15	2.94	6.62	3.67	0.200	0.475
New Forest	Jun-15	4.19	7.77	3.59	0.200	0.713
New Forest	Jul-15	3.04	6.32	3.28	0.200	0.430
New Forest	Aug-15	5.15	8.34	3.18	0.200	0.468
New Forest	Sep-15	5.56	10.40	4.83	0.200	0.481
New Forest	Oct-15	7.50	12.38	4.88	0.200	0.624
New Forest	Nov-15	2.92	4.27	1.34	0.200	0.249
New Forest	Dec-15	3.03	5.34	2.31	0.200	0.140
Skipwith Common	Jan-15	8.55	11.10	2.54	0.200	0.860
Skipwith Common	Feb-15	9.23	10.81	1.58	0.200	1.197
Skipwith Common	Mar-15	6.92	9.79	2.87	0.430	2.923
Skipwith Common	Apr-15	5.30	7.29	2.00	0.463	2.196
Skipwith Common	May-15	3.58	6.89	3.31	0.200	1.057
Skipwith Common	Jun-15	3.97	7.21	3.24	0.483	1.443
Skipwith Common	Jul-15	3.97	8.44	4.47	0.200	1.060
Skipwith Common	Aug-15	4.73	9.26	4.53	0.373	1.522
Skipwith Common	Sep-15	4.82	8.29	3.47	0.327	1.125
Skipwith Common	Oct-15	8.80	12.45	3.66	0.333	0.918
Skipwith Common	Nov-15	8.09	9.23	1.14	0.200	0.861
Skipwith Common	Dec-15	8.28	9.38	1.10	0.557	0.820
Thorne Moor	Jan-15	9.85	12.15	2.30	0.200	0.379
Thorne Moor	Feb-15	9.85	11.03	1.18	0.200	0.484
Thorne Moor	Mar-15	7.76	10.97	3.20	0.543	2.296
Thorne Moor	Apr-15	6.38	9.85	3.47	0.663	2.067
Thorne Moor	May-15	4.54	7.96	3.42	0.200	0.759
Thorne Moor	Jun-15	4.38	8.06	3.68	0.463	0.984
Thorne Moor	Jul-15	4.52	9.17	4.65	0.200	1.045
Thorne Moor	Aug-15	4.87	8.95	4.08	0.310	1.271
Thorne Moor	Sep-15	5.75	9.68	3.93	0.370	0.729
Thorne Moor	Oct-15	8.12	12.09	3.97	0.230	0.606
Thorne Moor	Nov-15	7.57	9.27	1.70	0.200	0.403
Thorne Moor	Dec-15	7.25	9.18	1.93	0.240	0.436

**Table 6.1.2 Annual mean concentrations of gaseous concentrations 2012-2015**

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
	2015	0.20	7.57	11.33	3.76	0.89
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
	2015	0.23	7.70	10.57	2.87	1.34
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
	2015	0.25	1.27	4.15	2.88	0.59
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
	2015	0.33	3.38	6.20	2.80	0.33
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
	2015	0.20	4.86	7.95	3.10	0.52
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
	2015	0.33	6.35	9.18	2.83	1.33
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
	2015	0.32	6.74	9.86	3.13	0.95

**Figure 6.1.1 Gaseous concentrations (2015): Manchester Mosses SAC**  
 SO<sub>2</sub> samples recorded as below limit of detection set to zero.

**Manchester Mosses – gaseous concentrations**

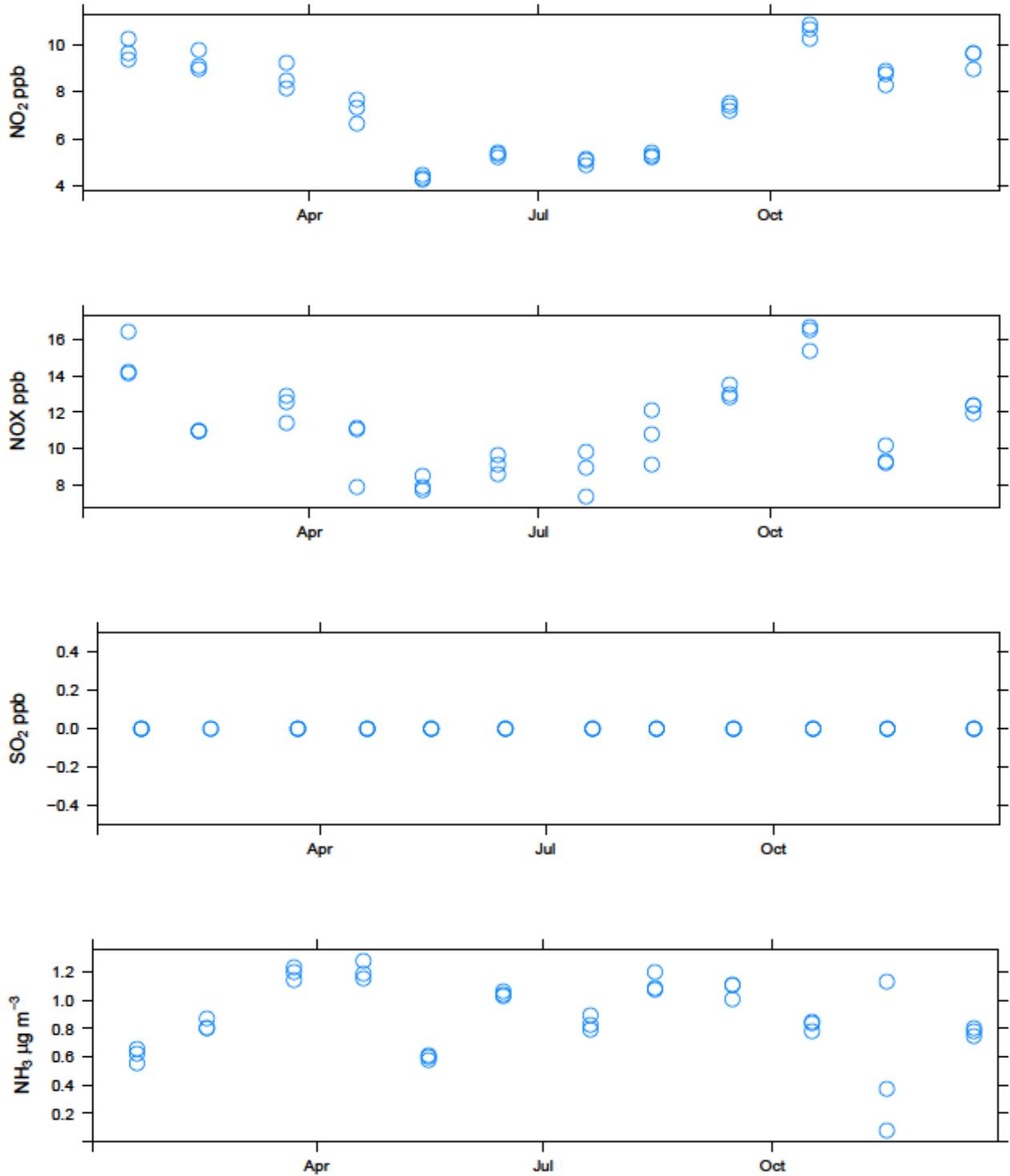


Figure 6.1.2 Gaseous concentrations (2015): Cannock Chase SAC

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

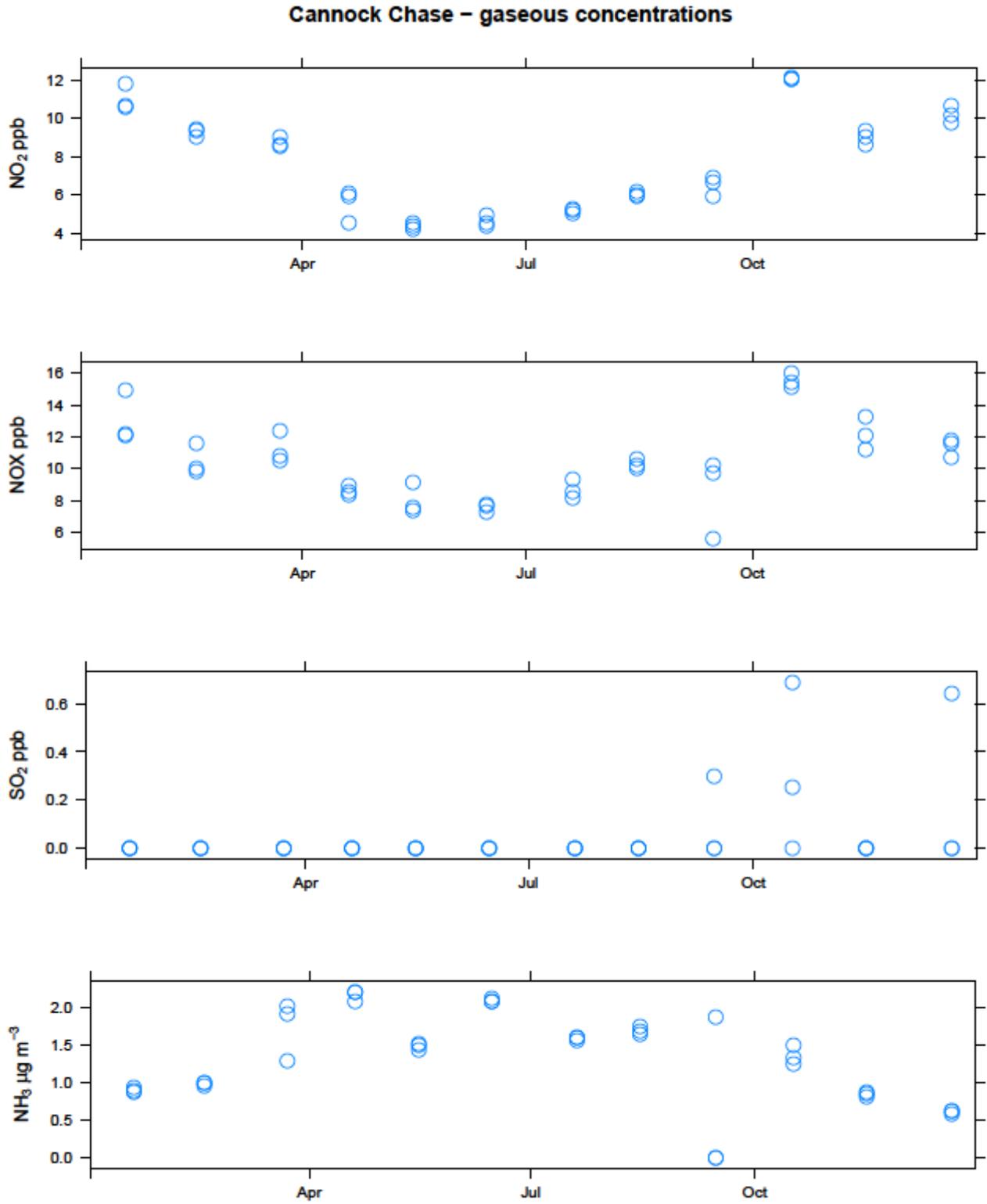
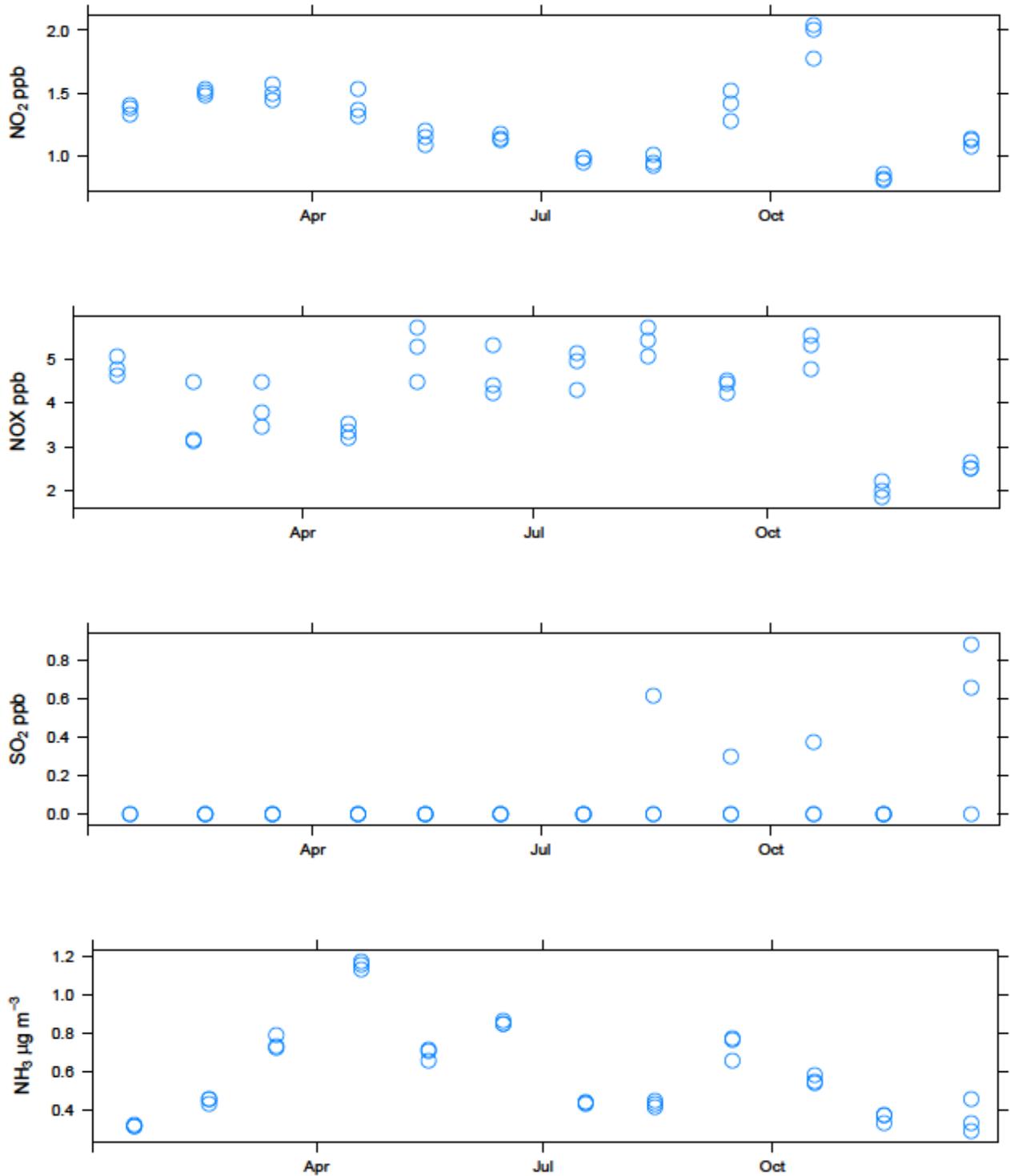


Figure 6.1.3 Gaseous concentrations (2015

): Cleddau Rivers SAC

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

Cleddau Rivers – gaseous concentrations



**Figure 6.1.4 Gaseous concentrations (2015): Usk Bat sites SAC**

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

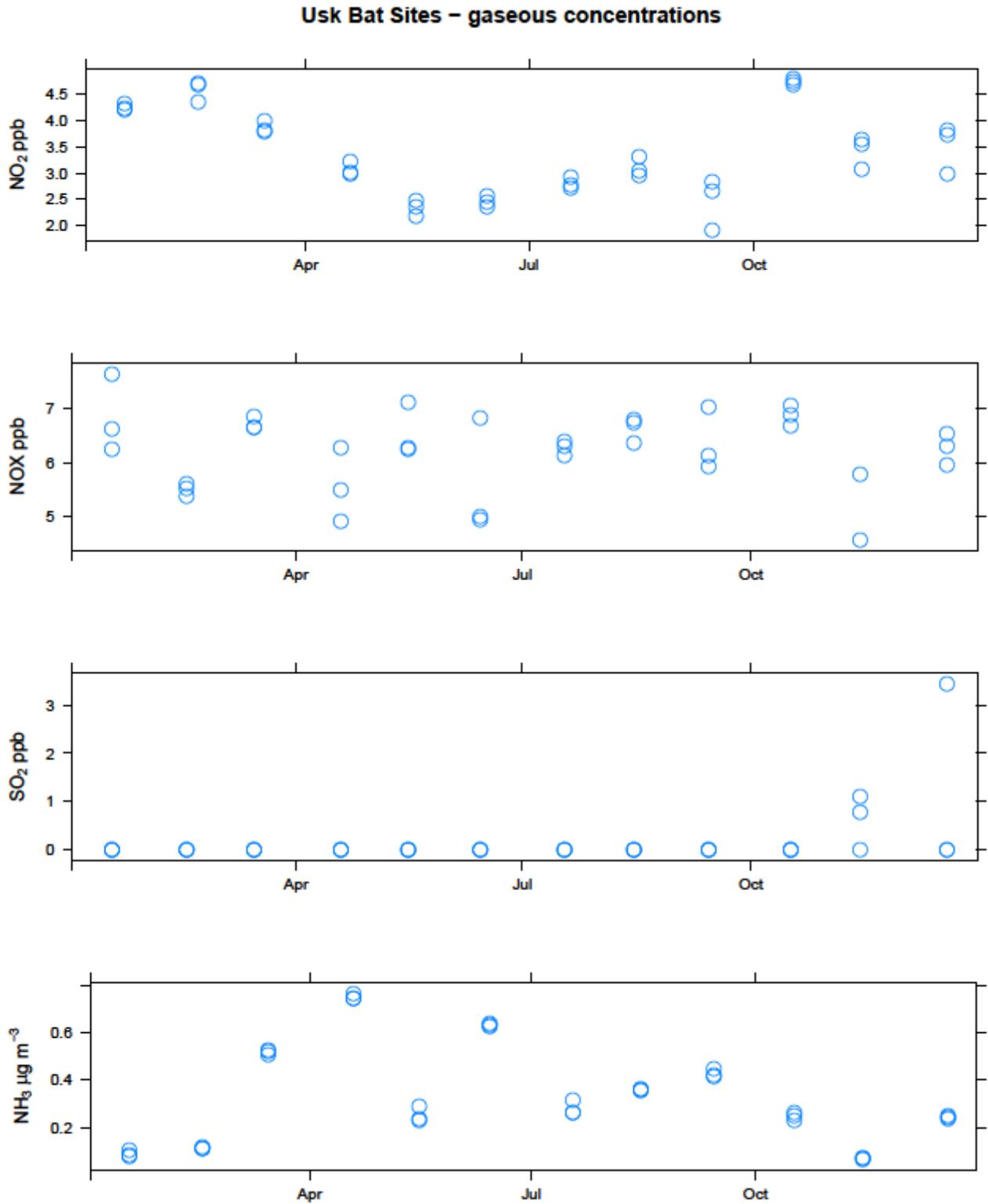


Figure 6.1.5 Gaseous concentrations (2015): New Forest SAC

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

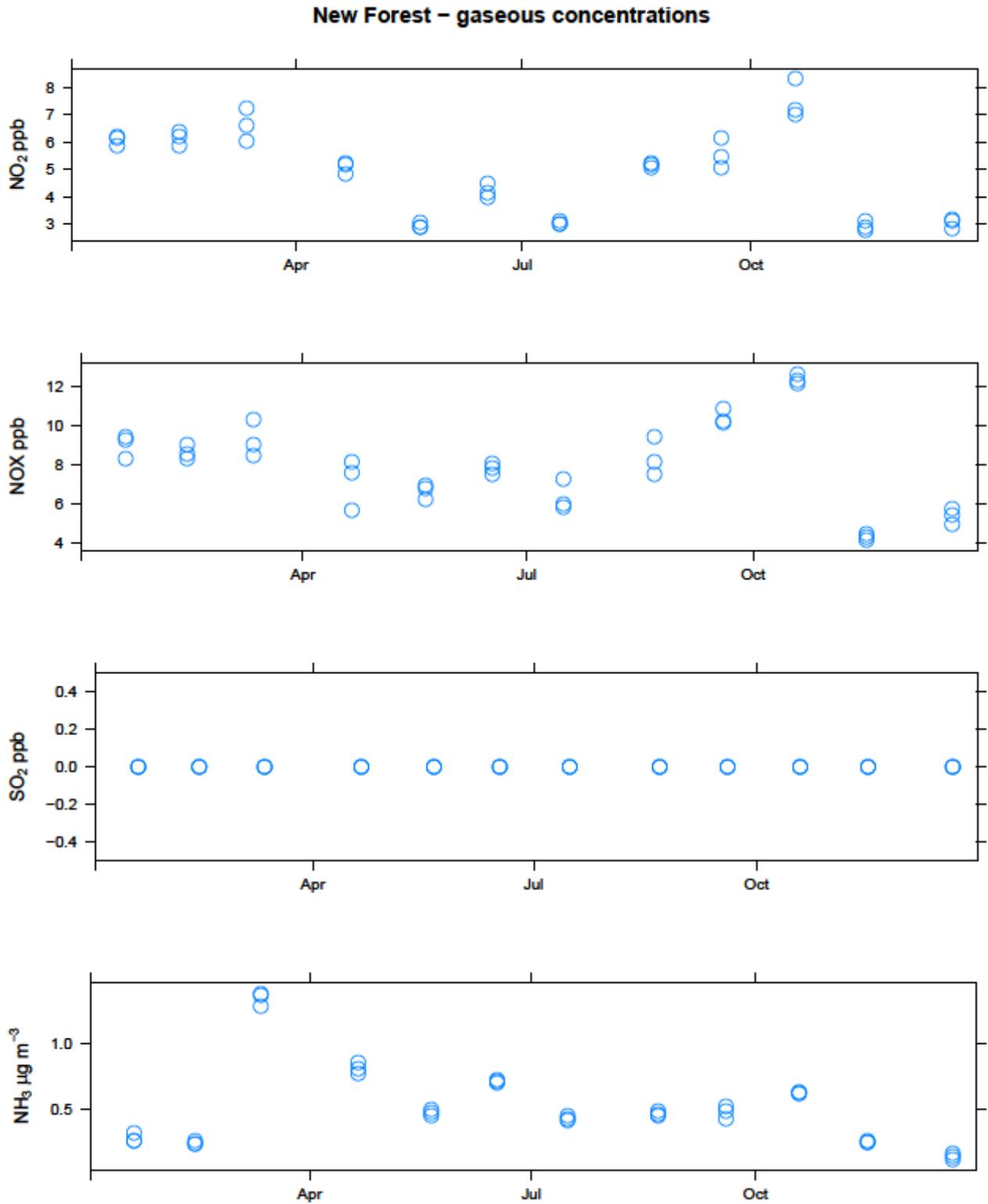


Figure 6.1.6 Gaseous concentrations (2015): Skipwith Common SAC

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

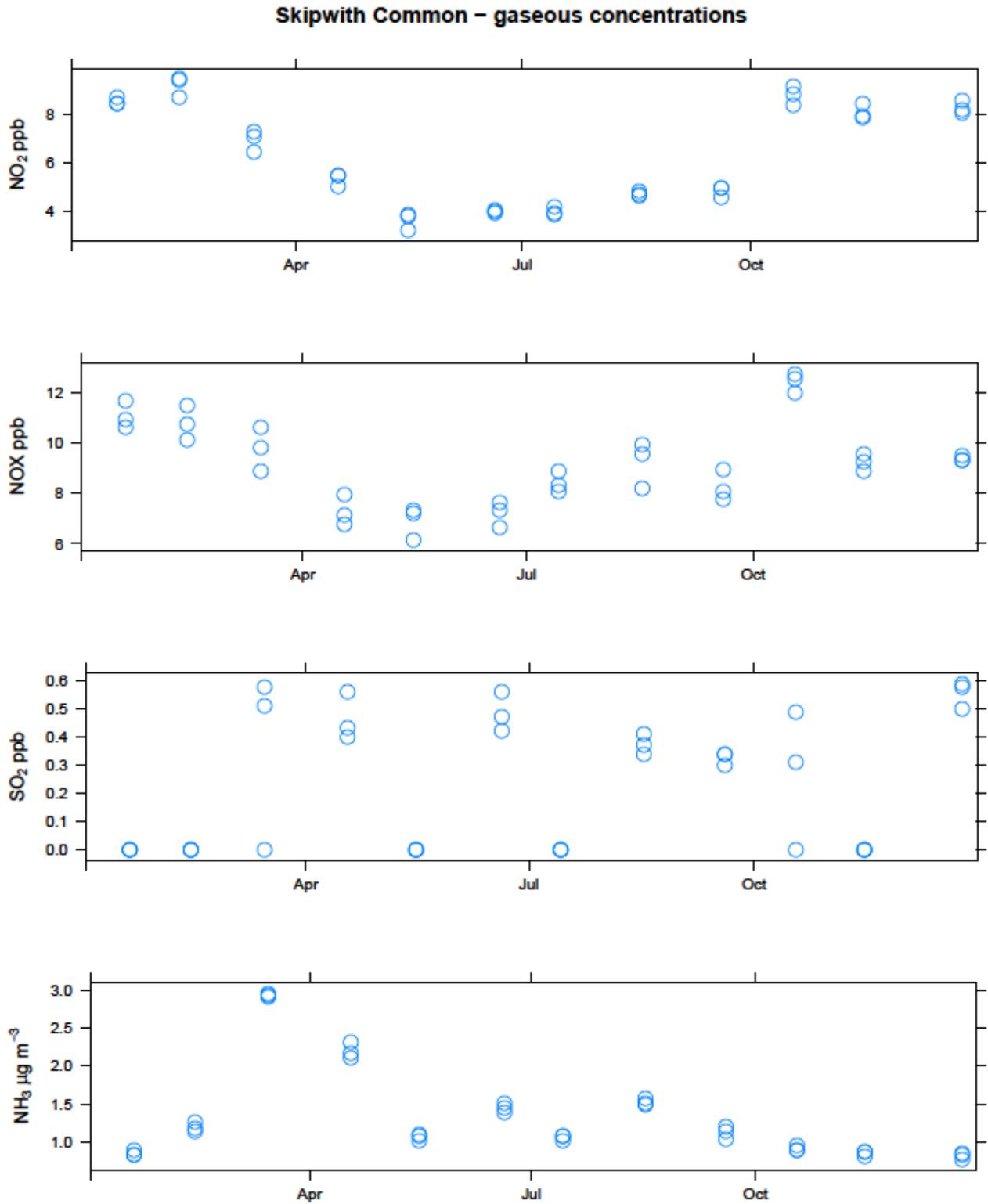
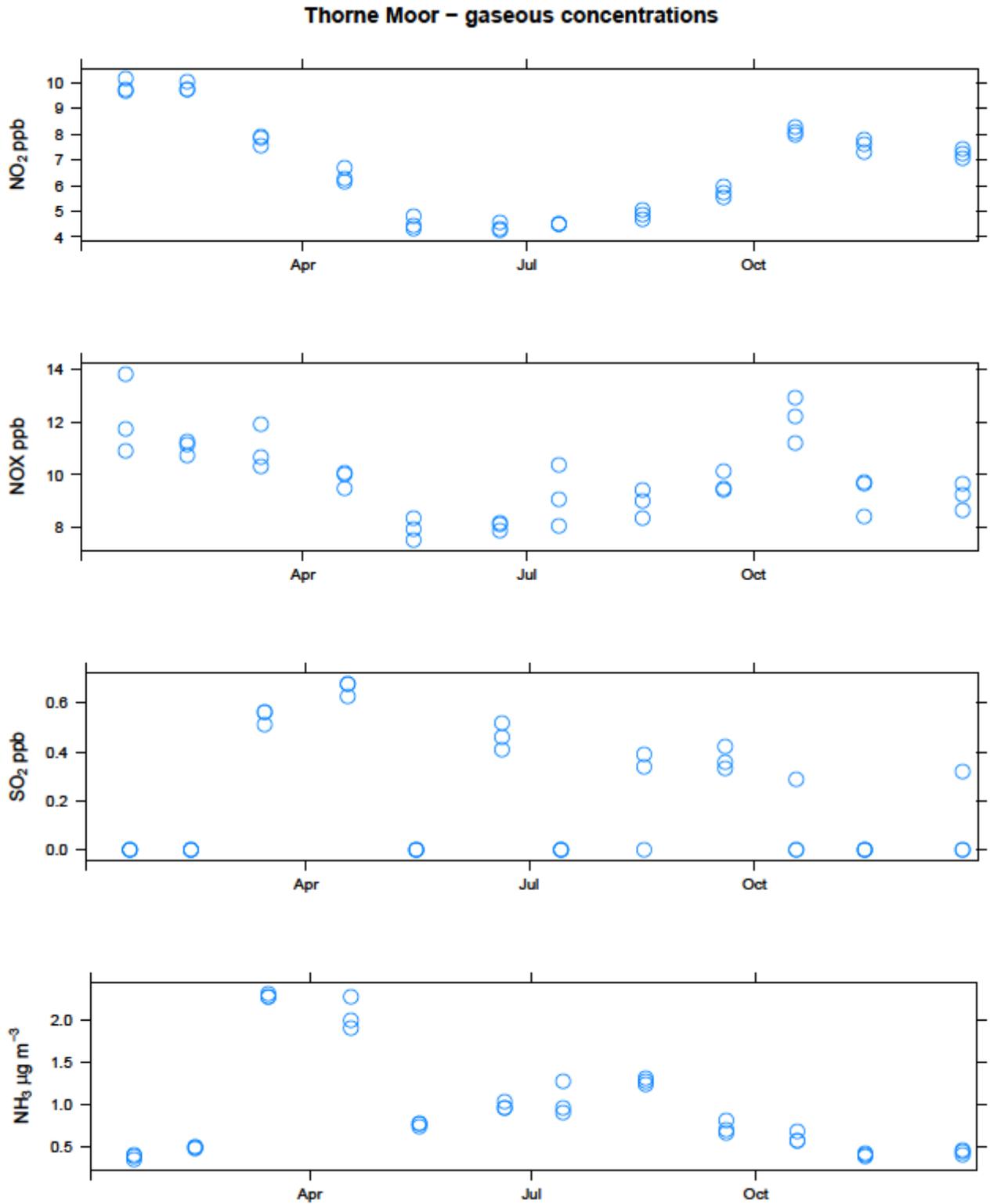


Figure 6.1.6 Gaseous concentrations (2015): Thorne Moor SAC

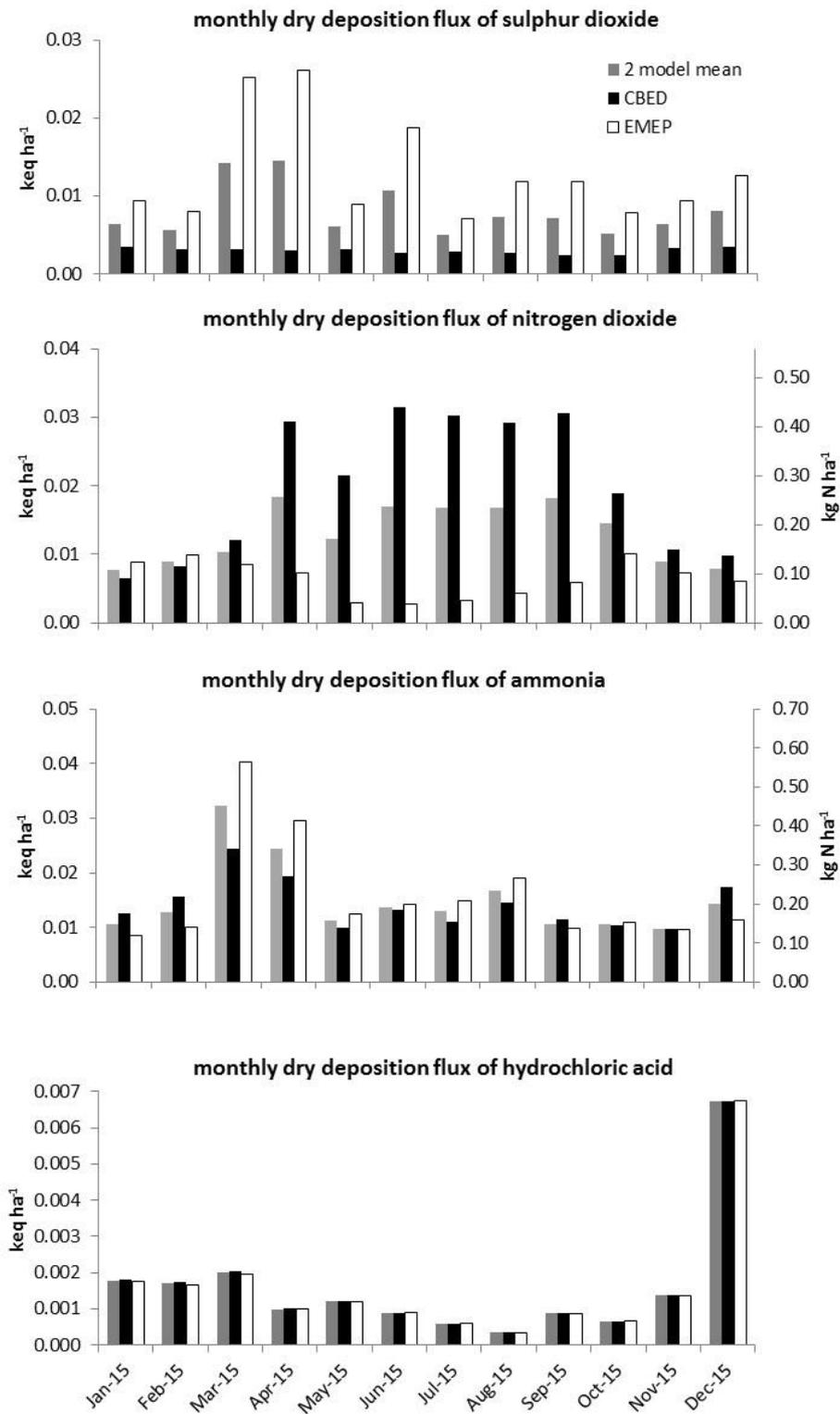
SO<sub>2</sub> samples recorded as below limit of detection set to zero.



## 6.2 Dry deposition estimates - 2015

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**

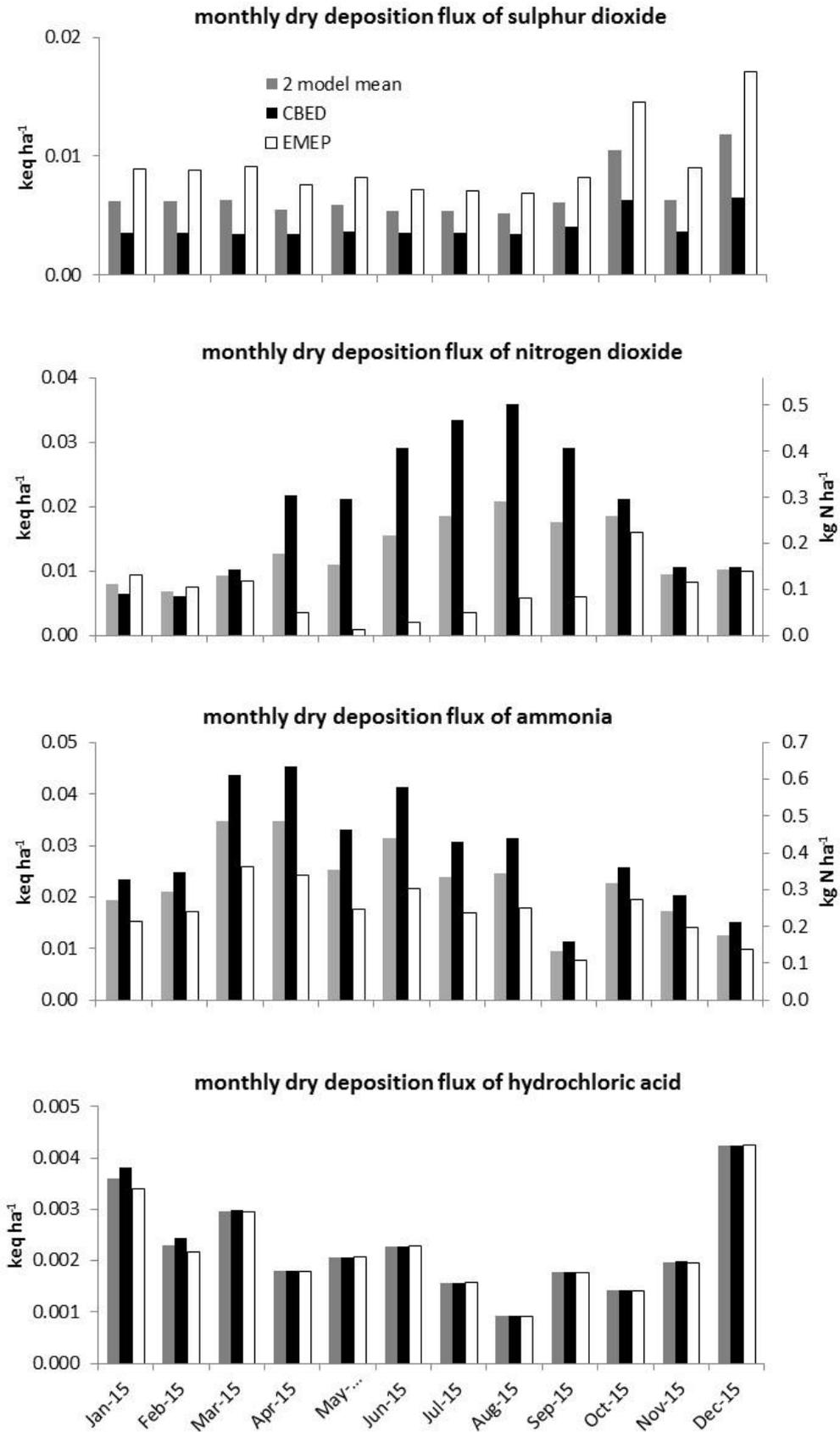
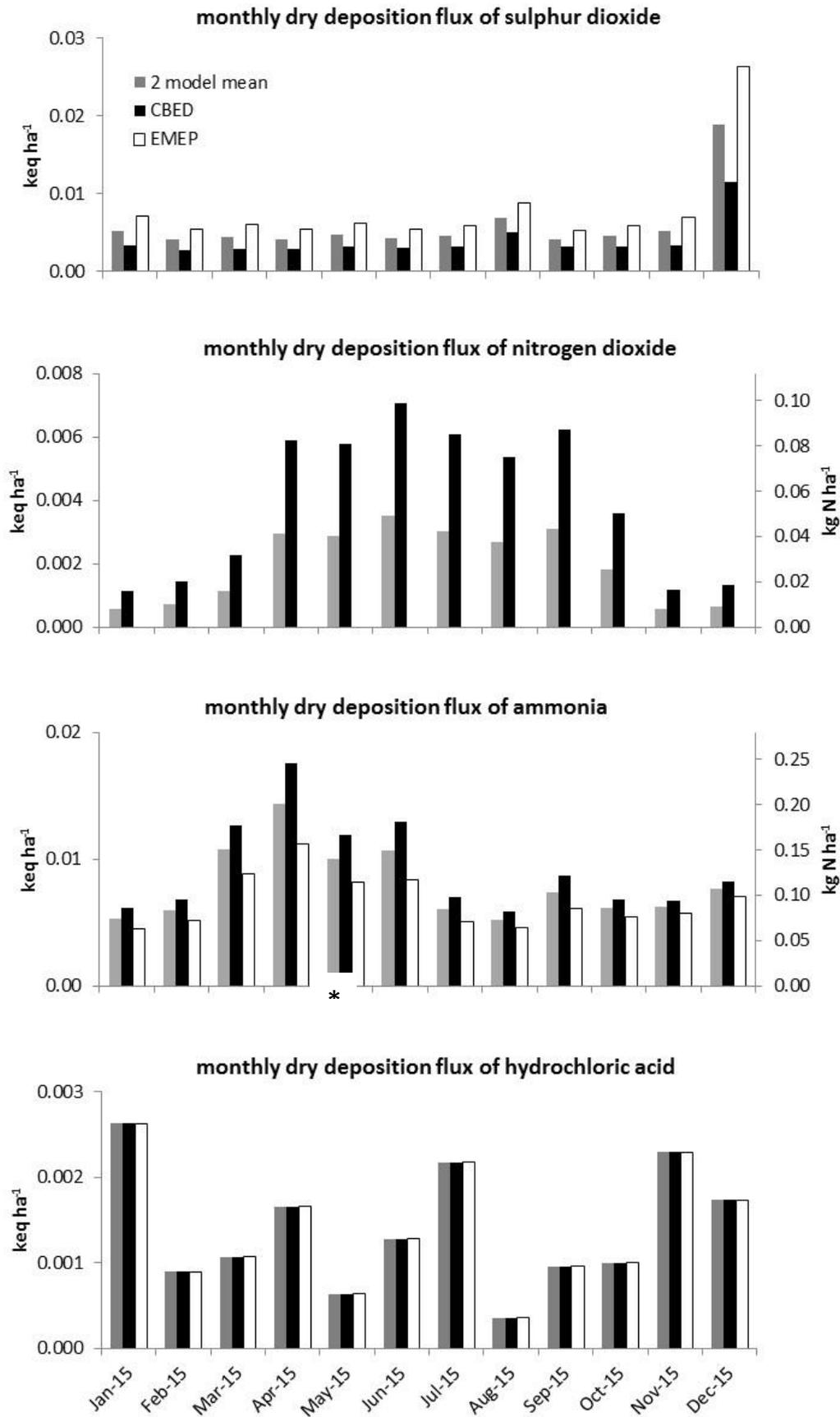


Figure 6.2.3 Monthly dry deposition estimates: Cleddau Rivers SAC



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

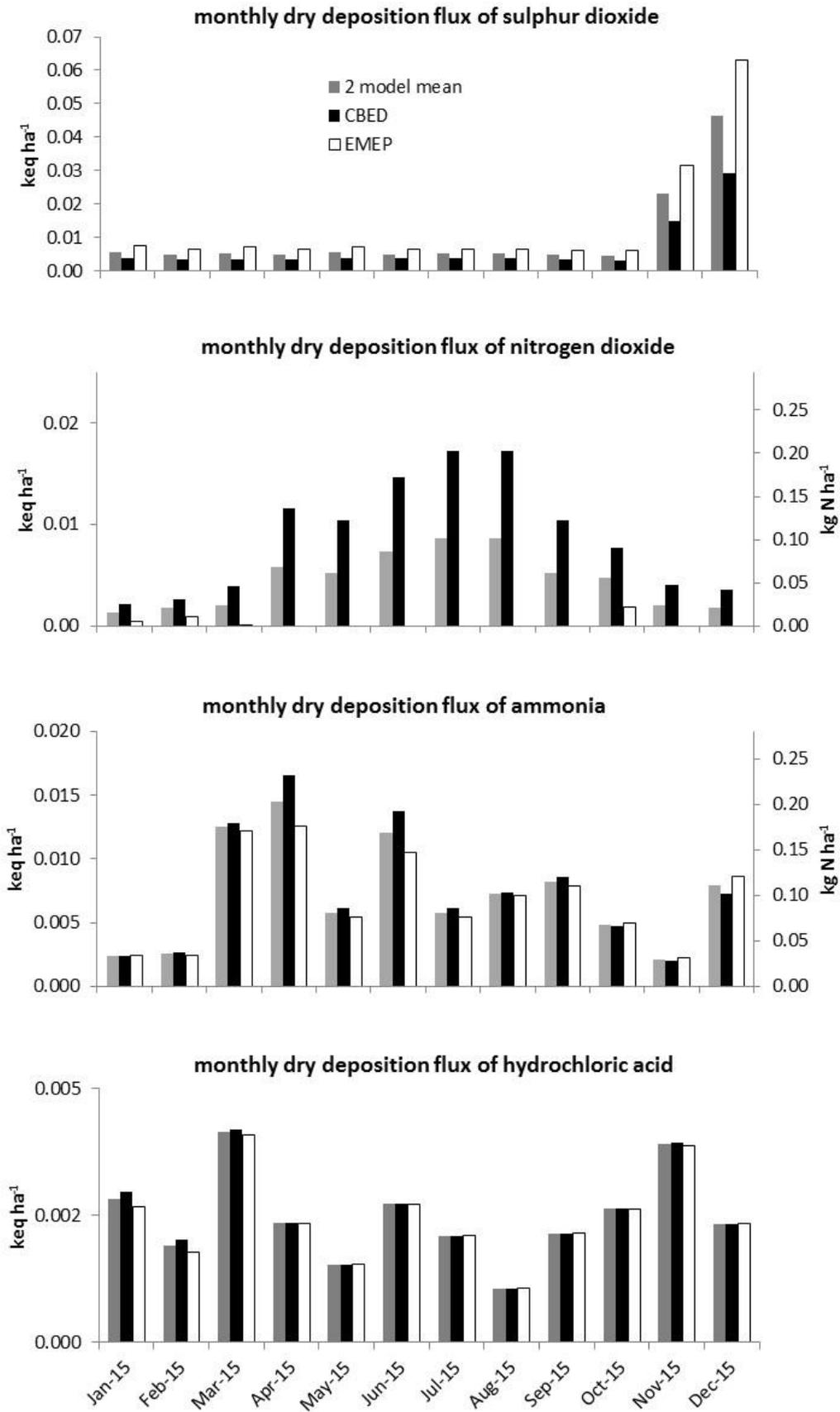
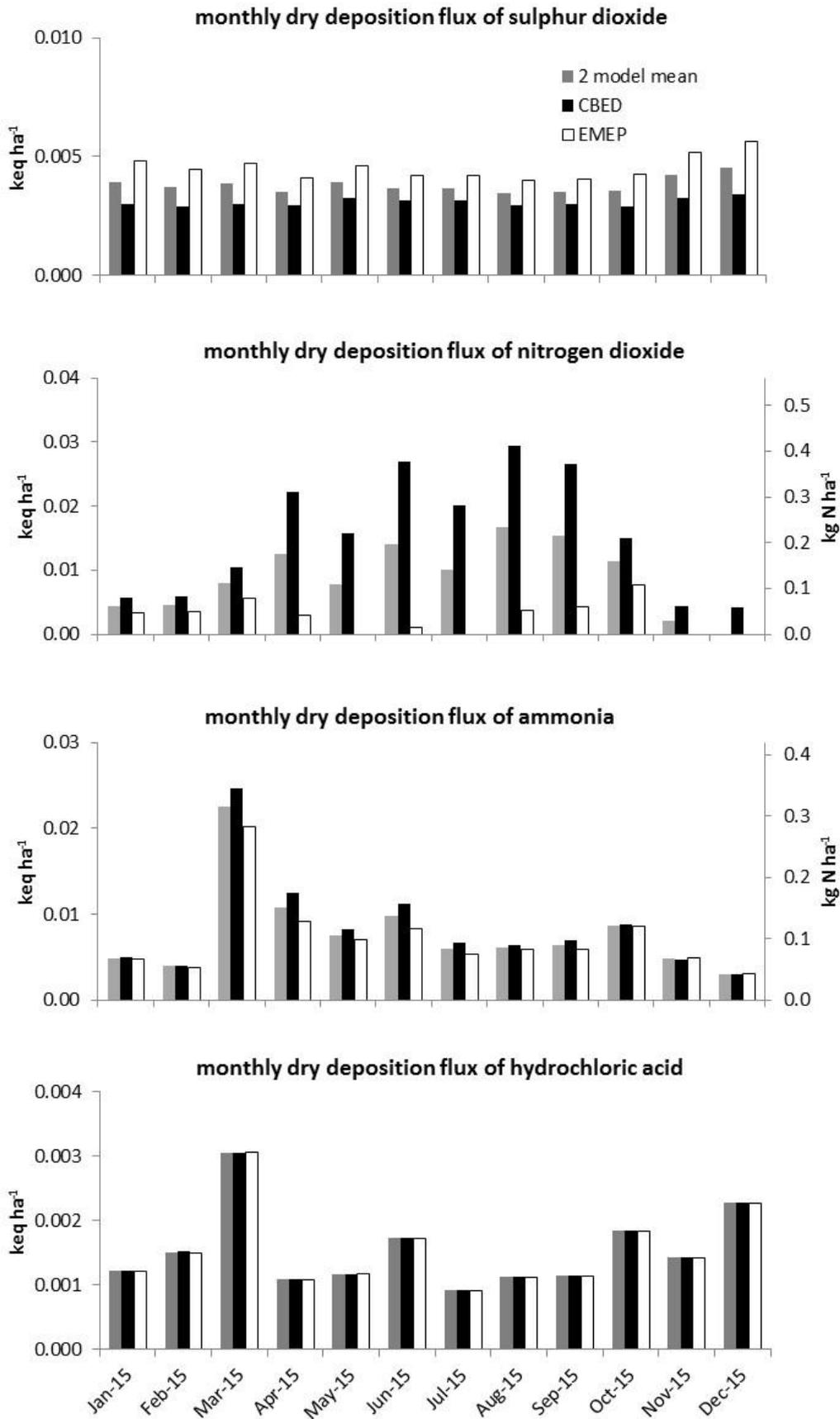
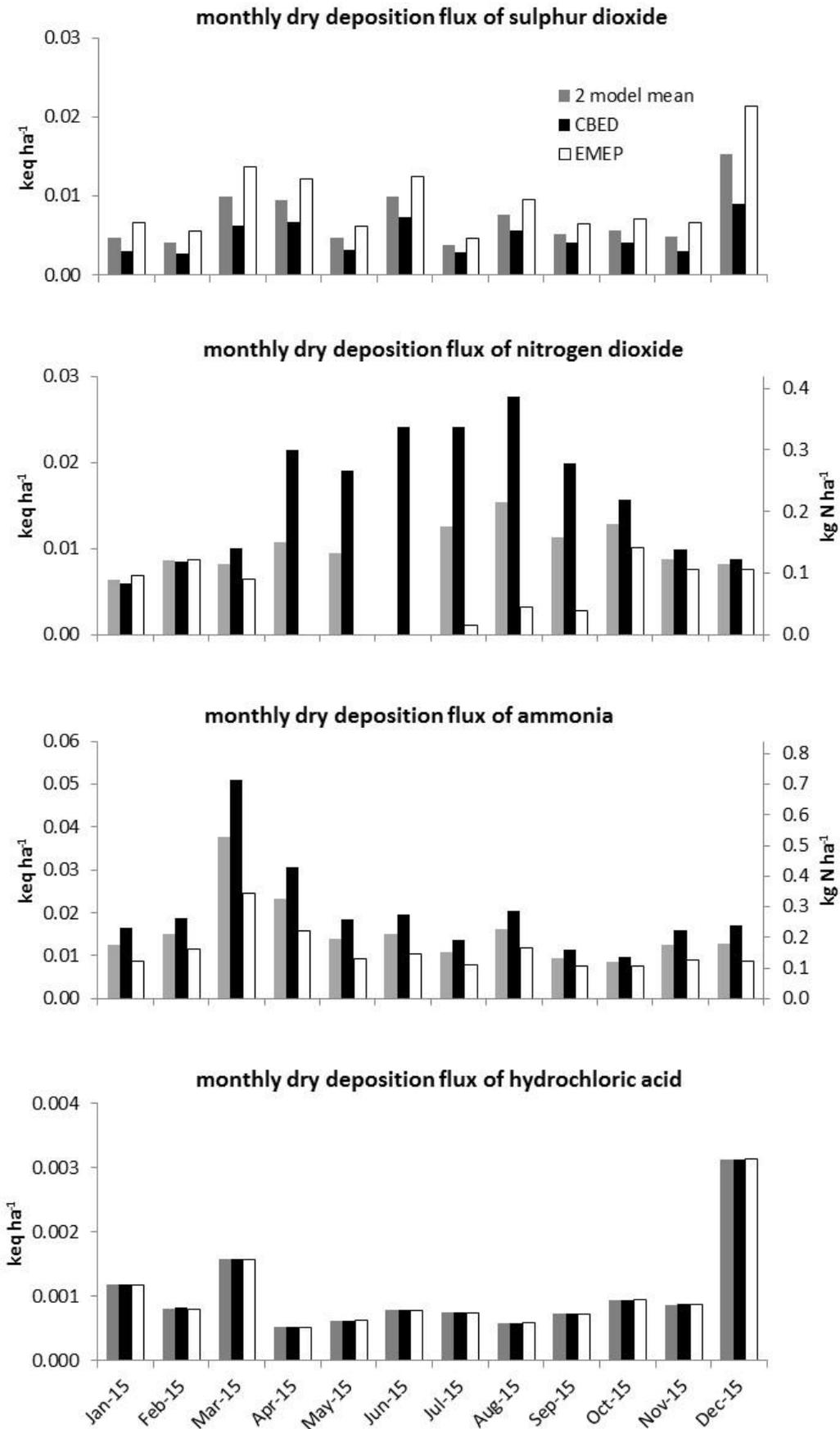


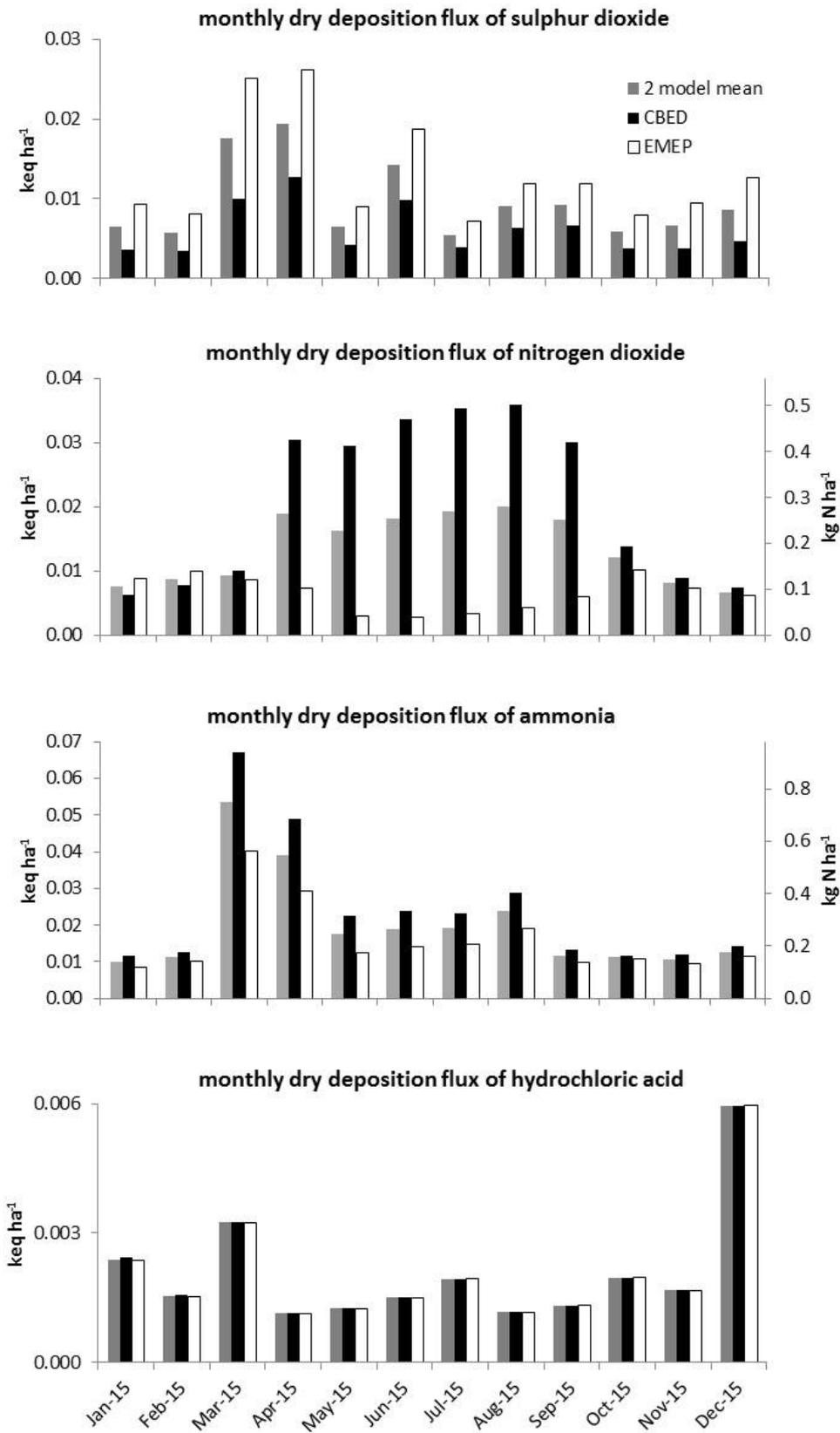
Figure 6.2.5 Monthly dry deposition estimates: New Forest SAC



**Figure 6.2.6 Monthly dry deposition estimates: Skipwith Common SAC**

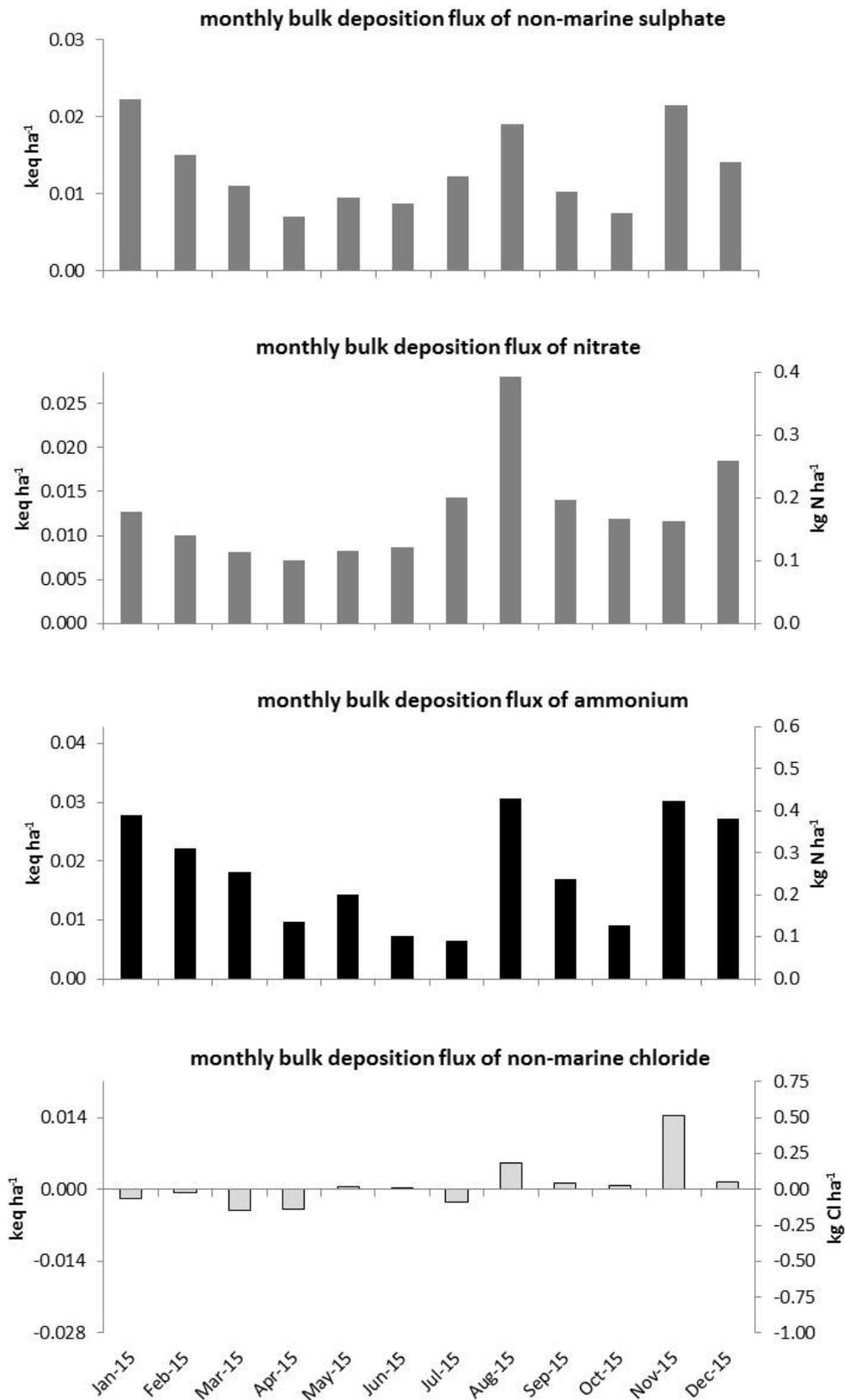


**Figure 6.2.7 Monthly dry deposition estimates: Thorne Moor SAC**

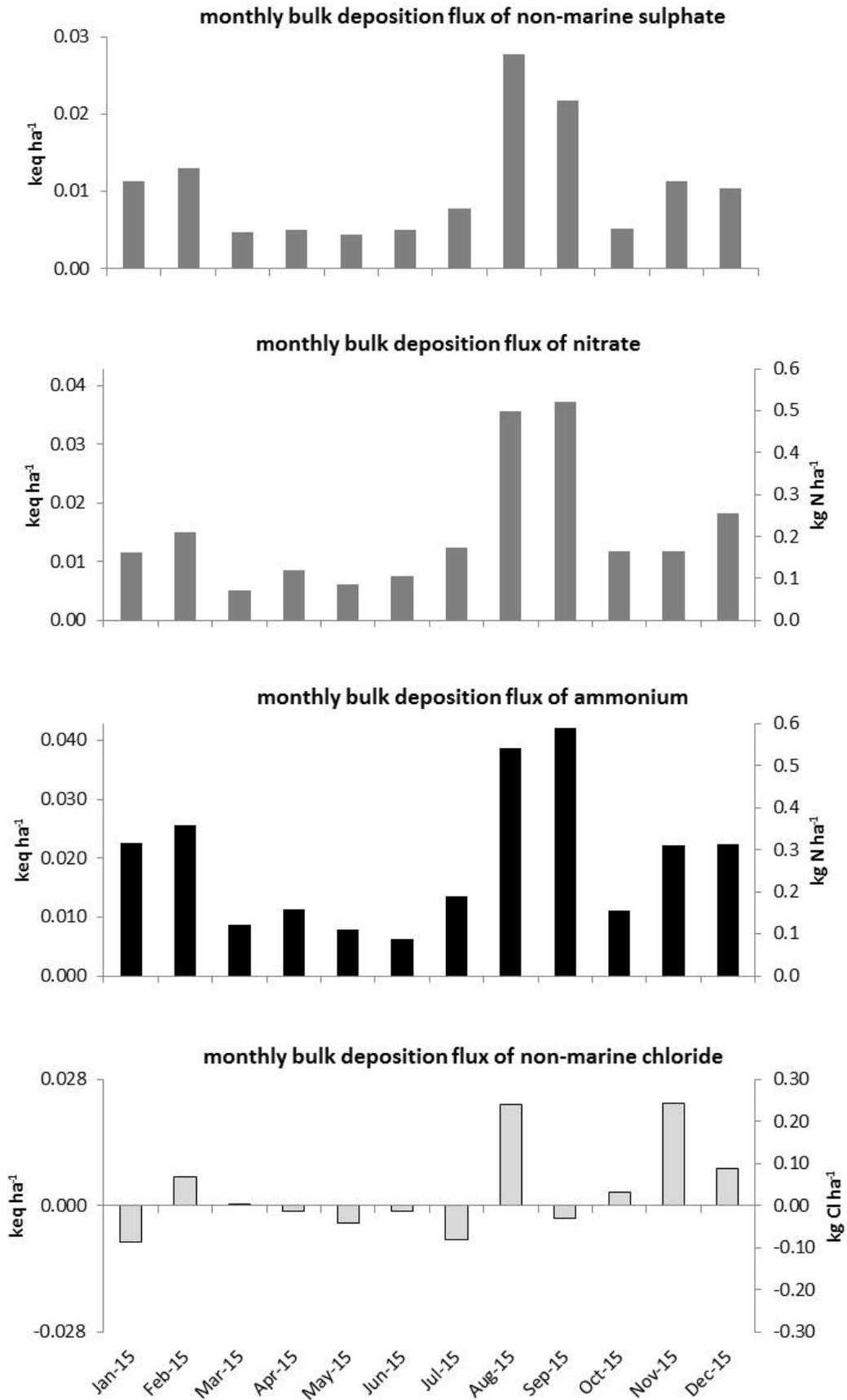


### 6.3 Bulk wet deposition concentrations

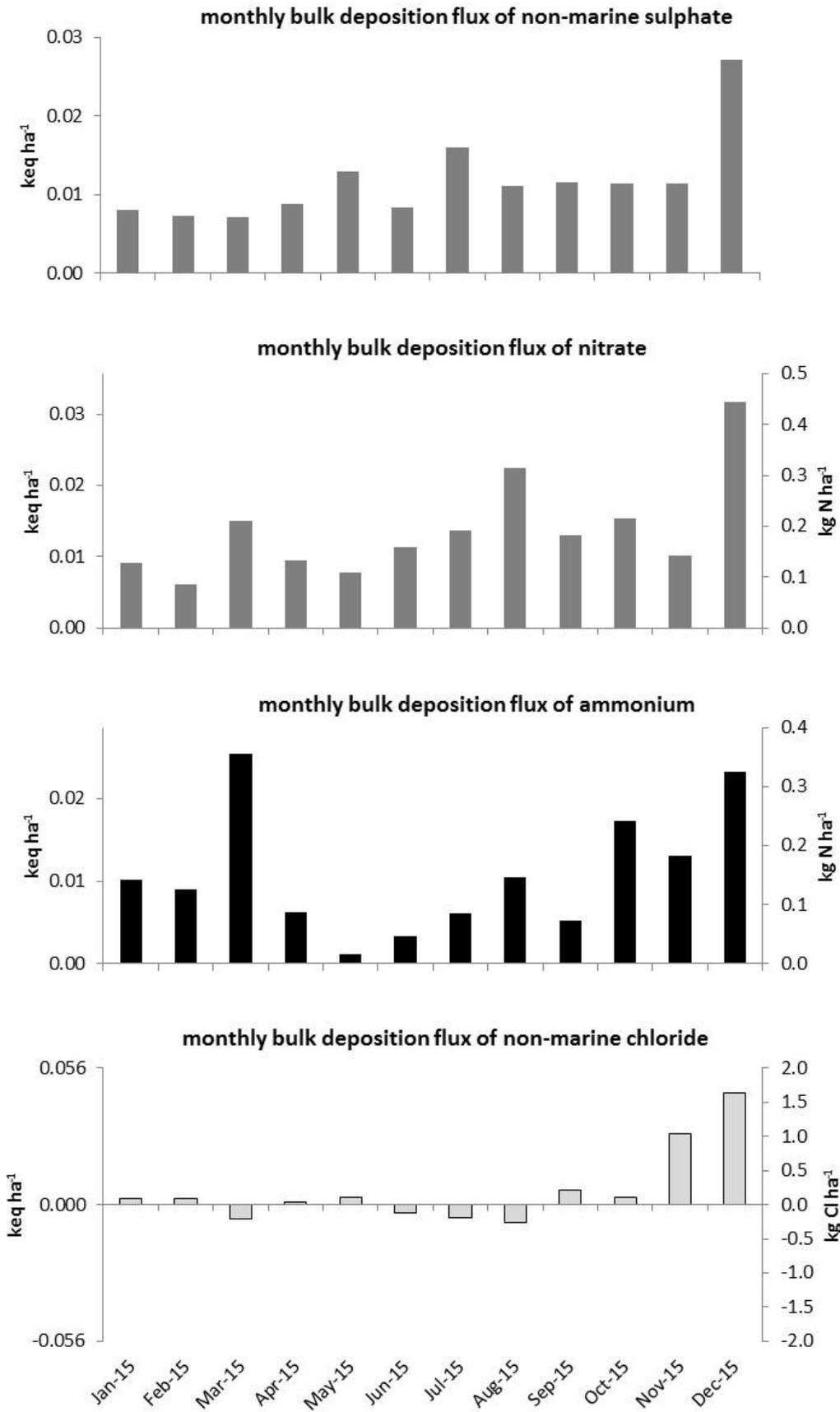
Figure 6.3.1 Monthly bulk wet deposition estimates: Manchester Mosses SAC



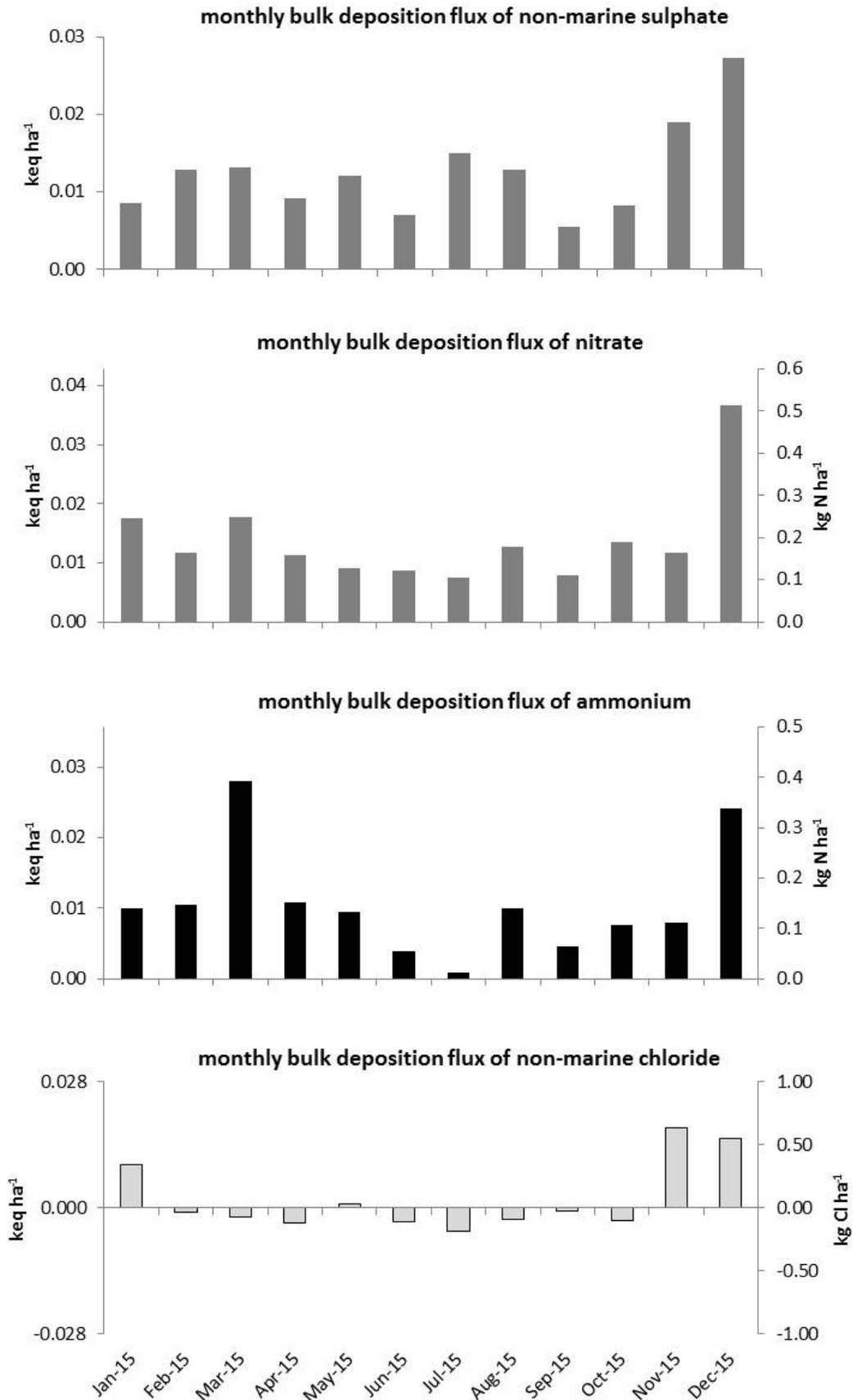
**Figure 6.3.2 Monthly bulk wet deposition estimates: Cannock Chase SAC**



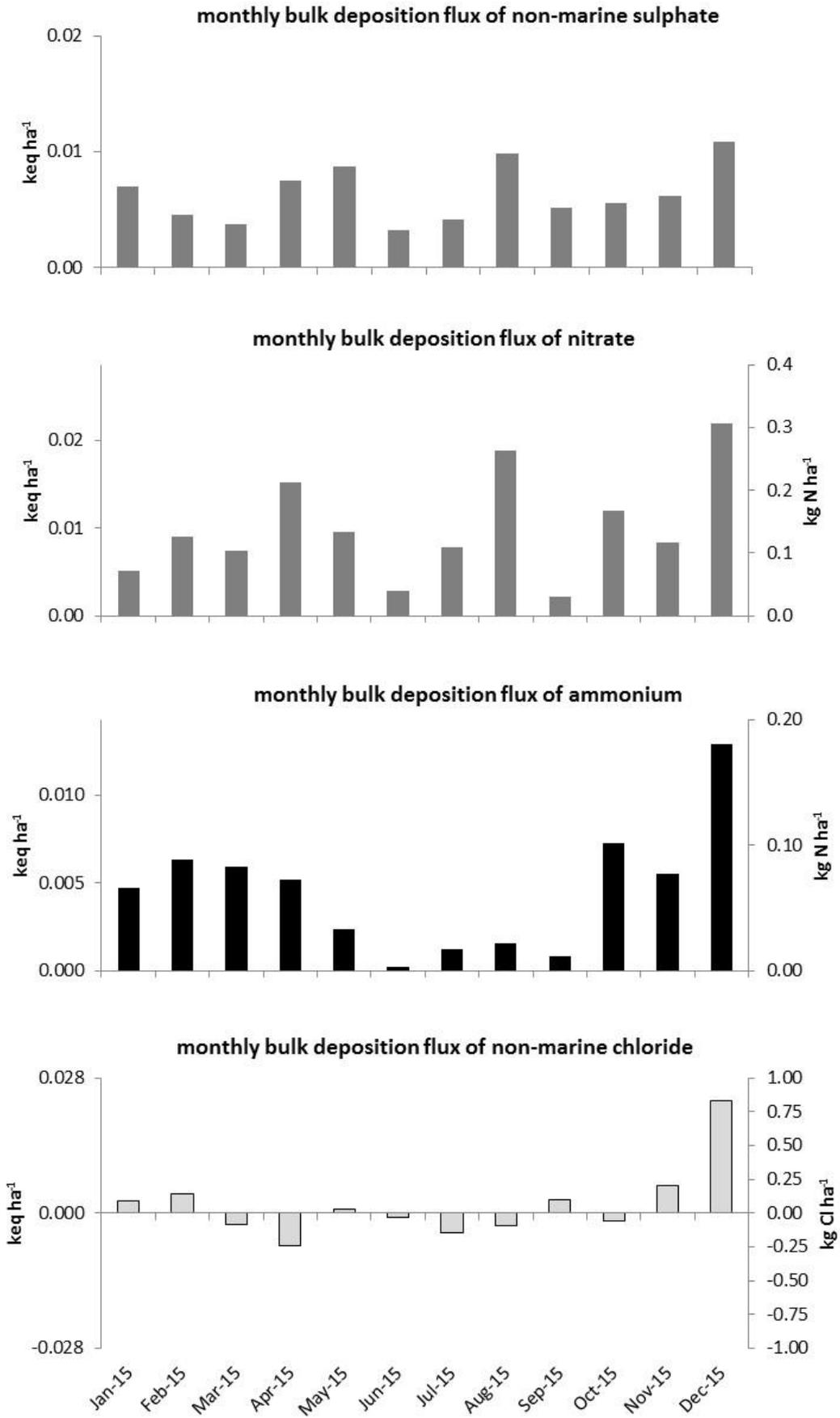
**Figure 6.3.3 Monthly bulk wet deposition estimates: Cleddau Rivers SAC**



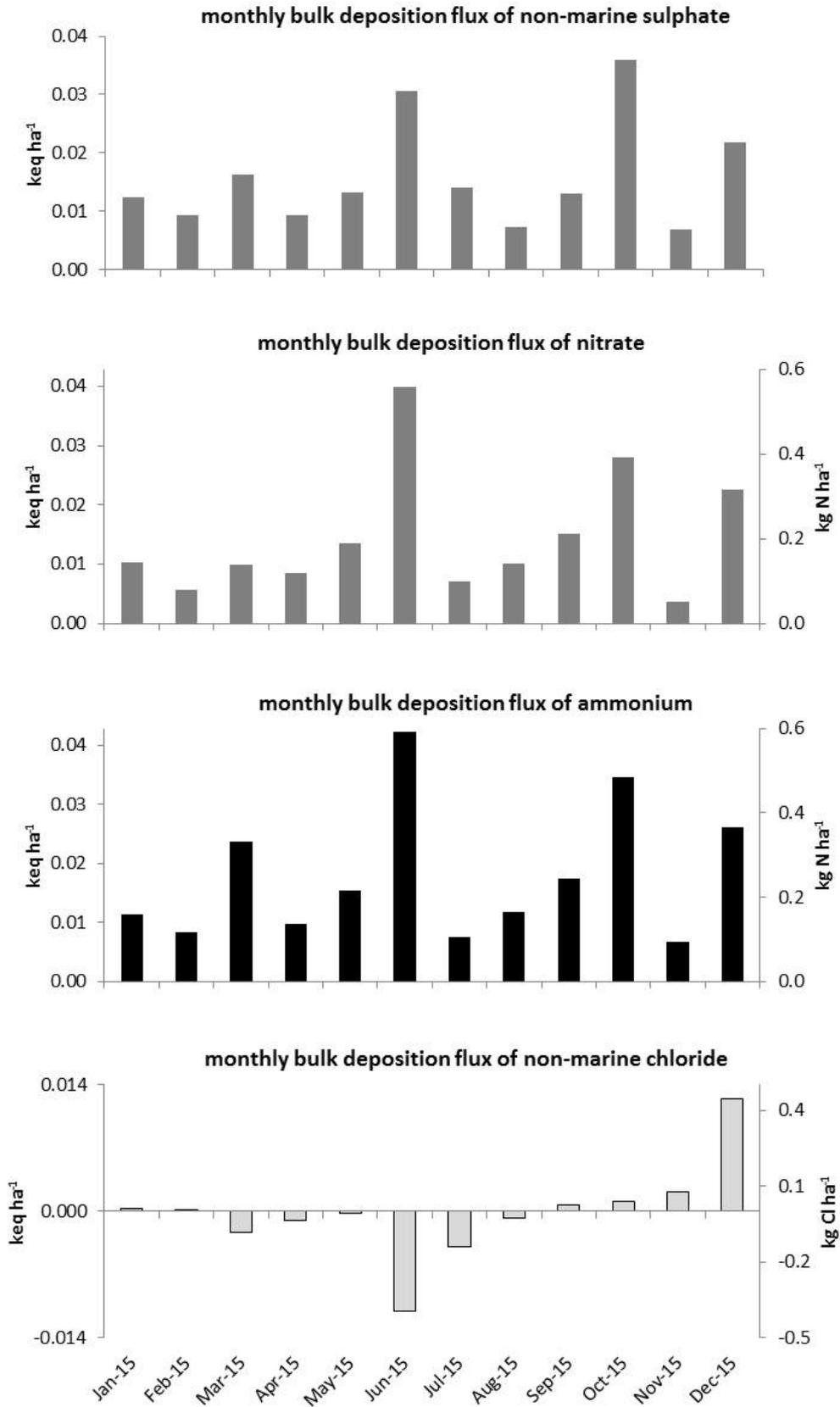
**Figure 6.3.4 Monthly bulk wet deposition estimates: Usk Bats site SAC**



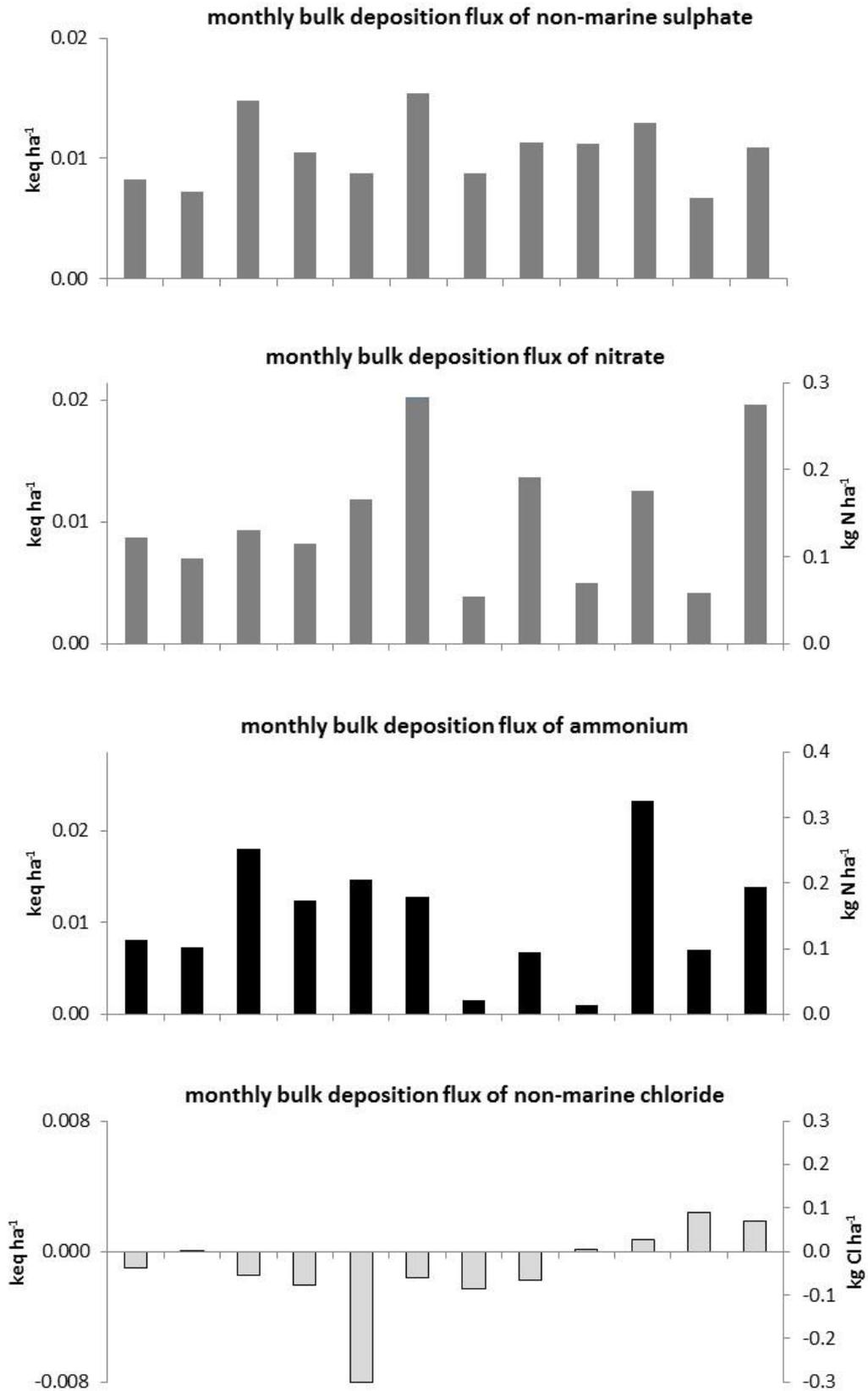
**Figure 6.3.5 Monthly bulk wet deposition estimates: New Forest SAC**



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



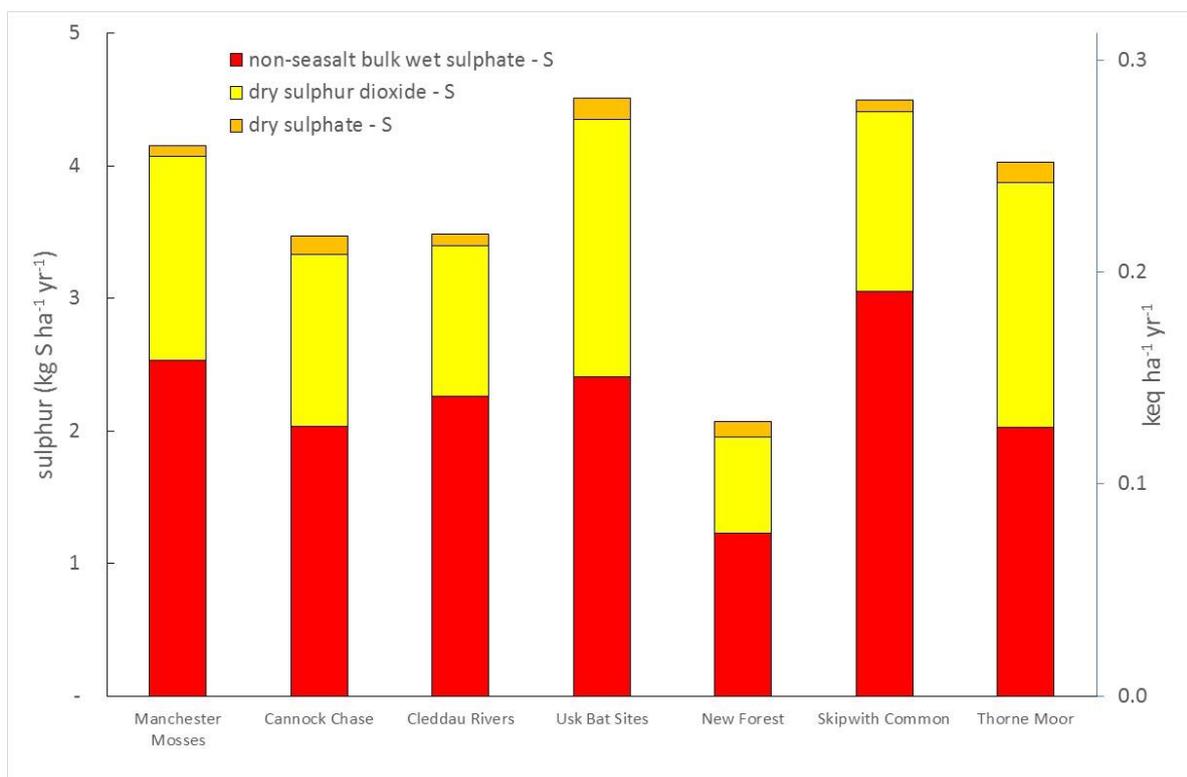
**Figure 6.3.7 Monthly bulk wet deposition estimates: Thorne Moor SAC**



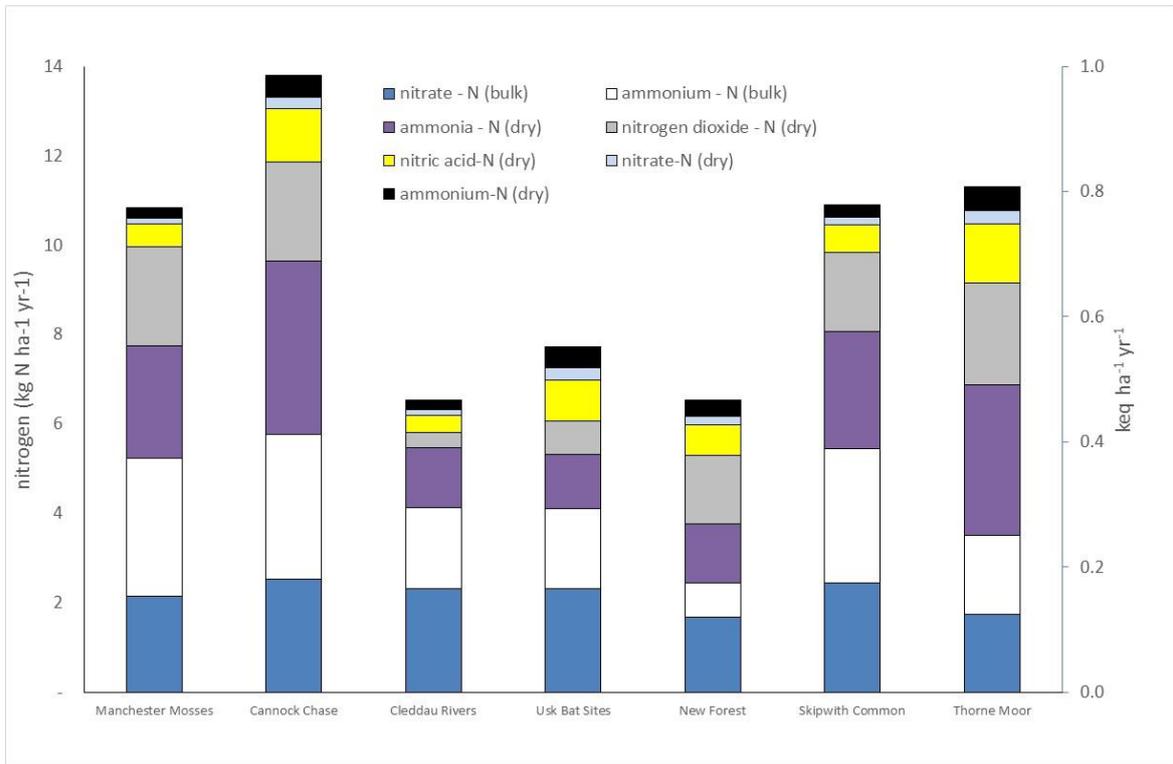
## 6.4 Annual deposition summaries for 2015

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 (2015) bulk wet and dry sulphur deposition. Dry sulphur dioxide contribution derived from original measured concentrations.



**Figure 6.4.2. Estimated annual (2015) bulk wet and dry nitrogen deposition.**



**Figure 6.4.3. Estimated total acidity contributed by bulk wet and dry non-seasalt sulphur (amalgamated), oxidised and reduced nitrogen, non-seasalt bulk wet chloride and dry deposited hydrochloric acid. Dry sulphur dioxide contribution derived from original measured concentrations.**

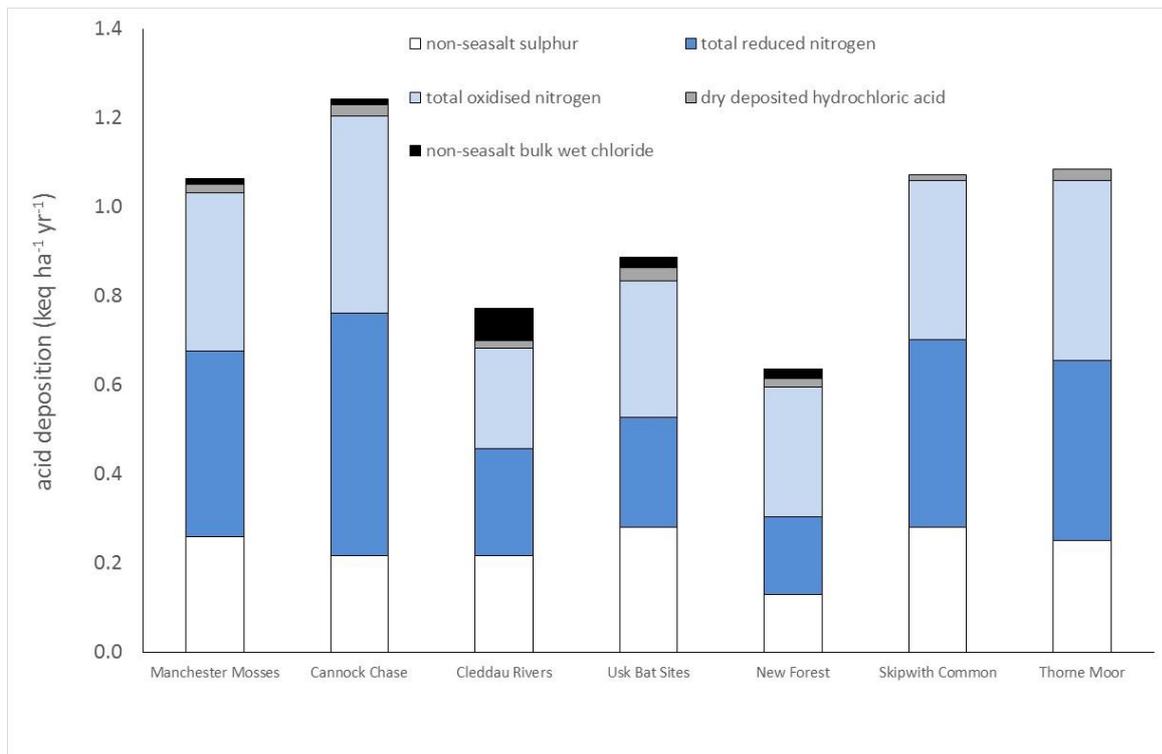


Table 6.4.1

Estimated annual wet and dry sulphur, nitrogen, chloride and total deposition as acidity. 2012-2105. Dry sulphur dioxide contribution derived from original measured concentrations. Corrections to bulk wet deposition estimates for Usk Bat Sites for 2014, and dry nitric acid and total deposition estimates for years 2012-14, highlighted in bold.

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
	2015	0.005	0.009	0.005	0.010	0.007	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
	2015	0.096	0.081	0.071	0.121	0.046	0.085	0.115
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	<b>0.213</b>	0.154	0.209	0.183
	2015	0.158	0.127	0.141	0.151	0.077	0.191	0.127
Dry nitric acid-N	2012	<b>0.052</b>	<b>0.105</b>	<b>0.037</b>	<b>0.069</b>	<b>0.073</b>	<b>0.057</b>	<b>0.121</b>
	2013	<b>0.093</b>	<b>0.156</b>	<b>0.073</b>	<b>0.132</b>	<b>0.114</b>	<b>0.089</b>	<b>0.189</b>
	2014	<b>0.046</b>	<b>0.099</b>	<b>0.031</b>	<b>0.072</b>	<b>0.058</b>	<b>0.061</b>	<b>0.139</b>
	2015	0.036	0.084	0.028	0.065	0.049	0.044	0.094
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
	2015	0.010	0.019	0.009	0.020	0.014	0.012	0.022
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
	2015	0.016	0.035	0.015	0.033	0.026	0.020	0.038
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
	2015	0.180	0.277	0.096	0.086	0.094	0.188	0.240
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
	2015	0.158	0.158	0.024	0.053	0.109	0.127	0.163
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	<b>0.210</b>	0.187	0.204	0.163
	2015	0.153	0.181	0.165	0.166	0.120	0.174	0.124

<b>Bulk wet NH<sub>4</sub>-N</b>	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	<b>0.211</b>	0.177	0.193	0.097
	2015	0.220	0.232	0.131	0.128	0.054	0.215	0.127
<b>Non-seasalt bulk wet chloride</b>	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	<b>0.043</b>	-0.003	0.028	-0.008
	2015	0.011	0.012	0.072	0.023	0.021	-0.002	-0.014
<b>Dry HCl</b>	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
	2015	0.019	0.027	0.017	0.030	0.019	0.012	0.025
<b>TOTAL ACID DEPOSITION</b>	2012	<b>1.182</b>	<b>1.271</b>	<b>0.772</b>	<b>1.124</b>	<b>0.879</b>	<b>1.310</b>	<b>1.696</b>
	2013	<b>1.138</b>	<b>1.500</b>	<b>0.842</b>	<b>1.161</b>	<b>0.983</b>	<b>1.219</b>	<b>1.449</b>
	2014	<b>1.093</b>	<b>1.457</b>	<b>0.728</b>	<b>1.100</b>	<b>0.941</b>	<b>1.191</b>	<b>1.288</b>
	2015	1.062	1.242	0.774	0.886	0.636	1.071	1.071

**Table 6.4.2 Estimated annual wet and dry nitrogen deposition 2012 - 2015. Corrections to bulk wet deposition estimates for Usk Bat Sites for 2014, and dry nitric acid and total deposition estimates for years 2012-14, highlighted in bold.**

species (kg N 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 nitric acid_N	2012	<b>0.726</b>	<b>1.477</b>	<b>0.522</b>	<b>0.962</b>	<b>1.019</b>	<b>0.797</b>	<b>1.695</b>
	2013	<b>1.302</b>	<b>2.184</b>	<b>1.031</b>	<b>1.843</b>	<b>1.591</b>	<b>1.250</b>	<b>2.642</b>
	2014	<b>0.647</b>	<b>1.383</b>	<b>0.437</b>	<b>1.003</b>	<b>0.809</b>	<b>0.851</b>	<b>1.941</b>
	2015	0.510	1.181	0.390	0.915	0.685	0.619	1.316
Dry NO <sub>3</sub> -N	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
	2015	0.139	0.265	0.123	0.282	0.197	0.164	0.307
Dry NH <sub>4</sub> -N	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
	2015	0.226	0.497	0.204	0.464	0.368	0.278	0.533
Dry NH <sub>3</sub> -N	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
	2015	2.523	3.875	1.340	1.203	1.322	2.628	3.360
Dry NO <sub>2</sub> N	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
	2015	2.207	2.217	0.332	0.748	1.531	1.774	2.285
Bulk wet NO <sub>3</sub> -N	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	2.943	<b>2.612</b>	2.862	2.276
	2015	2.147	2.531	2.311	2.325	1.682	2.437	1.736
Bulk wet NH <sub>4</sub> -N	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	2.948	<b>2.475</b>	2.703	1.356
	2015	3.078	3.243	1.828	1.789	0.757	3.006	1.773
TOTAL N DEPOSITION	2012	<b>11.005</b>	<b>13.551</b>	<b>7.111</b>	<b>10.080</b>	<b>9.457</b>	<b>12.119</b>	<b>15.769</b>
	2013	<b>11.708</b>	<b>16.324</b>	<b>7.243</b>	<b>11.475</b>	<b>9.113</b>	<b>11.295</b>	<b>14.127</b>
	2014	<b>11.283</b>	<b>16.121</b>	<b>6.968</b>	<b>9.830</b>	<b>9.727</b>	<b>11.553</b>	<b>12.782</b>
	2015	10.830	13.809	6.528	7.726	6.542	10.906	11.310

## 6.5 Soil solution chemistry (2015)

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 (2015) 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-15	dipwell	4.15	5.74	0.11	0.92	0.75	0.13	0.014	0.028	0.079	10.83	0.225	25.53
Manchester Mosses	Feb-15	dipwell	4.02	5.62	0.11	0.88	0.69	0.13	0.002	0.026	0.061	10.09	0.121	25.67
Manchester Mosses	Mar-15	dipwell	3.96	5.75	0.24	0.82	0.68	0.15	0.003	0.043	0.047	10.60	0.131	27.40
Manchester Mosses	Apr-15	dipwell	4.00	5.96	0.32	1.03	0.76	0.16	0.002	0.056	0.157	11.47	0.189	29.30
Manchester Mosses	May-15	dipwell	4.53	5.54	0.32	0.99	0.66	0.15	0.158	0.028	1.595	10.80	0.057	31.10
Manchester Mosses	Jun-15	dipwell	4.31	5.55	0.19	0.99	0.72	0.16	0.037	0.025	0.526	11.80	0.104	29.57
Manchester Mosses	Jul-15	dipwell	4.27	5.70	0.11	1.10	0.73	0.15	0.066	0.070	0.665	12.20	0.514	31.30
Manchester Mosses	Aug-15	dipwell	4.01	5.61	0.06	1.20	0.73	0.17	0.004	0.024	0.072	11.93	0.229	32.30
Manchester Mosses	Sep-15	dipwell	4.31	5.23	0.17	0.98	0.63	0.14	0.116	0.105	1.005	8.62	0.510	29.03
Manchester Mosses	Oct-15	dipwell	4.04	5.15	0.21	0.93	0.63	0.13	0.005	0.027	0.123	11.17	0.295	24.83
Manchester Mosses	Nov-15	dipwell	3.96	5.39	0.33	1.03	0.75	0.16	0.004	0.053	0.094	11.53	0.224	33.17
Manchester Mosses	Dec-15	dipwell	4.10	5.00	0.53	1.11	0.76	0.26	0.000	0.000	0.162	9.86	0.071	38.80
Cannock Chase	Jan-15	deep	4.72	3.43	1.23	0.32	0.19	1.11	0.008	0.065	0.022	5.12	1.370	9.47
Cannock Chase	Jan-15	shallow	4.47	4.99	2.05	0.13	0.05	1.69	0.022	0.063	0.050	5.63	1.565	20.35
Cannock Chase	Feb-15	deep	4.60	3.60	1.28	0.39	0.26	1.14	0.000	0.034	0.019	5.71	1.255	8.58
Cannock Chase	Feb-15	shallow	4.29	5.05	1.97	0.10	0.06	1.61	0.006	0.057	0.031	4.93	1.704	19.30
Cannock Chase	Mar-15	deep	4.53	3.84	1.42	0.35	0.25	1.08	0.000	0.062	0.000	6.64	1.455	7.44
Cannock Chase	Mar-15	shallow	4.30	5.12	2.07	0.00	0.05	1.48	0.005	0.051	0.022	5.72	1.703	18.35
Cannock Chase	Apr-15	deep	4.57	3.68	1.44	0.36	0.27	1.07	0.004	0.059	0.013	7.19	1.255	7.57

Cannock Chase	Apr-15	shallow	4.26	5.07	2.29	0.00	0.06	1.48	0.062	0.109	0.043	7.27	1.710	18.25
Cannock Chase	May-15	deep	4.62	3.53	1.40	0.46	0.25	1.04	0.000	0.049	0.000	5.24	1.400	8.74
Cannock Chase	May-15	shallow	*	*	*	*	*	*	*	*	*	*	*	*
Cannock Chase	Jun-15	deep	4.66	3.55	1.43	0.29	0.21	1.07	0.003	0.065	0.018	6.20	1.280	10.18
Cannock Chase	Jun-15	shallow	4.42	5.70	2.74	0.08	0.08	1.62	0.003	0.549	0.053	6.71	1.537	18.25
Cannock Chase	Jul-15	deep	4.76	*	*	*	*	*	0.043	0.668	0.052	5.99	1.420	11.90
Cannock Chase	Jul-15	shallow	4.30	*	*	*	*	*	0.118	1.440	0.112	7.55	1.780	13.90
Cannock Chase	Aug-15	deep	*	*	*	*	*	*	0.013	1.070	0.156	6.42	1.670	*
Cannock Chase	Aug-15	shallow	4.22	3.91	2.74	0.16	0.08	1.73	0.008	1.480	0.050	6.00	1.780	10.70
Cannock Chase	Sep-15	deep	4.84	3.29	1.35	0.20	0.18	1.21	0.000	0.215	0.035	2.56	1.050	20.20
Cannock Chase	Sep-15	shallow	4.18	3.78	2.64	0.00	0.08	1.68	0.010	0.746	0.062	9.67	0.975	19.15
Cannock Chase	Oct-15	deep	*	*	*	*	*	*	0.000	0.576	0.043	3.77	1.250	13.70
Cannock Chase	Oct-15	shallow	4.23	3.78	2.58	0.00	0.08	1.72	0.007	1.010	0.033	6.39	2.000	12.00
Cannock Chase	Nov-15	deep	4.60	3.31	1.21	0.47	0.29	0.89	0.000	0.364	0.027	6.47	1.128	10.19
Cannock Chase	Nov-15	shallow	4.28	4.20	2.62	0.07	0.07	1.79	0.013	0.421	0.028	8.07	2.090	12.80
Cannock Chase	Dec-15	deep	4.66	3.92	1.18	0.44	0.35	1.02	0.007	0.061	0.000	7.94	0.966	8.56
Cannock Chase	Dec-15	shallow	4.33	5.12	2.49	0.00	0.07	1.81	0.010	0.276	0.033	8.90	2.320	14.50
Cleddau Rivers	Jan-15	dipwell	4.63	6.91	0.47	1.69	0.80	0.09	0.016	0.027	0.726	10.90	0.275	32.07
Cleddau Rivers	Feb-15	dipwell	4.38	6.99	0.35	1.42	0.78	0.08	0.236	0.028	0.241	11.39	0.273	26.97
Cleddau Rivers	Mar-15	dipwell	4.31	6.68	0.36	1.25	0.70	0.10	0.084	0.041	0.180	10.12	0.180	31.20
Cleddau Rivers	Apr-15	dipwell	4.42	6.46	0.60	0.89	0.68	0.12	0.142	0.048	0.544	9.87	0.374	37.00
Cleddau Rivers	May-15	dipwell	4.84	6.29	0.66	0.84	0.67	0.11	0.136	0.031	2.012	9.08	0.156	36.90
Cleddau Rivers	Jun-15	dipwell	5.57	6.75	0.73	2.63	0.75	0.13	0.148	0.051	1.699	8.87	0.376	44.87
Cleddau Rivers	Jul-15	dipwell	5.28	6.81	0.76	0.89	0.76	0.16	0.289	0.021	3.979	8.12	0.161	57.70
Cleddau Rivers	Aug-15	dipwell	4.38	6.60	0.18	0.58	0.80	0.19	0.011	0.037	0.564	7.12	0.057	58.67
Cleddau Rivers	Sep-15	dipwell	4.21	6.05	0.18	0.37	0.72	0.17	0.009	0.054	0.194	7.50	0.205	51.73
Cleddau Rivers	Oct-15	dipwell	4.86	6.10	0.33	0.42	0.66	0.13	0.486	0.029	4.805	8.42	0.338	41.23
Cleddau Rivers	Nov-15	dipwell	4.16	6.06	0.24	0.59	0.73	0.10	0.050	0.026	0.150	9.70	0.177	36.57

Cleddau Rivers	Dec-15	dipwell	4.54	6.25	0.26	0.39	0.69	0.10	0.085	0.044	0.583	10.68	0.193	30.90
Usk Bat Sites	Jan-15	dipwell	4.21	4.16	0.20	0.60	0.59	0.10	0.014	0.045	0.501	7.34	0.625	26.10
Usk Bat Sites	Feb-15	dipwell	4.02	4.54	0.19	0.57	0.67	0.08	0.004	0.046	0.488	9.43	0.677	18.57
Usk Bat Sites	Mar-15	dipwell	3.97	4.50	0.32	0.58	0.64	0.14	0.012	0.060	0.693	7.74	0.618	34.03
Usk Bat Sites	Apr-15	dipwell	3.99	4.69	0.20	0.72	0.74	0.15	0.023	0.244	0.704	7.55	1.203	32.00
Usk Bat Sites	May-15	dipwell	4.06	4.25	0.21	0.61	0.63	0.14	0.000	0.036	0.655	7.23	0.671	33.17
Usk Bat Sites	Jun-15	dipwell	4.24	4.31	0.16	0.56	0.62	0.11	0.003	0.151	0.692	6.97	0.934	22.75
Usk Bat Sites	Jul-15	dipwell	4.23	3.70	0.26	0.57	0.60	0.10	0.004	0.072	0.461	6.47	1.149	23.60
Usk Bat Sites	Aug-15	dipwell	4.09	4.31	0.14	0.71	0.70	0.23	0.000	0.056	0.575	7.34	0.457	41.40
Usk Bat Sites	Sep-15	dipwell	4.09	3.94	0.11	0.55	0.63	0.16	0.014	0.066	0.574	7.10	0.449	34.57
Usk Bat Sites	Oct-15	dipwell	4.09	3.89	0.17	0.53	0.65	0.09	0.000	0.073	0.284	6.90	0.624	22.47
Usk Bat Sites	Nov-15	dipwell	4.05	4.23	0.16	0.65	0.74	0.18	0.002	0.046	0.568	7.21	0.494	39.83
Usk Bat Sites	Dec-15	dipwell	4.14	4.32	0.12	0.69	0.72	0.20	0.005	0.038	0.666	7.51	0.400	40.37
New Forest	Jan-15	deep	4.64	15.75	0.05	1.44	1.37	1.30	0.006	0.026	0.000	20.40	5.270	3.42
New Forest	Jan-15	shallow	4.43	14.75	0.08	0.74	1.17	2.25	0.010	0.037	0.038	18.40	4.426	29.75
New Forest	Feb-15	deep	4.81	16.93	0.17	2.41	2.06	0.98	0.000	0.032	0.000	23.23	6.647	3.17
New Forest	Feb-15	shallow	4.39	13.75	0.13	0.69	1.13	2.47	0.004	0.025	0.020	18.15	3.508	36.55
New Forest	Mar-15	deep	4.73	16.53	0.16	2.30	1.78	0.94	0.000	0.037	0.000	21.70	5.898	2.94
New Forest	Mar-15	shallow	4.31	13.15	0.20	0.66	0.99	2.17	0.000	0.033	0.018	17.00	3.194	32.75
New Forest	Apr-15	deep	4.89	16.10	0.18	2.22	1.86	0.84	0.000	0.047	0.000	22.23	6.440	3.25
New Forest	Apr-15	shallow	4.39	10.29	0.53	0.48	0.93	4.22	0.021	0.049	0.021	15.40	2.226	25.18
New Forest	May-15	deep	4.90	16.53	0.15	2.59	2.06	0.65	0.000	0.028	0.000	22.98	6.795	2.95
New Forest	May-15	shallow	4.49	12.65	0.19	0.59	0.93	1.46	0.000	0.103	0.000	15.40	2.392	20.25
New Forest	Jun-15	deep	4.86	17.40	0.18	2.55	2.09	0.79	0.000	0.028	0.027	22.30	6.513	3.26
New Forest	Jun-15	shallow	4.55	13.20	0.21	0.61	0.95	1.32	0.000	0.023	0.000	19.30	2.987	16.35
New Forest	Jul-15	deep	4.68	16.50	0.24	1.81	1.56	0.88	0.000	0.016	0.007	22.23	6.133	3.21
New Forest	Jul-15	shallow	4.38	14.75	0.18	0.73	1.07	1.32	0.000	0.021	0.037	18.23	2.805	17.55
New Forest	Aug-15	deep	4.54	15.10	0.22	1.19	1.04	0.90	0.000	0.019	0.000	18.80	5.175	3.50

New Forest	Aug-15	shallow	4.27	13.00	0.26	0.80	0.69	0.76	0.002	0.031	0.030	20.00	3.420	16.87
New Forest	Sep-15	deep	4.76	14.85	0.17	2.39	1.86	0.39	0.000	0.048	0.000	21.25	6.225	2.98
New Forest	Sep-15	shallow	4.36	10.90	0.26	0.53	0.55	0.84	0.027	0.027	0.000	14.80	1.070	31.00
New Forest	Oct-15	deep	4.73	15.33	0.25	2.04	1.74	0.71	0.000	0.020	0.000	21.57	6.253	2.78
New Forest	Oct-15	shallow	4.35	14.45	0.19	0.76	1.17	1.56	0.004	0.032	0.047	23.25	3.715	18.93
New Forest	Nov-15	deep	4.77	16.88	0.31	2.64	2.13	0.64	0.000	0.024	0.000	23.75	6.363	3.06
New Forest	Nov-15	shallow	4.28	15.35	0.25	0.75	1.22	1.92	0.005	0.027	0.016	22.85	2.950	27.60
New Forest	Dec-15	deep	4.73	16.07	0.23	2.27	1.88	0.83	0.000	0.000	0.000	23.83	6.173	2.71
New Forest	Dec-15	shallow	4.34	14.40	0.27	0.87	1.16	1.94	0.000	0.000	0.013	22.75	2.928	32.50
Skipwith Common	Jan-15	deep	4.49	3.96	1.06	0.32	0.33	4.70	0.011	0.037	0.187	4.78	4.493	30.58
Skipwith Common	Jan-15	shallow	4.08	4.68	2.15	0.47	0.56	6.63	0.012	0.026	1.565	3.79	2.745	90.75
Skipwith Common	Feb-15	deep	4.31	4.67	1.00	0.31	0.38	5.50	0.000	0.047	0.159	6.89	7.300	26.75
Skipwith Common	Feb-15	shallow	4.04	4.44	1.98	0.49	0.49	5.69	0.003	0.030	1.408	4.29	2.553	83.33
Skipwith Common	Mar-15	deep	4.37	4.26	1.24	0.37	0.34	4.84	0.000	0.093	0.232	4.73	5.223	30.65
Skipwith Common	Mar-15	shallow	4.02	4.62	2.13	0.52	0.47	5.51	0.000	0.078	1.450	4.71	2.600	85.53
Skipwith Common	Apr-15	deep	4.32	6.99	0.72	0.42	0.34	2.38	0.006	0.080	0.160	6.93	7.025	26.50
Skipwith Common	Apr-15	shallow	4.02	4.52	2.22	0.64	0.46	5.49	0.004	0.045	1.600	4.98	2.343	90.58
Skipwith Common	May-15	deep	4.44	4.15	1.37	0.43	0.32	4.75	0.000	0.128	0.145	4.99	5.078	31.63
Skipwith Common	May-15	shallow	4.09	4.25	2.57	0.50	0.52	5.89	0.000	0.037	1.765	4.39	2.513	89.00
Skipwith Common	Jun-15	deep	4.44	4.23	1.30	0.30	0.30	4.67	0.000	0.071	0.171	5.26	4.893	30.90
Skipwith Common	Jun-15	shallow	4.12	4.04	2.25	0.40	0.45	5.54	0.000	0.018	1.342	4.24	2.203	84.78
Skipwith Common	Jul-15	deep	4.41	4.56	1.11	0.34	0.30	4.79	0.000	0.072	0.097	6.39	5.183	28.70
Skipwith Common	Jul-15	shallow	4.05	4.19	2.16	0.47	0.40	5.56	0.000	0.019	1.123	4.68	1.803	90.20
Skipwith Common	Aug-15	deep	4.41	4.37	1.17	0.44	0.30	4.76	0.002	0.242	0.111	6.44	5.040	28.90
Skipwith Common	Aug-15	shallow	4.02	4.59	2.41	0.62	0.45	5.32	0.003	0.034	1.368	4.82	3.295	85.40
Skipwith Common	Sep-15	deep	4.45	3.73	0.95	0.29	0.28	3.68	0.004	0.219	0.104	5.45	3.933	29.20
Skipwith Common	Sep-15	shallow	4.01	4.72	2.17	0.55	0.58	5.01	0.010	0.032	1.261	3.60	4.503	69.15
Skipwith Common	Oct-15	deep	4.40	4.06	0.95	0.31	0.32	4.25	0.002	0.050	0.096	5.61	4.933	24.77

Skipwith Common	Oct-15	shallow	3.97	5.43	2.66	0.71	0.65	5.10	0.003	0.024	1.703	4.31	6.113	67.00
Skipwith Common	Nov-15	deep	4.34	4.56	1.15	0.39	0.34	5.05	0.000	0.041	0.137	7.85	6.438	22.83
Skipwith Common	Nov-15	shallow	3.98	5.58	2.41	0.68	0.63	5.98	0.002	0.031	1.238	4.34	5.120	81.47
Skipwith Common	Dec-15	deep	4.44	4.35	0.99	0.38	0.39	4.51	0.003	0.000	0.113	7.82	5.080	24.77
Skipwith Common	Dec-15	shallow	4.03	5.40	2.20	0.71	0.61	6.05	0.005	0.000	1.361	4.21	4.760	82.90
Thorne Moor	Jan-15	dipwell	3.64	6.96	0.55	2.83	1.18	0.91	0.028	0.032	0.372	12.17	0.262	113.20
Thorne Moor	Feb-15	dipwell	3.58	7.10	0.44	2.46	1.13	0.96	0.017	0.031	0.489	11.93	0.204	107.20
Thorne Moor	Mar-15	dipwell	3.56	6.94	0.87	2.71	1.07	0.90	0.005	0.174	0.468	12.23	0.314	114.20
Thorne Moor	Apr-15	dipwell	3.57	6.71	0.87	2.73	1.09	0.98	0.013	0.049	0.405	11.93	0.404	127.33
Thorne Moor	May-15	dipwell	3.57	7.04	0.47	3.20	1.18	1.09	0.000	0.025	0.340	12.22	0.108	143.33
Thorne Moor	Jun-15	dipwell	3.59	7.87	0.09	3.96	1.45	1.60	0.006	0.030	0.282	12.63	0.258	148.67
Thorne Moor	Jul-15	dipwell	3.55	7.96	0.37	4.23	1.45	1.45	0.000	0.019	0.299	14.44	0.303	171.00
Thorne Moor	Aug-15	dipwell	3.56	7.27	0.56	3.96	1.31	1.45	0.004	0.023	0.303	12.93	0.259	178.33
Thorne Moor	Sep-15	dipwell	3.57	6.50	0.36	3.09	1.11	1.02	0.005	0.026	0.302	12.37	0.269	126.33
Thorne Moor	Oct-15	dipwell	3.59	6.72	0.41	3.25	1.15	1.09	0.003	0.026	0.291	12.13	0.247	130.00
Thorne Moor	Nov-15	dipwell	3.65	6.90	0.99	3.41	1.26	1.11	0.005	0.029	0.392	12.43	0.361	131.67
Thorne Moor	Dec-15	dipwell	3.63	6.67	0.88	3.32	1.26	1.34	0.060	0.047	0.329	11.83	0.344	147.67

**Table 6.5.2. Annual (2012 - 2015) mean concentrations of pH and solutes in monthly soil solution samples.**

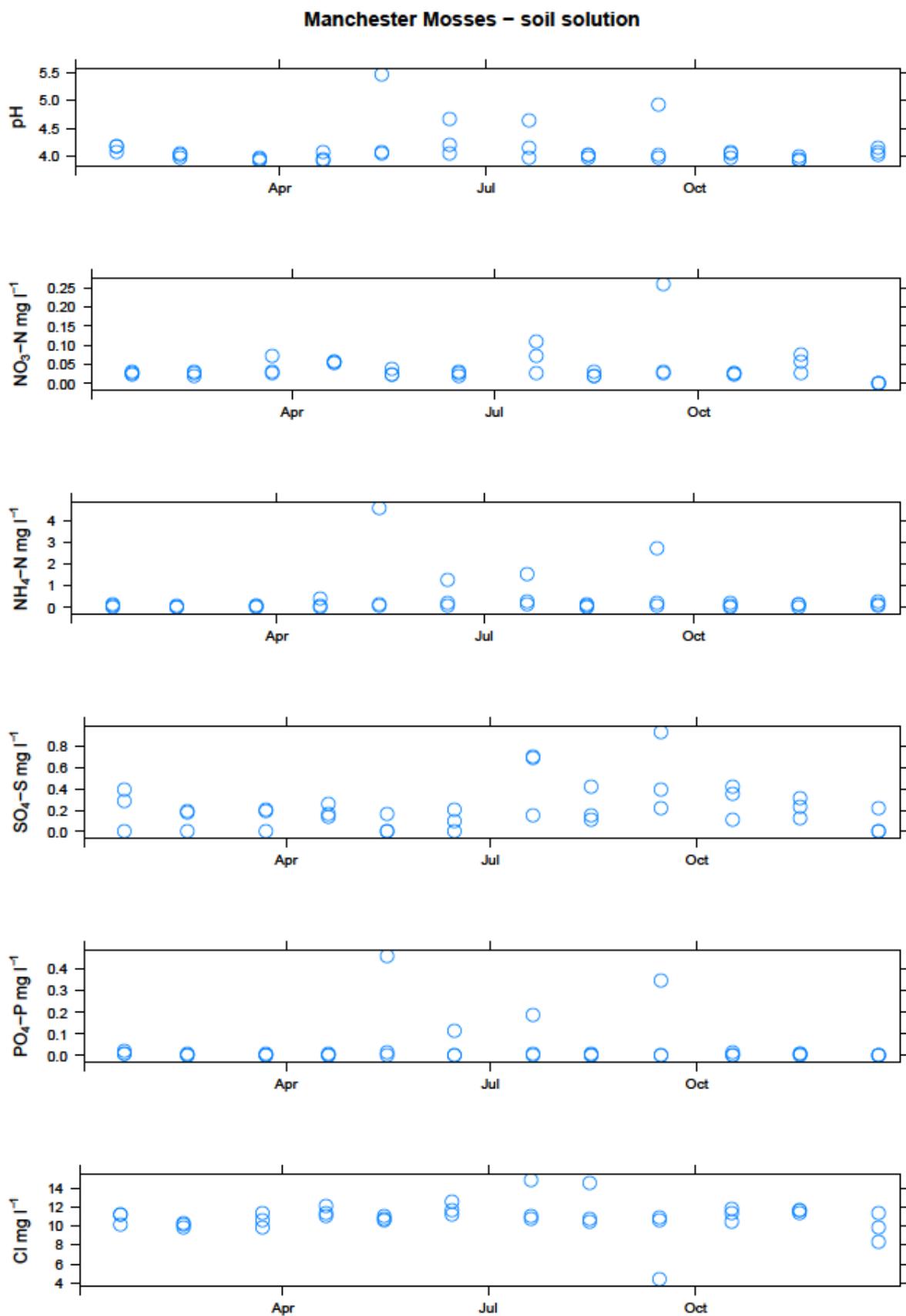
**Determined as means of monthly means. All units with exception of pH in mg L<sup>-1</sup>. Heathland soils, sampled at two depths, shaded.**

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> <b>(dipwell)</b>	2012	4.33	4.38	0.27	1.32	0.59	0.20	0.022	0.031	0.336	8.87	0.117	42.00
	2013	4.29	4.71	1.08	1.04	0.62	0.26	0.027	0.028	0.161	9.13	0.170	40.46
	2014	4.27	5.22	0.67	0.97	0.69	0.19	0.020	0.034	0.210	9.84	0.167	35.23
	2015	4.14	5.52	0.23	1.00	0.71	0.16	0.036	0.041	0.383	10.91	0.234	29.83
<b>Cannock Chase</b> <b>(shallow)</b>	2012	4.59	4.04	3.50	1.05	0.21	1.05	0.046	0.032	0.188	5.61	1.538	26.61
	2013	4.38	3.52	2.42	0.18	0.10	1.18	0.007	0.055	0.049	5.58	1.590	16.61
	2014	4.48	3.92	2.08	0.25	0.07	1.51	0.012	0.066	0.047	6.14	1.404	15.23
	2015	4.31	4.67	2.42	0.07	0.07	1.66	0.022	0.457	0.046	6.87	1.671	17.13
<b>Cannock Chase</b> <b>(deep)</b>	2012	5.23	3.40	1.76	1.38	0.30	0.63	0.041	0.047	0.357	5.74	1.977	13.14
	2013	4.63	2.64	1.81	0.42	0.18	0.99	0.004	0.075	0.038	5.23	1.568	7.01
	2014	4.72	3.63	1.67	0.38	0.23	1.19	0.011	0.064	0.025	6.46	1.293	7.88
	2015	4.64	3.59	1.32	0.37	0.25	1.06	0.006	0.202	0.027	5.99	1.280	9.85
<b>Cleddau Rivers</b> <b>(dipwell)</b>	2012	5.69	5.31	0.91	3.86	0.74	0.17	0.427	0.032	3.155	7.73	0.618	35.65
	2013	5.55	6.26	0.96	4.22	0.88	0.10	1.428	0.025	8.183	9.08	0.757	31.04
	2014	4.71	7.27	0.67	1.87	0.87	0.10	0.242	0.028	1.423	10.31	0.612	30.94
	2015	4.63	6.50	0.43	1.00	0.73	0.12	0.141	0.037	1.306	9.31	0.234	40.48
<b>Usk Bats Site</b> <b>(dipwell)</b>	2012	4.80	3.69	0.38	2.04	0.55	0.20	0.047	0.087	0.819	6.36	0.779	28.87
	2013	4.38	4.35	0.38	0.97	0.76	0.19	0.026	0.165	0.612	6.87	1.706	15.95
	2014	4.35	4.17	0.26	0.66	0.53	0.14	0.010	0.078	0.422	6.74	0.860	21.41
	2015	4.10	4.25	0.19	0.61	0.66	0.14	0.008	0.078	0.572	7.40	0.693	31.18

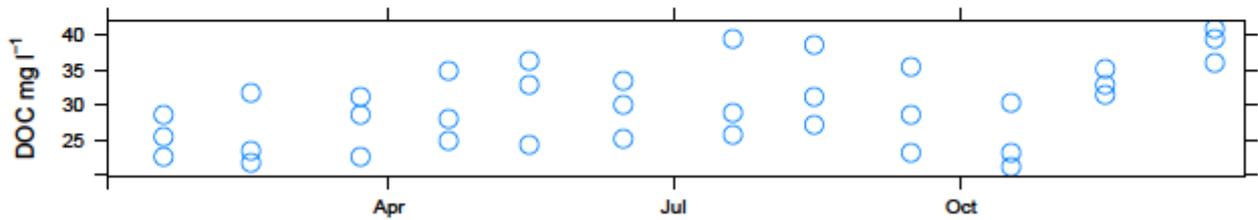
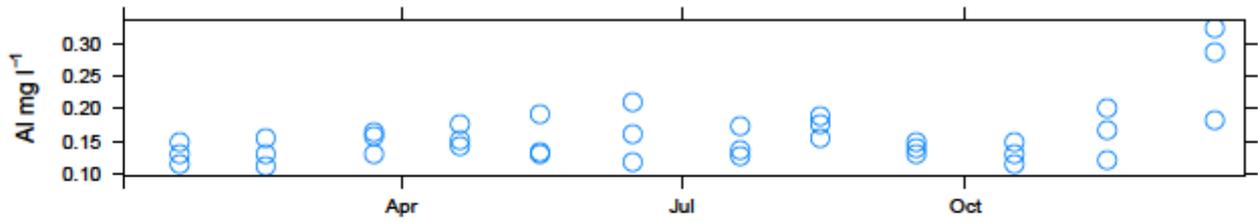
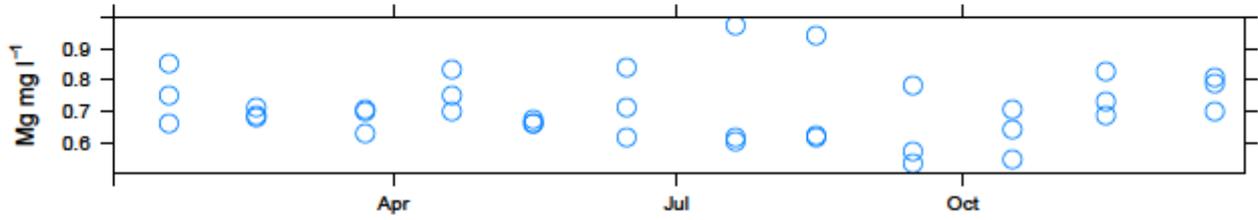
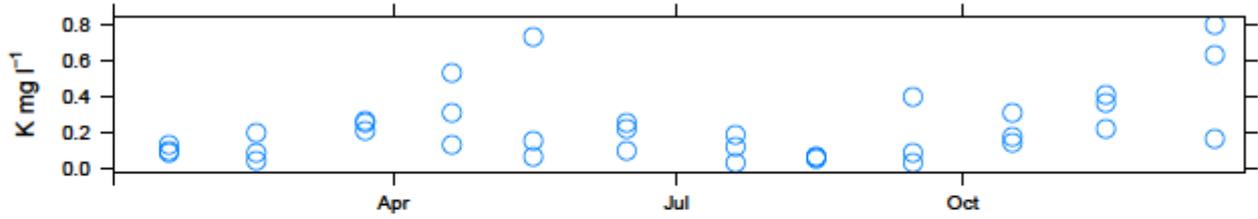
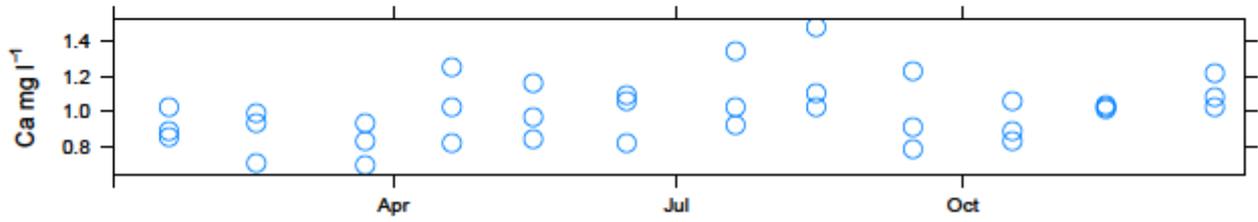
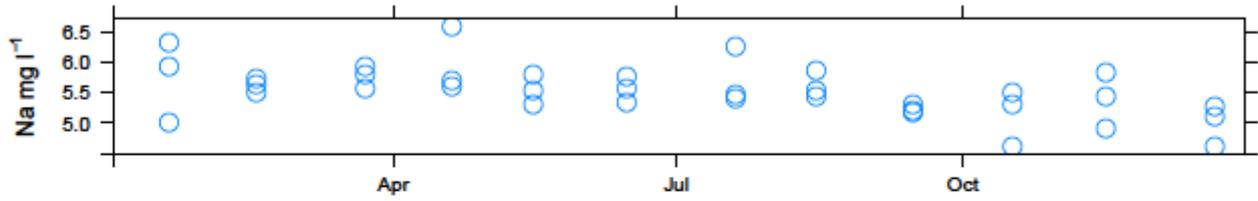
Table 6.5.2. continued

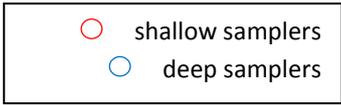
site	Year	pH	Na	K	Ca	Mg	Al	PO <sub>4</sub> -P	NO <sub>3</sub> -N	NH <sub>4</sub> -N	Cl	SO <sub>4</sub> -S	DOC
<b>New Forest (shallow)</b>	2012	4.38	14.28	0.26	0.79	1.06	2.04	0.009	0.022	0.087	20.72	2.663	37.59
	2013	4.43	13.03	0.27	0.76	1.04	1.68	0.006	0.025	0.043	17.29	3.724	31.78
	2014	4.41	13.91	0.33	0.77	1.09	1.74	0.021	0.028	0.043	17.91	3.247	27.06
	2015	4.39	13.52	0.23	0.69	1.03	1.95	0.008	0.037	0.025	18.77	3.077	24.89
<b>New Forest (deep)</b>	2012	4.63	18.35	0.24	2.50	2.07	1.00	0.003	0.018	0.052	27.00	6.551	5.09
	2013	4.50	17.42	0.21	2.31	1.90	0.80	0.005	0.019	0.025	26.08	6.924	3.19
	2014	4.78	16.71	0.25	2.28	1.86	0.79	0.005	0.024	0.013	20.97	6.368	3.50
	2015	4.75	16.14	0.19	2.14	1.78	0.83	0.003	0.027	0.008	21.93	6.143	3.12
<b>Skipwith Common (shallow)</b>	2012	3.98	5.34	2.12	0.76	0.65	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	0.006	0.028	1.132	7.29	3.135	78.41
	2014	4.08	4.70	2.62	0.61	0.61	5.70	0.009	0.025	1.659	8.26	2.598	83.86
	2015	4.03	4.71	2.20	0.56	0.51	5.59	0.005	0.032	1.382	4.36	3.284	82.69
<b>Skipwith Common (deep)</b>	2012	4.39	5.41	1.36	0.59	0.51	5.31	0.004	0.148	0.141	7.72	7.694	32.91
	2013	4.36	5.05	1.31	0.40	0.43	5.13	0.004	0.113	0.212	7.89	5.675	25.21
	2014	4.39	5.22	1.66	0.47	0.47	5.25	0.009	0.046	0.284	9.35	5.688	25.01
	2015	4.41	4.42	1.08	0.36	0.33	4.51	0.004	0.091	0.140	6.05	5.285	27.99
<b>Thorne Moor (dipwell)</b>	2012	3.71	6.68	0.93	3.62	1.33	1.37	0.016	0.026	0.449	10.83	1.677	132.79
	2013	3.73	6.63	0.57	3.47	1.16	1.29	0.060	0.027	0.873	11.70	0.776	109.88
	2014	3.71	6.89	0.57	3.52	1.28	1.46	0.053	0.035	0.783	12.47	0.805	143.36
	2015	3.59	7.03	0.59	3.27	1.22	1.15	0.013	0.043	0.356	12.44	0.280	136.58

Figure 6.5.1 Soil solution chemistry (2015): Manchester Mosses SAC

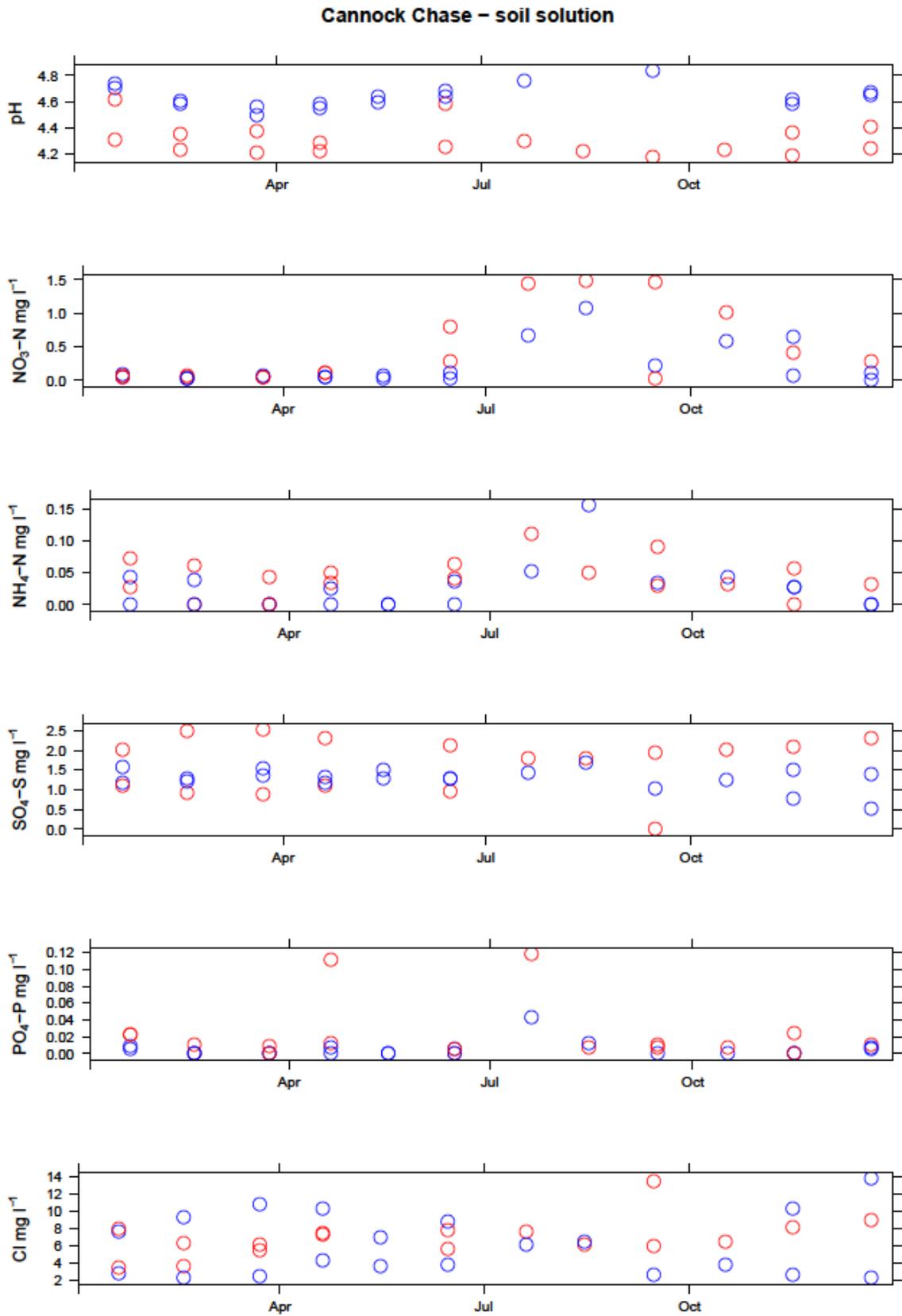


### Manchester Mosses – soil solution cont.





**Figure 6.5.2 Soil solution chemistry (2015): Cannock Chase SAC**



### Cannock Chase – soil solution cont.

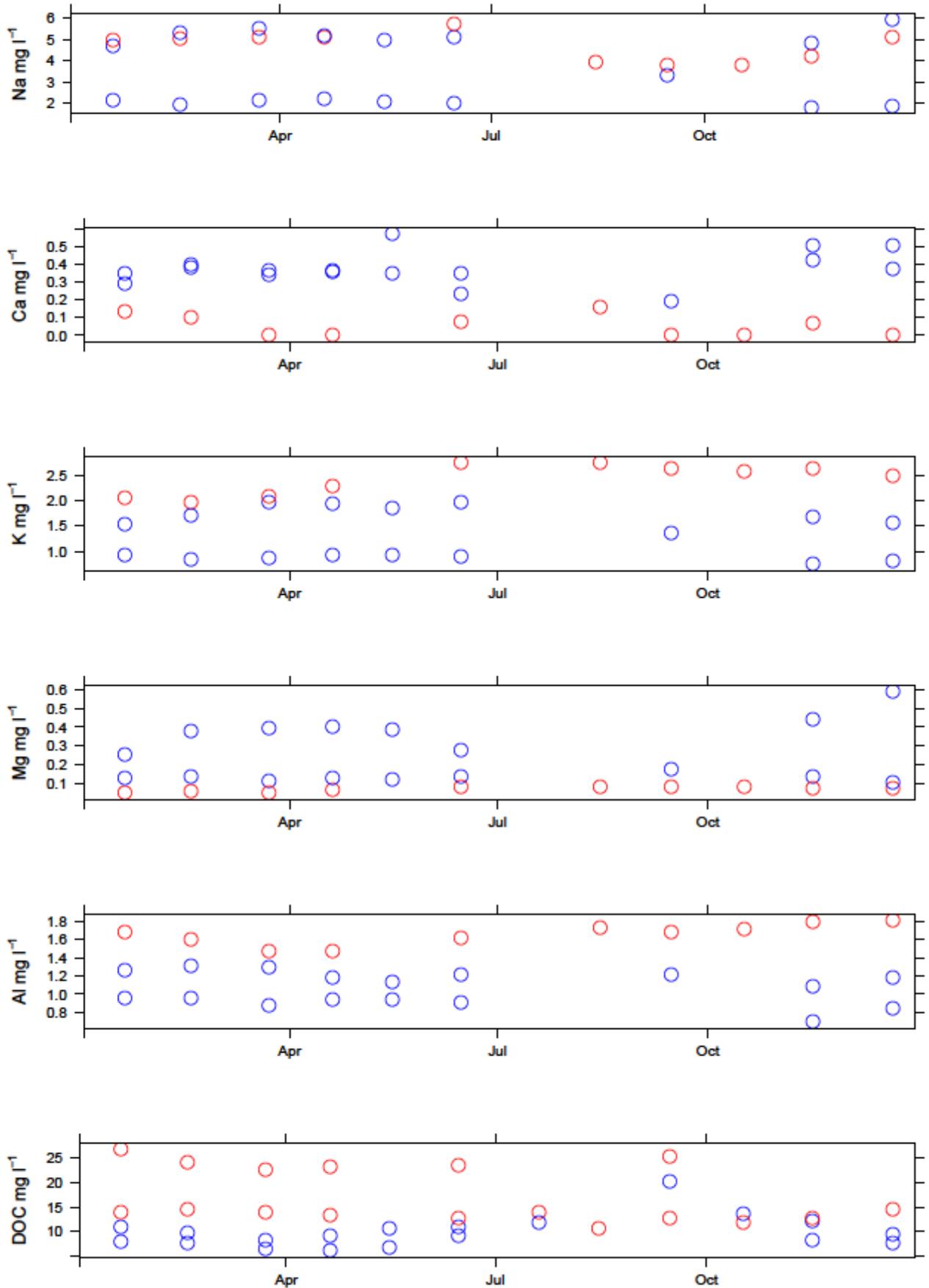
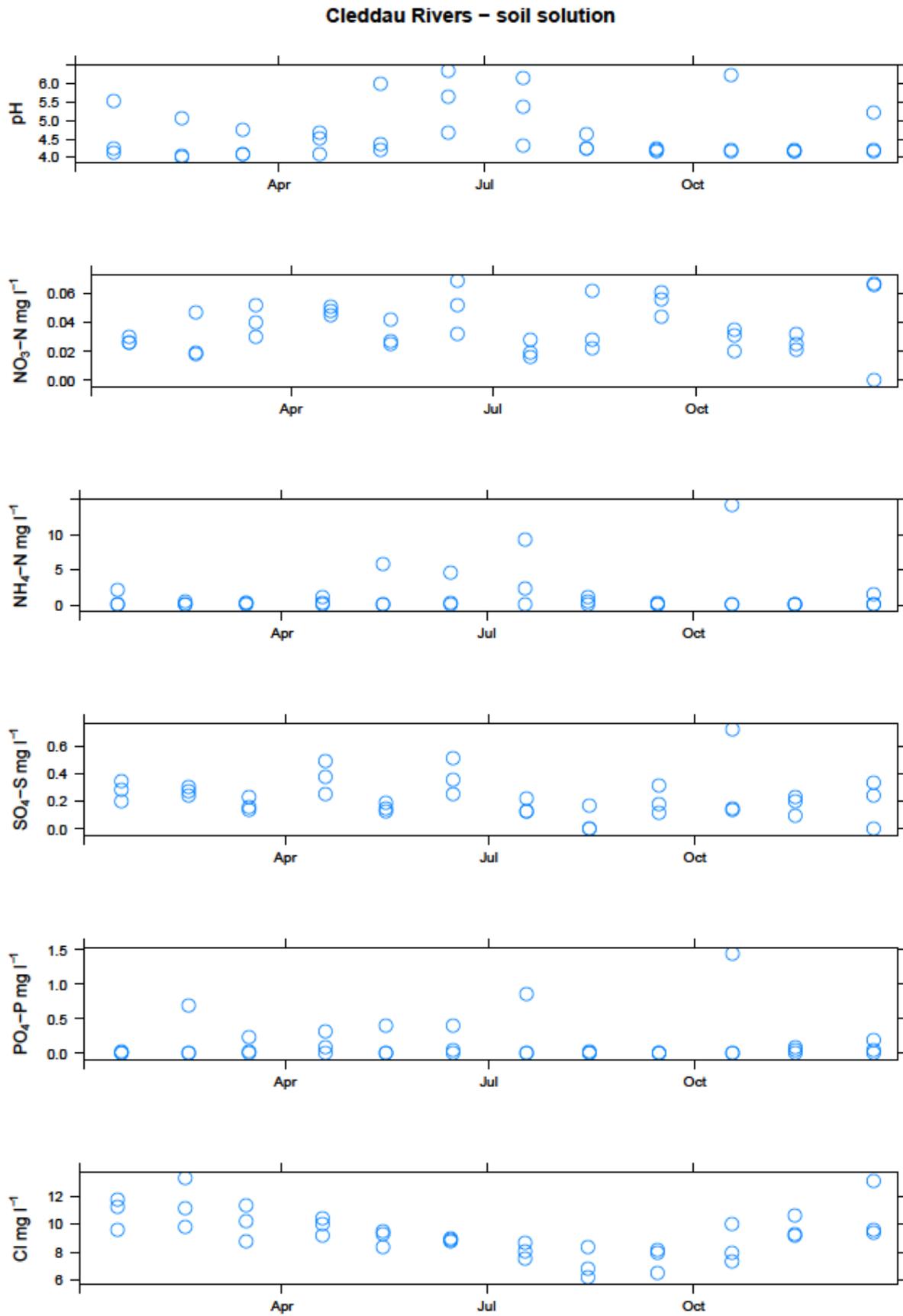


Figure 6.5.3 Soil solution chemistry (2015): Cleddau Rivers SAC



### Cleddau Rivers – soil solution – cont.

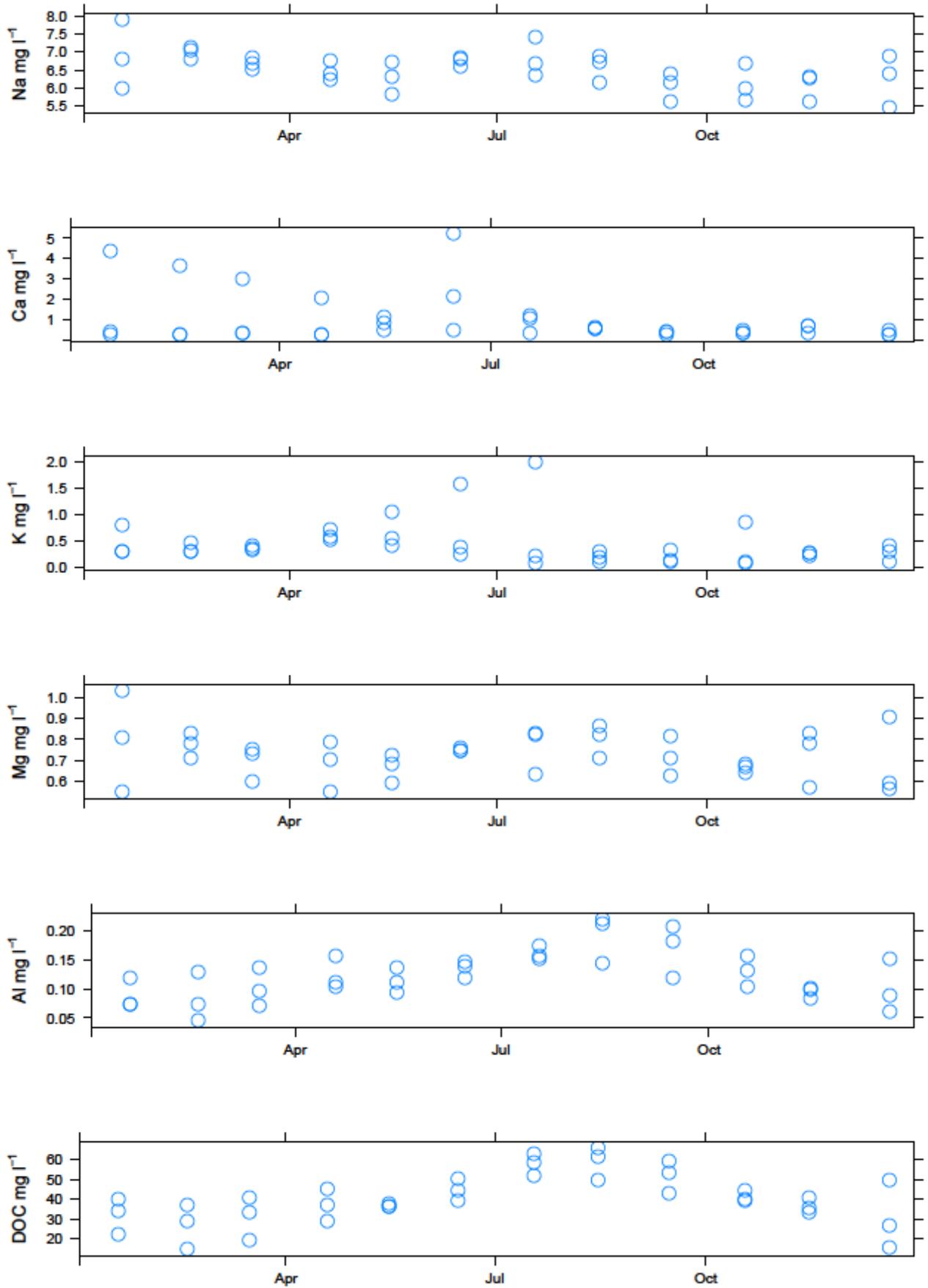
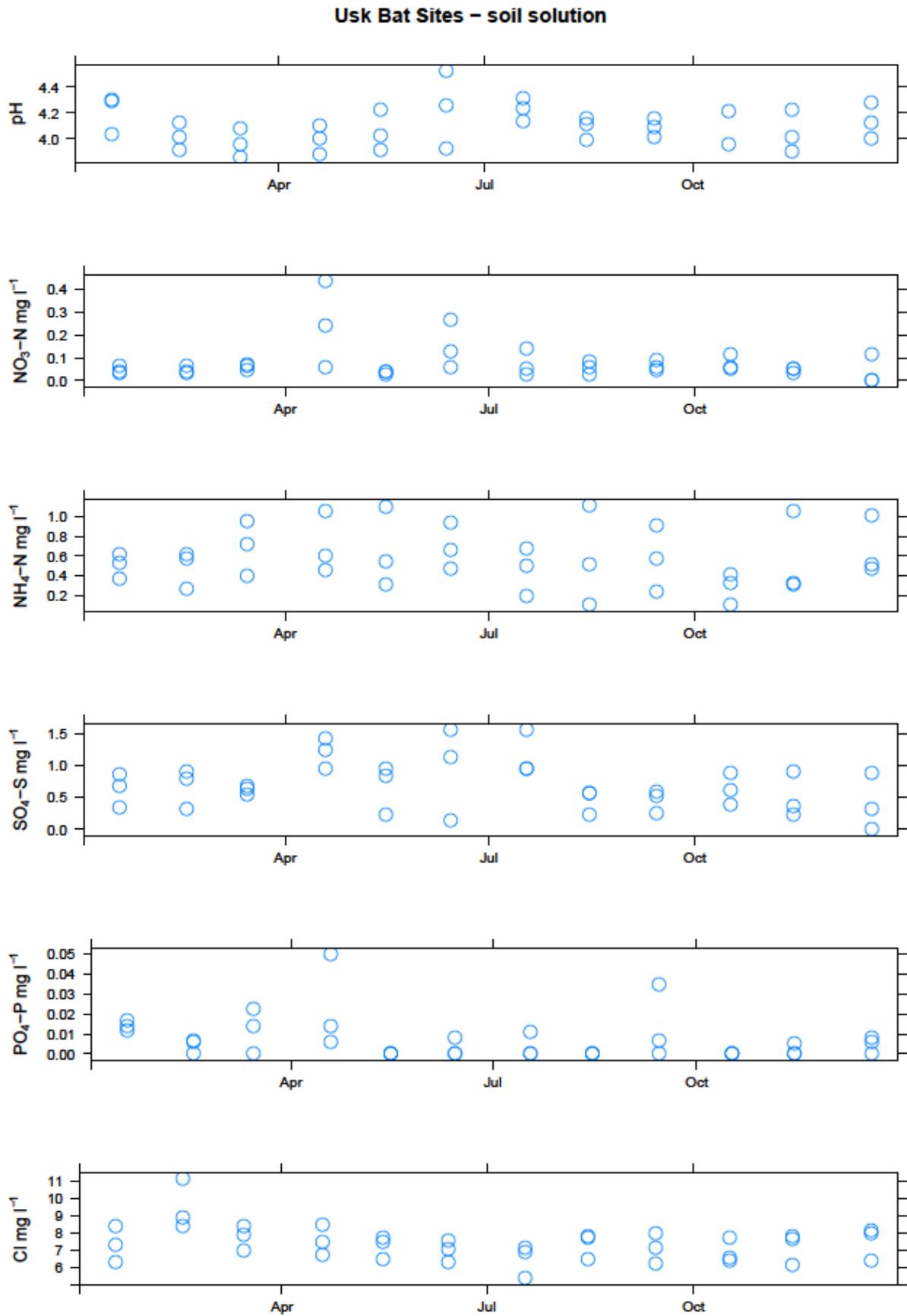


Figure 6.5.4 Soil solution chemistry (2015): Usk Bat Sites SAC



### Usk Bat Sites – soil solution – cont.

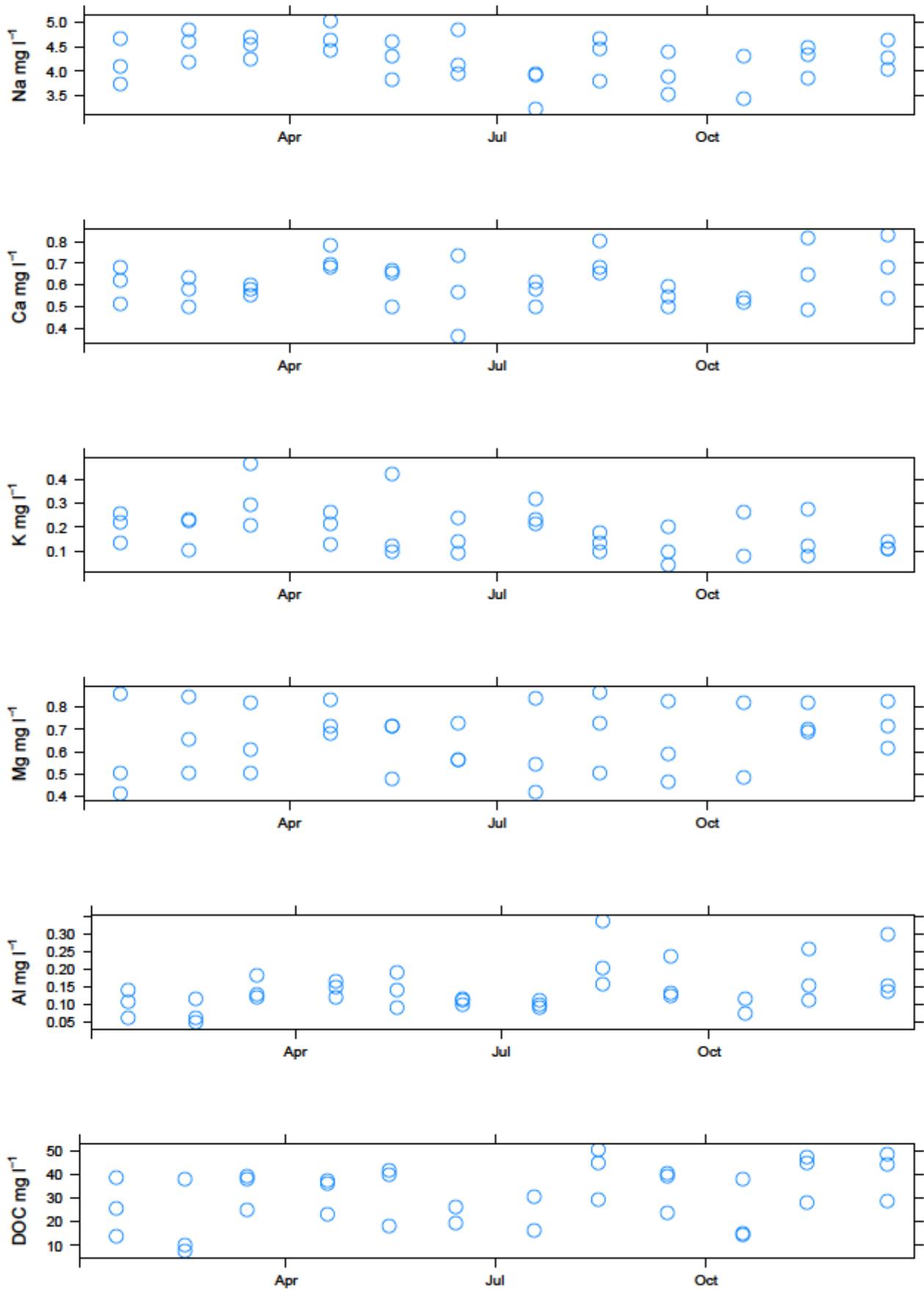
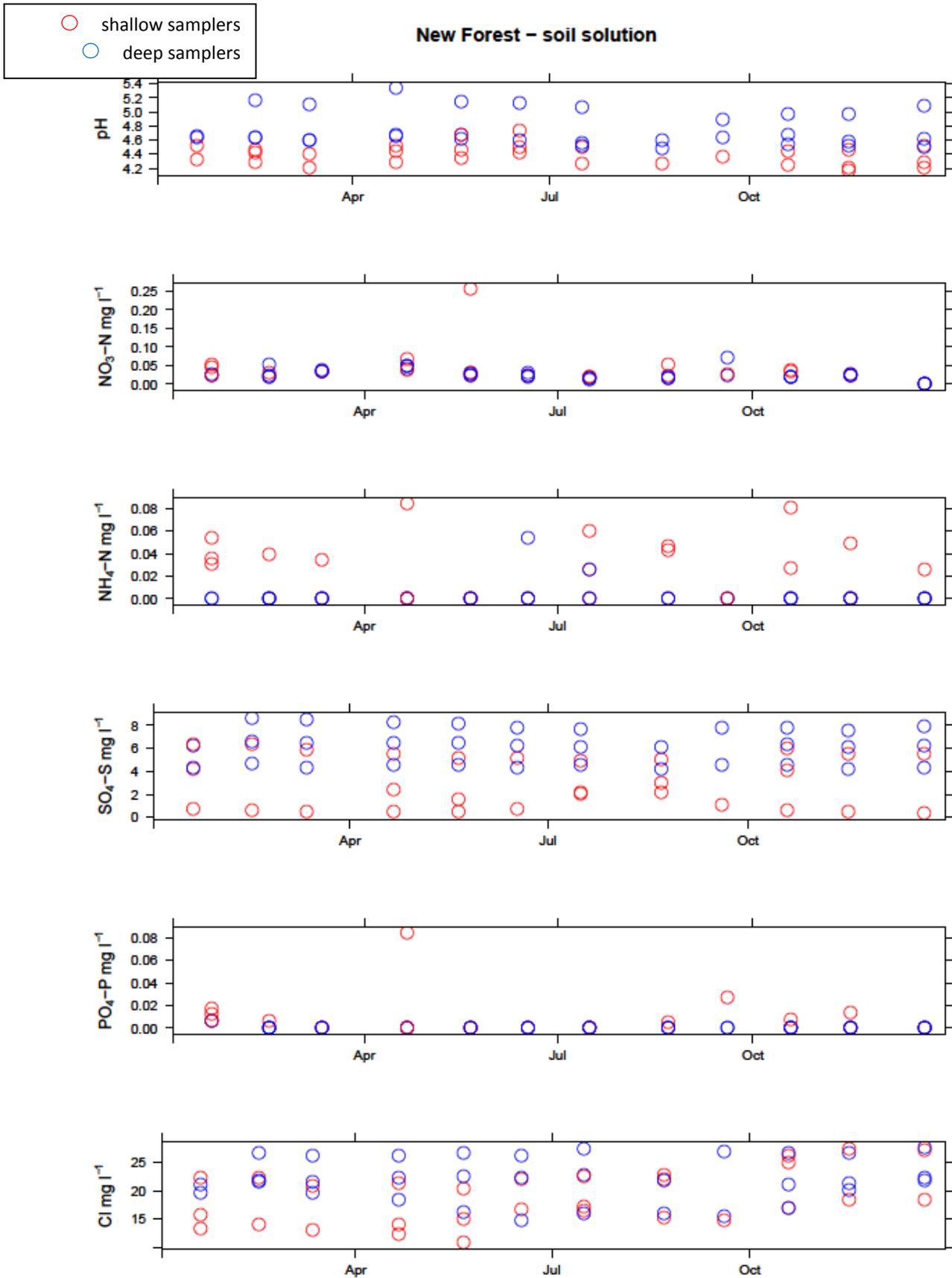


Figure 6.5.5 Soil solution chemistry (2015): New Forest SAC



### New Forest – soil solution – cont.

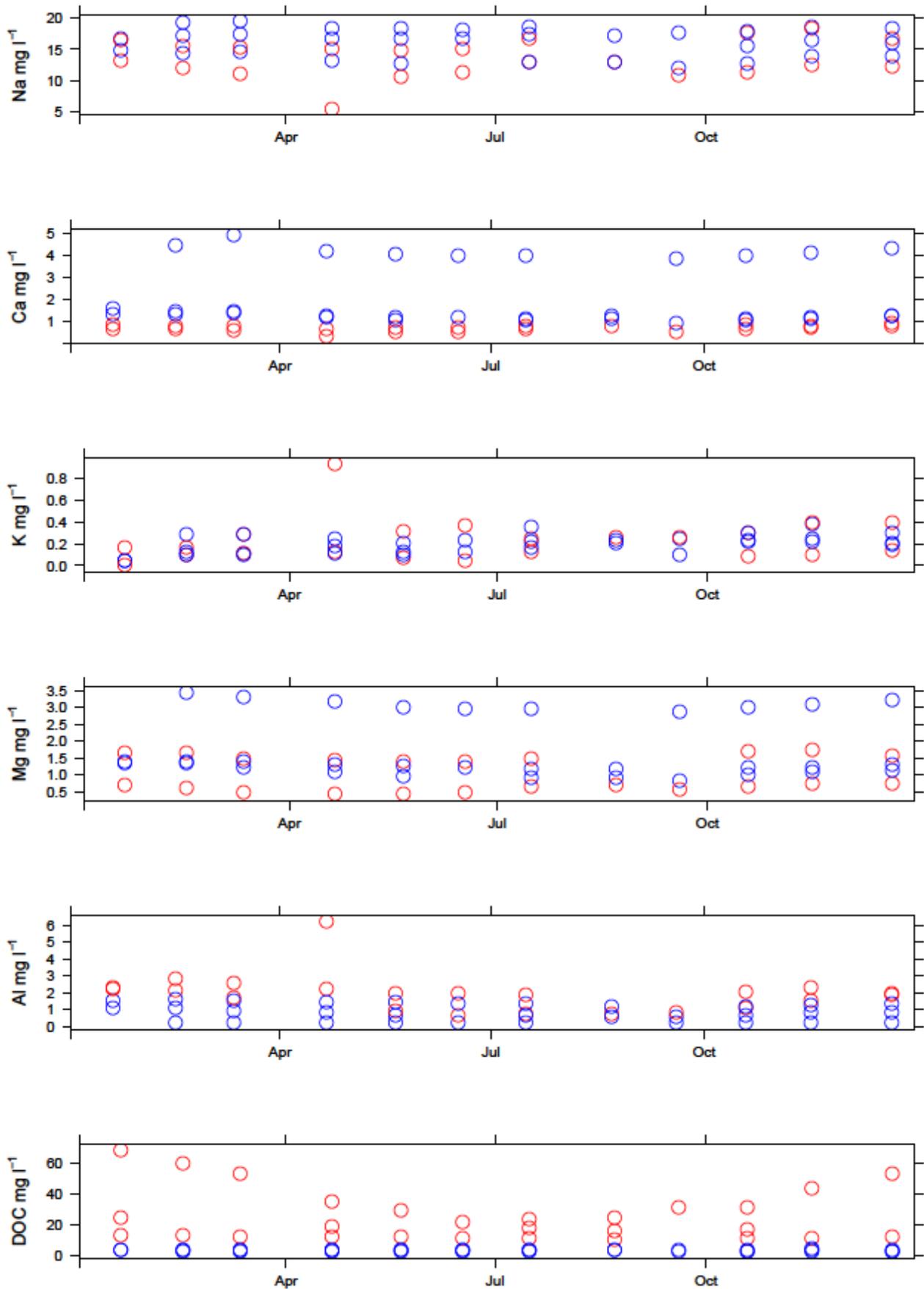
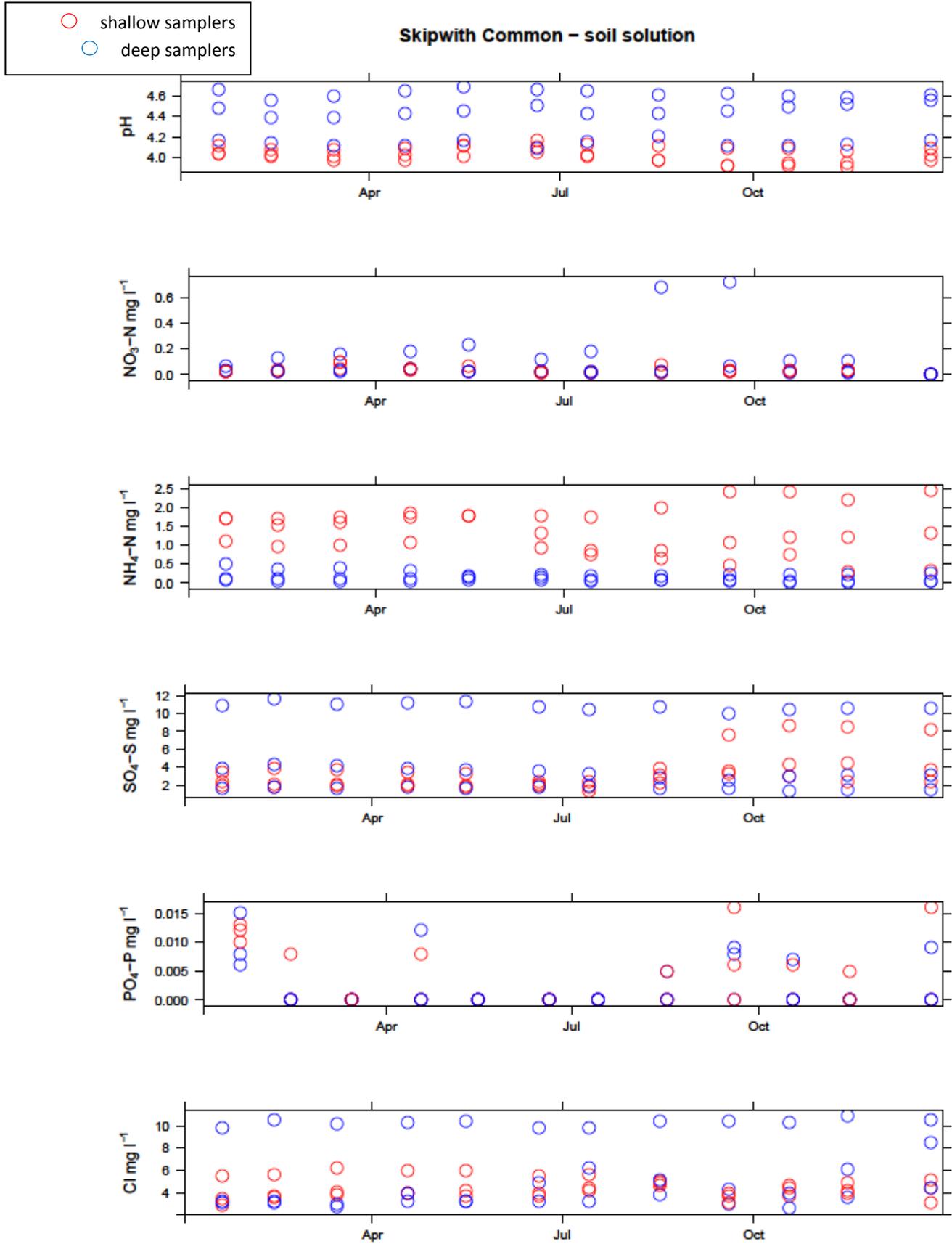


Figure 6.5.6 Soil solution chemistry (2015): Skipwith Common SAC



### Skipwith Common – soil solution – cont.

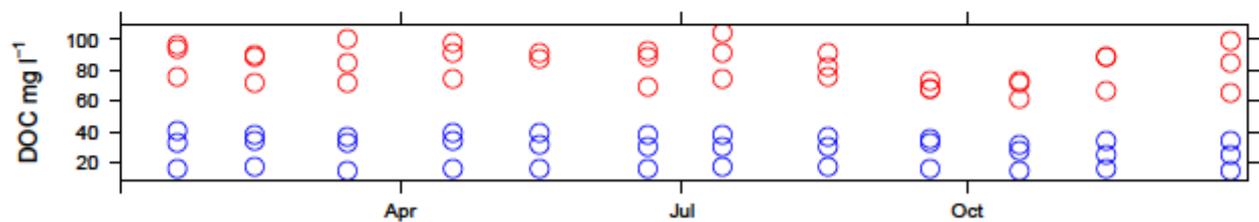
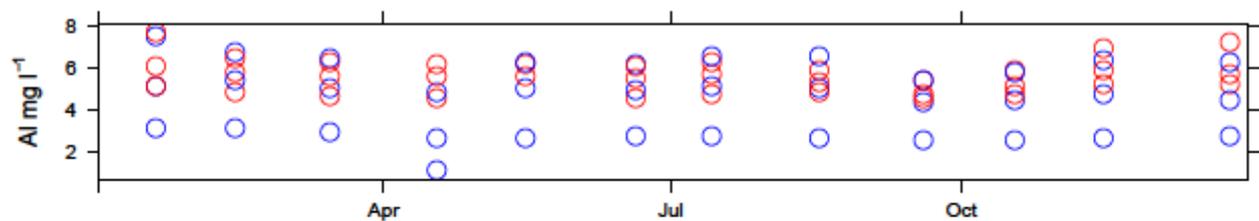
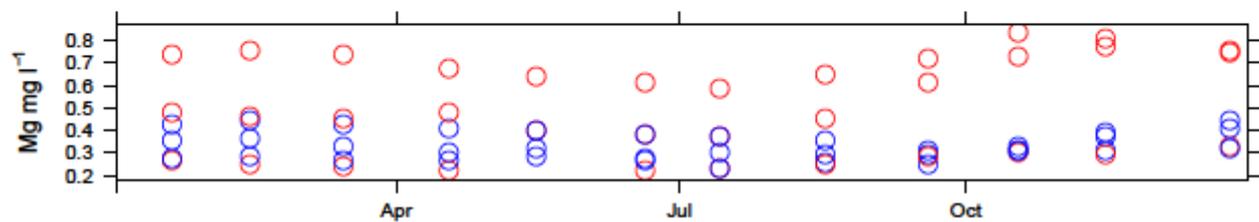
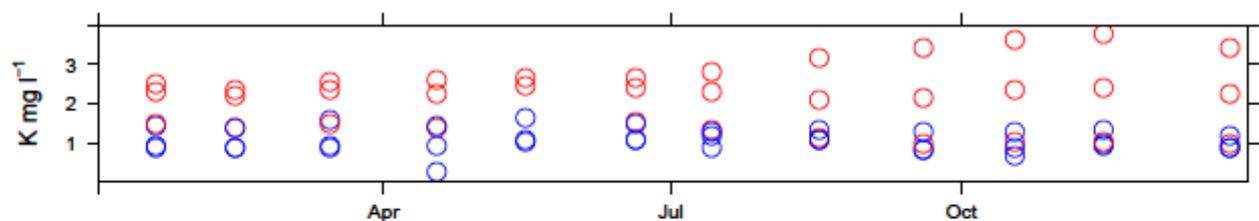
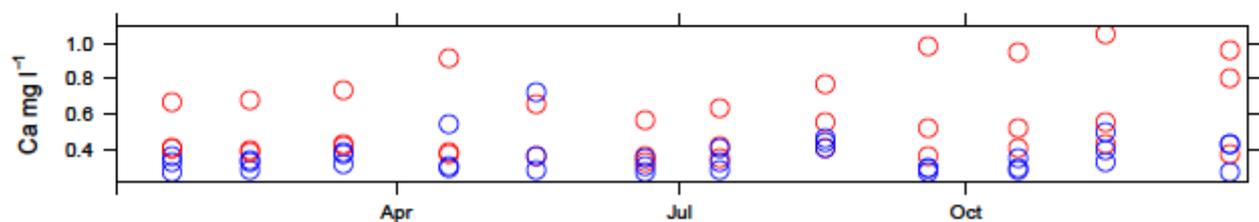
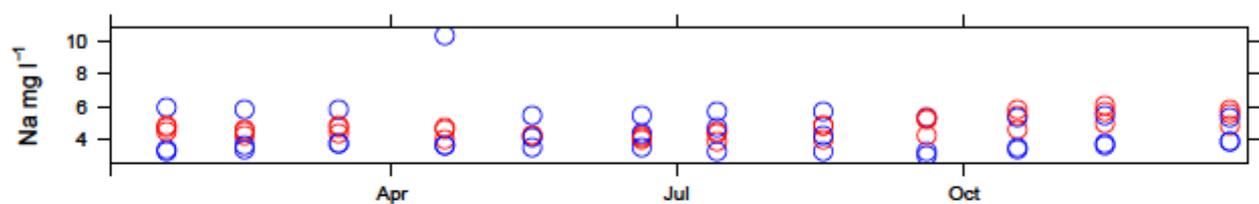
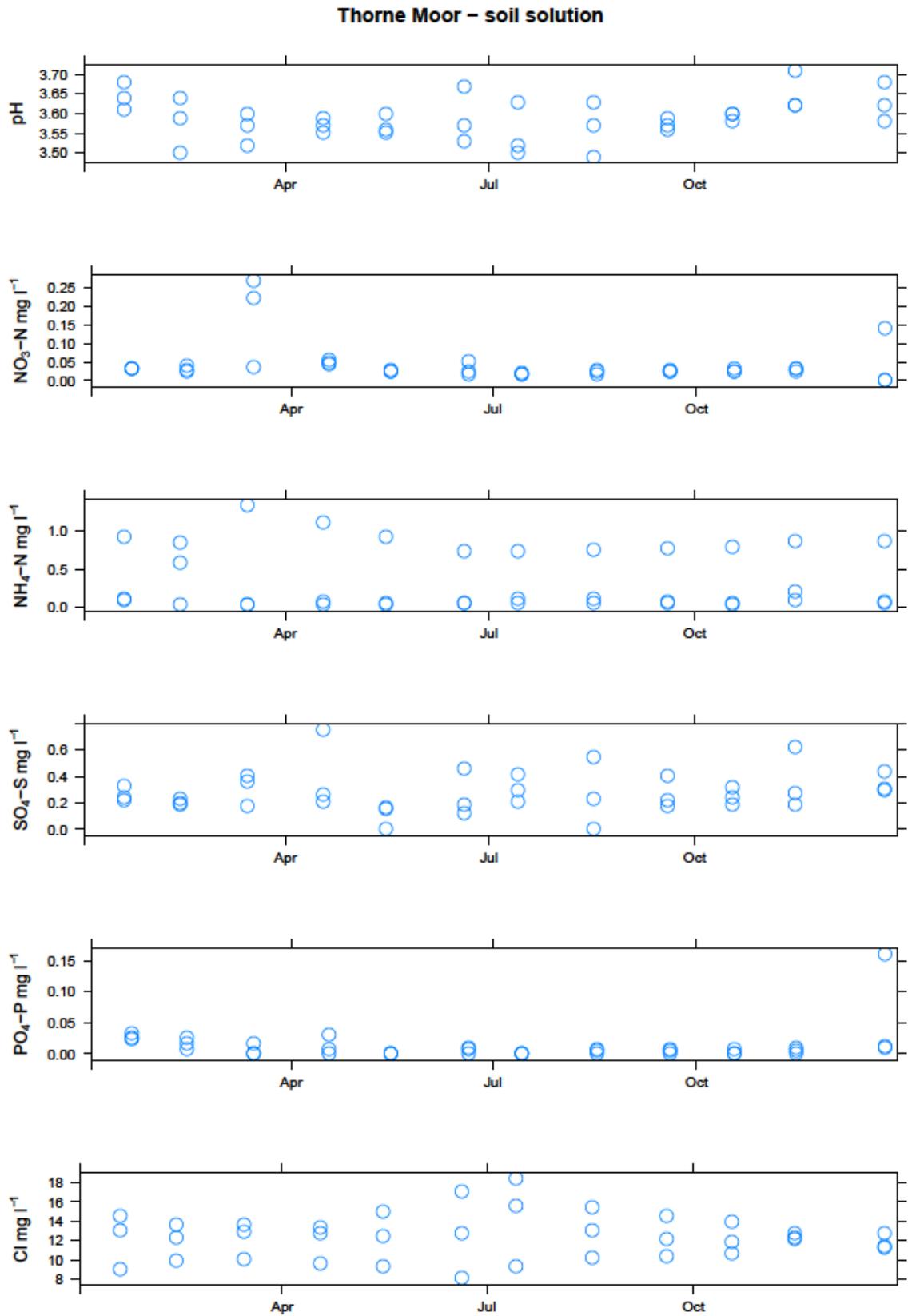
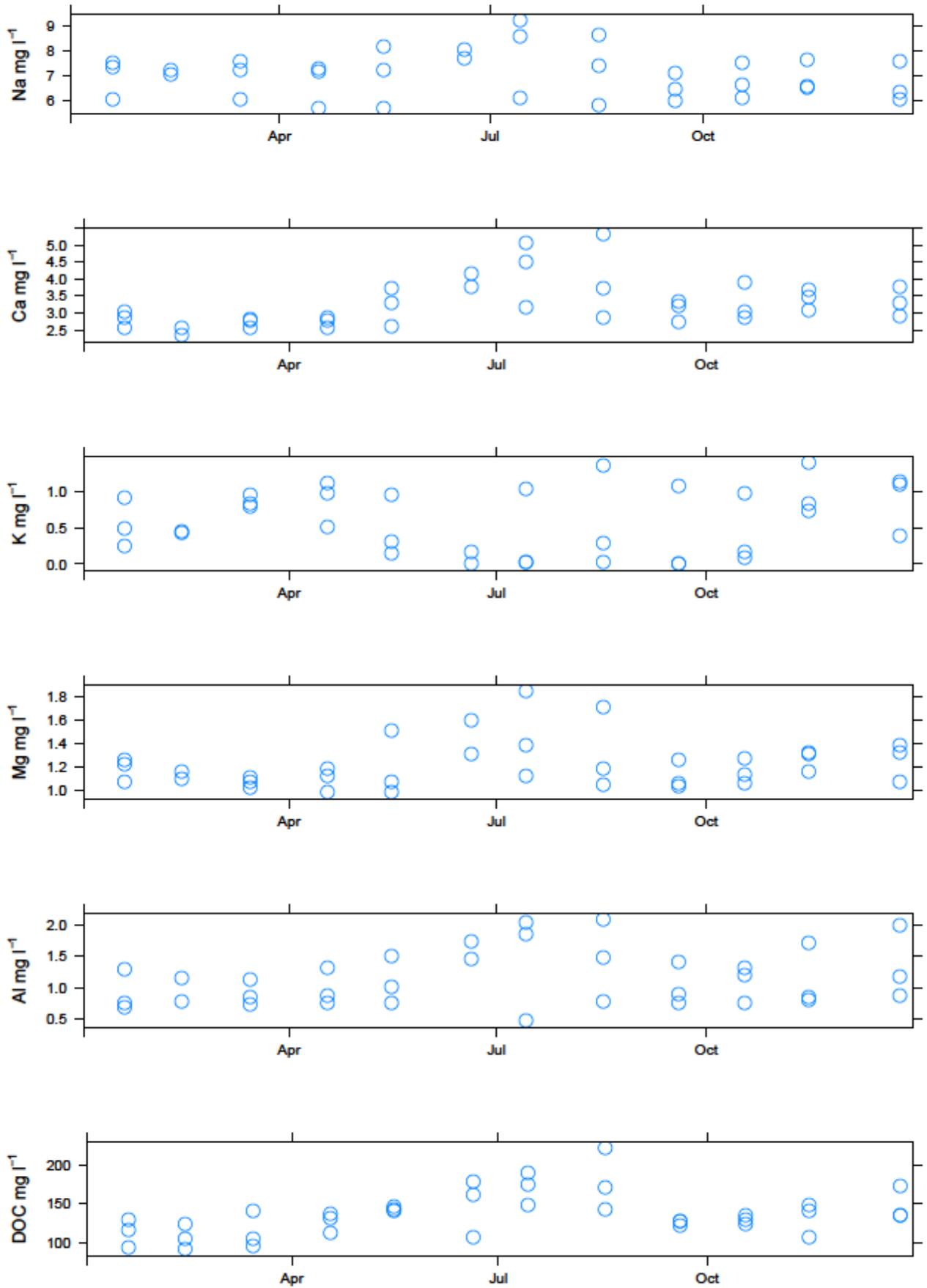


Figure 6.5.7 Soil solution chemistry (2015): Thorne Moor SAC



### Thorne Moor – soil solution – cont.



## 6.6 Comparison of annual summary data for 2012-15

### 6.6.1 Deposition measurements

Overall, the magnitude of deposition estimates of most chemical species for individual sites has remained relatively stable over the full 2012-15 monitoring period (see Figure 6.6.1), as did the ranking of sites with respect to their total acid deposition loads. There are indications of gradual cross-network reductions and convergence in total acid deposition, but four years is too short a period to determine the extent to which patterns are directional as opposed to a reflection of inter-annual variability. The clearest year-to-year reduction in total acid deposition was apparent for Thorne Moor, which experienced the largest acid load of all sites in 2012, but has since fallen below that for Cannock Chase, levels at which have remained more consistent over the four years. Cleddau Rivers received the lowest amounts of total acid deposition over the first three years, and while fluxes have again remained fairly constant here, total acid deposition at New Forest in 2015 became the lowest annual estimate for any site over the full monitoring period.

At most sites, nitrogen species dominated the acid load throughout the four years. Over the full monitoring period N species represented between 60 and 81% of total acid deposition, as opposed to 16 to 34% for sulphur species. Dry deposition of N tended to exceed wet deposition of N at most sites in most years, with a median ratio of 1.2. Deposition of oxidised N exceeded reduced N at most sites and in most years, with a median ratio of 1.3, however the ratio has fallen over the four years at all sites, and in 2015 reduced N exceeded oxidised N at all sites other than New Forest and Usk Bat sites.

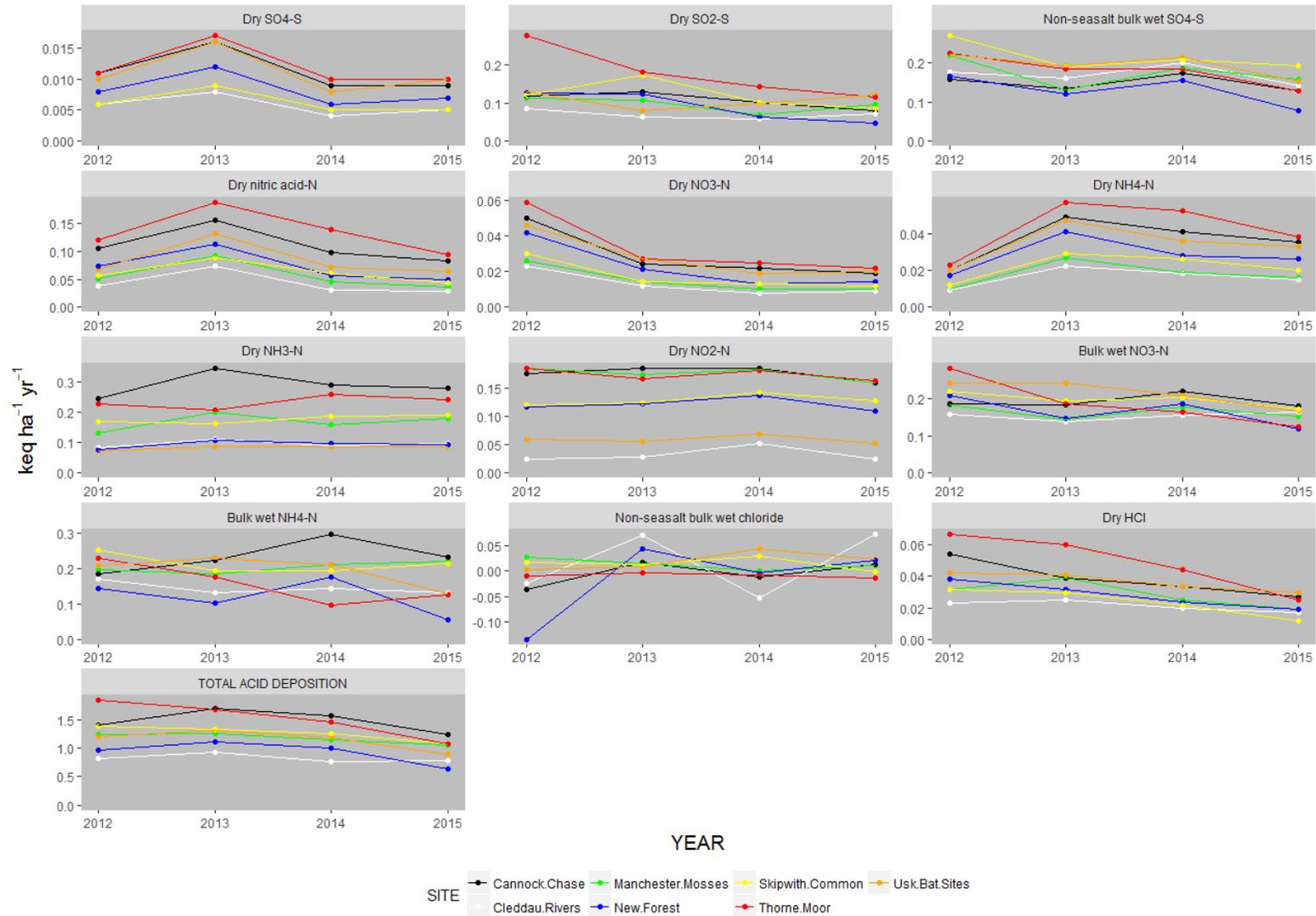
Of the N species, bulk wet  $\text{NO}_3$ , and dry  $\text{NO}_3$  and  $\text{HNO}_3$  showed progressive decline across the monitoring period, while the bulk wet deposition of  $\text{NH}_4$  showed the strongest year to year variation. Bulk wet non-seasalt  $\text{SO}_4$  deposition was highest at Skipwith Common in all four years, while dry  $\text{SO}_2$  (measured) and dry  $\text{SO}_4$  (modelled) deposition was highest at Thorne Moor. There was, however, a general tendency for deposition of both wet and dry sulphur species to decline over the four years at the majority of sites.

### 6.6.2 Soil chemistry measurements

Soil solution chemistry was also relatively stable over the four years of monitoring at most sites, although concentrations of sulphate declined markedly in both shallow and deep samplers at Skipwith Common, in the dip wells of Thorne Moor, and the deep samplers of Cannock Chase. These reductions appear to have been largely balanced by reductions in base cations and there was little evidence for concomitant increases in soil pH or reductions in aluminium concentration.

The pH of soil solution collected in the bog dipwells of Manchester Mosses, Cleddau Rivers, Usk Bat Sites and Thorne Moor, differed markedly between these sites. Thorne Moor soil solution was most acidic, with mean annual pH ranging from 3.59 to 3.73. The pH of Manchester Mosses and Usk Bat Sites soil water ranged mostly between pH 4.3 and 4.4. The pH of soil solution in the bog dipwells of Manchester Mosses, Usk Bat Sites and Thorne Moor was generally slightly lower in 2015 relative to earlier years. This is most likely due to higher seasalt inputs – as reflected by higher concentrations of sodium and chloride in the soil solution. Soil water chemistry of the Cleddau Rivers site has 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.

Figure 6.6.1 Trends in annual deposition estimates of all species used to derive the total acid deposition estimate



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. There was an indication of a gradual increase in soil pH in two of the three deep samplers at this site, but, if anything, pH in the third deep sampler declined slightly. Shallow soil solution pH at Cannock Chase and New Forest mostly ranged between pH 4.3 and 4.7 and showed no indication of trend. 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.

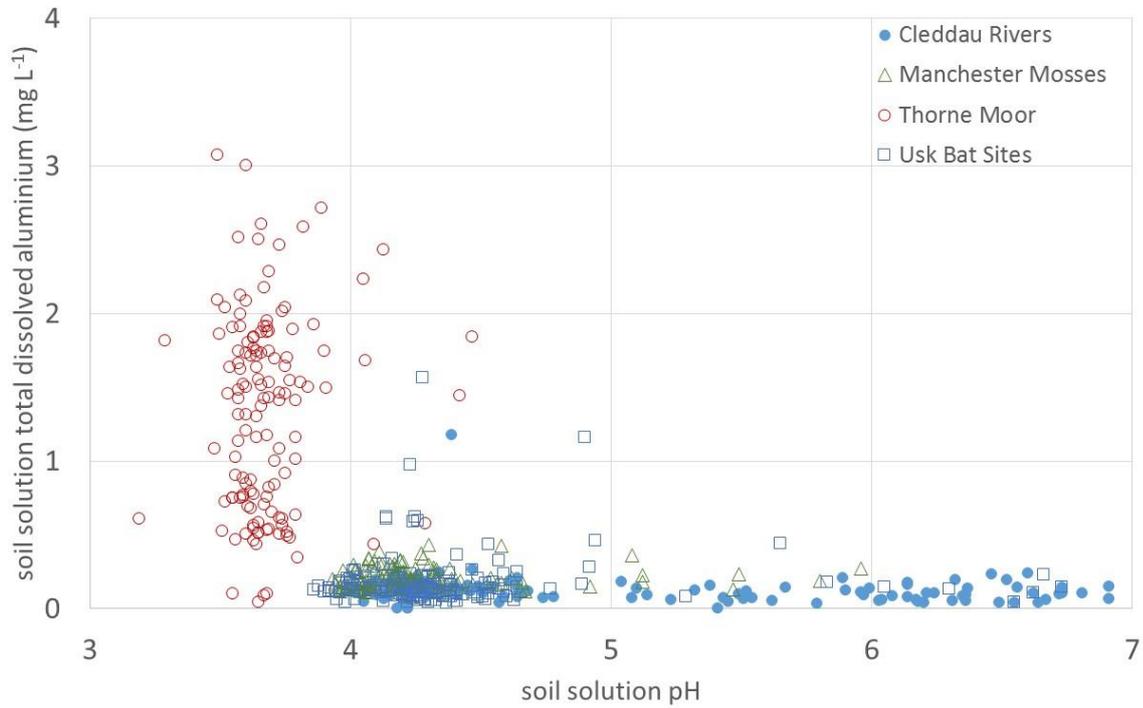
Figure 6.6.2a-b illustrates the relationship between total dissolved aluminium and soil water pH in the soil water of all samples collected over the four years of monitoring in bog and heathland sites respectively. This shows that aluminium levels in the bog waters (Figure 6.6.2a) were consistently low in samples with pH > 5 – mostly from the relatively lightly impacted Cleddau Rivers site, but maximum concentrations increased sharply as pH fell 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 many 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. With respect to the heathland sites, (Figure 6.6.2b), aluminium concentrations began to rise below a threshold of about pH 5.4 in the New Forest deep soil. 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.

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.

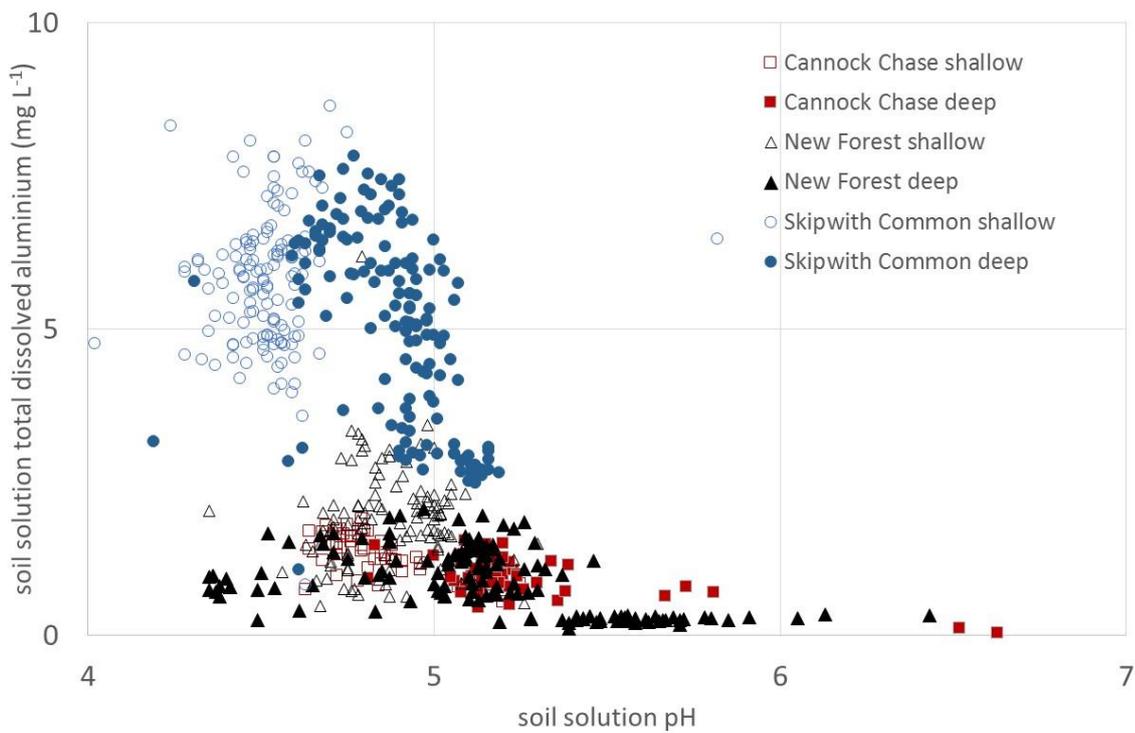
Nitrate concentrations were very stable from year to year in the bog soil solutions of all the bog sites. However, most N in solution in these soils is in the reduced form of  $\text{NH}_4$  which varied markedly between years. Ammonium concentrations also tended to be higher than  $\text{NO}_3$  in the heathland soils at both depths. In the dipwells at Manchester Mosses and Cleddau Rivers, and both the deep and shallow samplers at New Forest and Cannock Chase, mean  $\text{NO}_3$  concentrations were at their highest and mean  $\text{NH}_4$  concentrations at their lowest in 2015, thus hinting at increased rates of nitrification at these sites. Four 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.

**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)



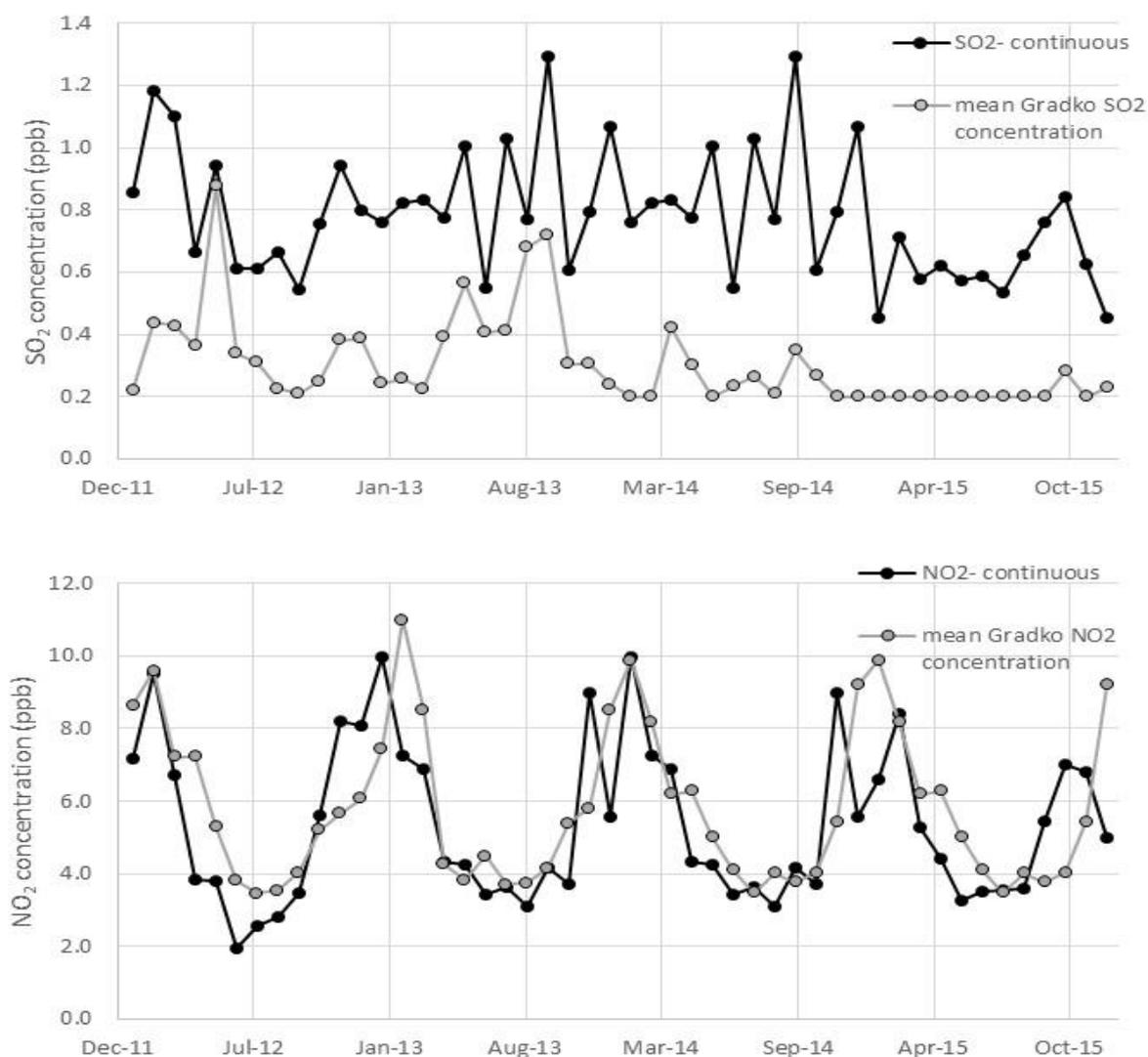
## **6.7 Considerations of uncertainty in deposition estimates with respect to sulphur dioxide concentration and diurnal variation in concentrations**

### *6.7.1 Comparison of diffusion tube and gas analyser SO<sub>2</sub> 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 three years, and the frequency of “below detection” samples in 2015 was the highest of all the years of monitoring . 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 NO<sub>2</sub> concentrations as these have invariably been recorded substantially above the limit of detection.

Over the monitoring period, additional SO<sub>2</sub> and NO<sub>2</sub> Gradko diffusion tubes were deployed alongside a gas analyser at a test site, Bottesford in the East Midlands. For the purpose of this study, hourly mean values were 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. The preceding deposition report based on the 2012 to 2014 data (Monteith et al., 2015) noted that mean monthly diffusion tube estimated concentrations of SO<sub>2</sub> at Bottesford were, on average, about half the monthly mean hourly concentrations measured by gas analyser. Figure 6.7.1 suggests poorer agreement between SO<sub>2</sub> diffusion tube data, which was consistently below the detection limit, and the gas analyser data over 2014 and 2015 relative to 2012 and 2013; after replacement of below detection values recorded by the SO<sub>2</sub> diffusion tubes with a standard value of 0.2 ppb, monthly mean hourly concentrations measured by gas analyser in the later two years were on average around 3 times the mean monthly diffusion tube estimated concentrations of SO<sub>2</sub> (Figure 6.7.1). In contrast, mean monthly diffusion tube concentrations of NO<sub>2</sub> 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 SO<sub>2</sub> and NO<sub>2</sub> at Bottesford measured using a gas analyser (calendar month means), and mean concentrations of triplicate SO<sub>2</sub> and NO<sub>2</sub> estimated using Gradko tubes deployed on an approximately monthly schedule.**



It also appears that mean SO<sub>2</sub> concentrations determined by diffusion tube for the monitoring period at the seven Habitats Monitoring Network sites are similarly consistently lower than SO<sub>2</sub> 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.

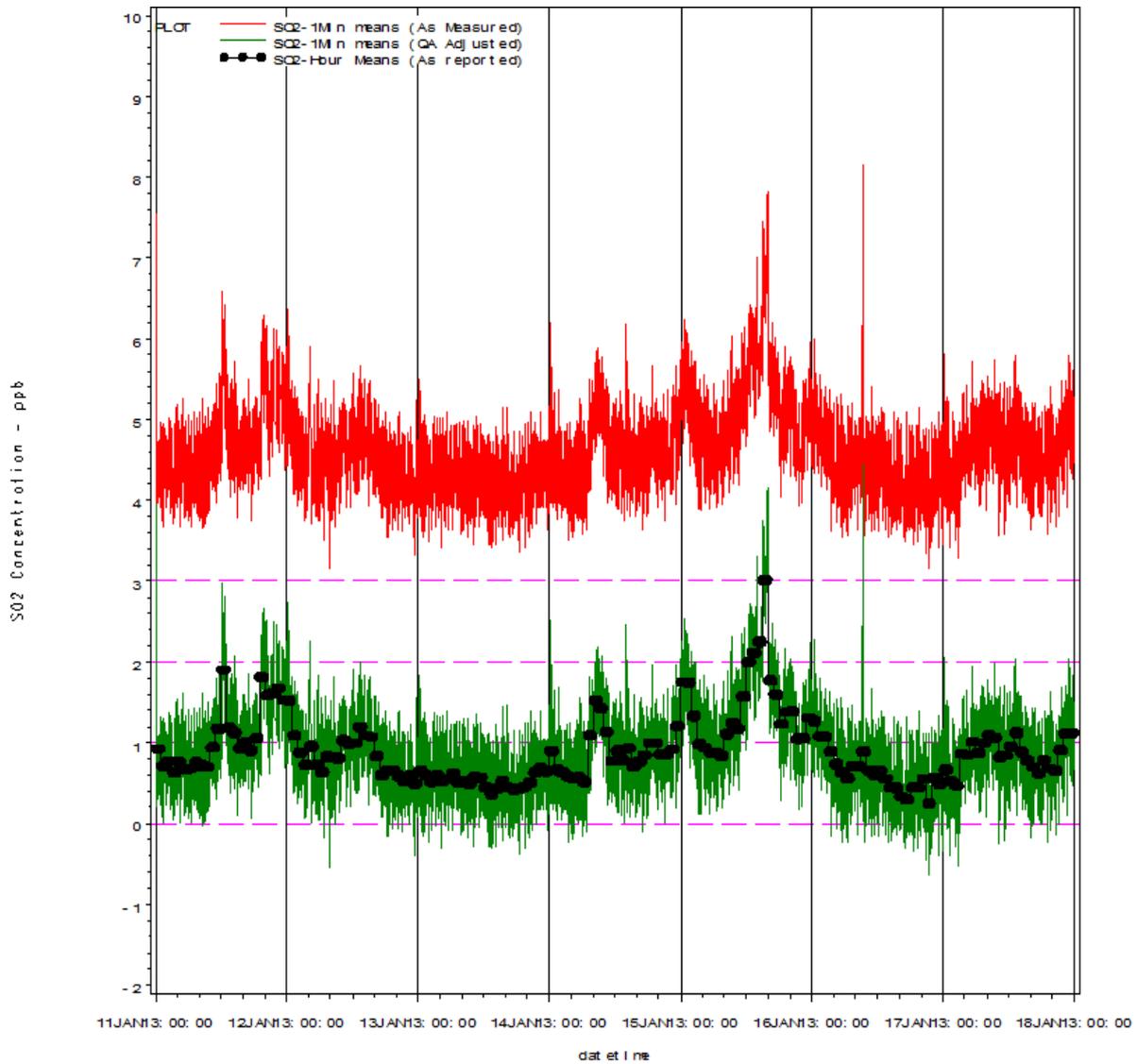
Most automatic monitoring of SO<sub>2</sub> in the UK is undertaken within UK Air Quality Strategy and EU Air Quality Directive guidelines. Analysers are typically configured to measure SO<sub>2</sub> concentration up to and above the limit values of 350 µg/m<sup>3</sup> averaged over one hour (not to 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).

Figure 6.7.2 also illustrates how the uncertainty reduces as the data are averaged over longer periods. If it is assumed that the sample of data presented by the green line has an uncertainty of, say, 100%, then the black dots (the hourly averages) would have a reduced uncertainty of 13%, and a diminution of the relative uncertainty can be seen in the distribution of the black dots. Moving to a monthly time step, the relative uncertainty of 100% at the minute time scale becomes a relative uncertainty of 0.5% on the monthly scale. Taking this back to Figure 6.7.1, these assumptions would mean the plot of the monthly means for SO<sub>2</sub> derived from the continuous measurements would have a relative uncertainty of 0.5%. It is therefore reasonable to conclude that the apparent underestimation shown by the Gradko tubes indicates a failure to identify a portion of the SO<sub>2</sub> concentration at the Bottesford site.

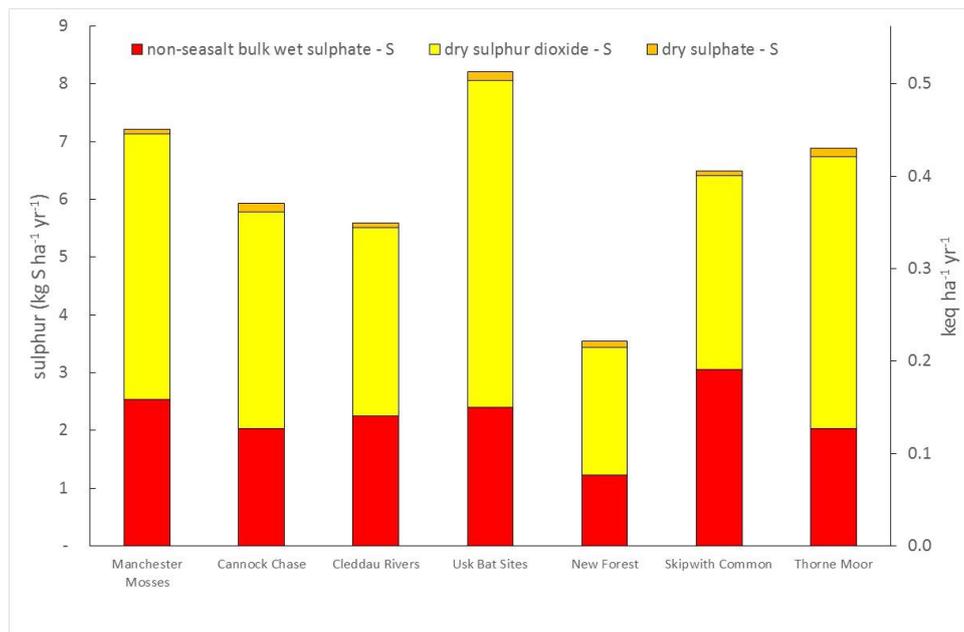
Figure 6.7.2. Sulphur dioxide (1 minute) data recorded by gas analyser at Bottesford between 11<sup>th</sup>-18<sup>th</sup> January 2013. The red line represents raw data, while the green line represents the corrected data following routine zero checks. Black dots represent hourly means.



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 annual SO<sub>2</sub> dry deposition estimates that have been adjusted by factors of between 2.0 – 3.0 (according to the approach described in Section 5.2.3) to allow for a potential 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 adjusted by a variable factor (see Section 5.2.3).



**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 adjusted by a variable factor (see Section 5.2.3).

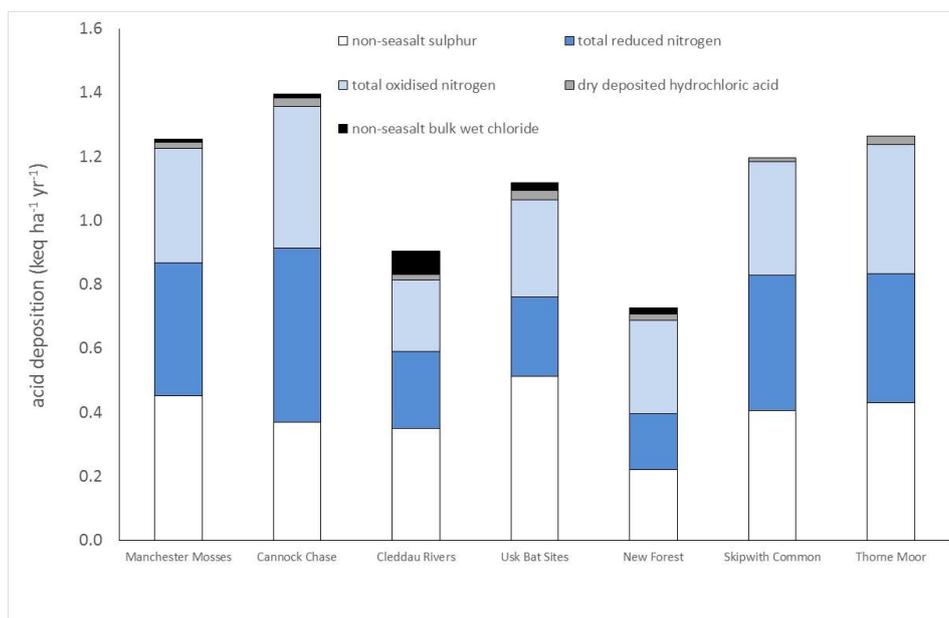


Table 6.7.1

Adjusted estimated annual wet and dry sulphur, nitrogen, chloride and total deposition as acidity. Original sulphur dioxide dry deposition estimate adjusted by a variable factor (see Section 5.2.3).

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
	2015	0.005	0.009	0.005	0.010	0.007	0.005	0.010
Dry SO <sub>2</sub> -S	2012	0.277	0.308	0.222	0.337	0.296	0.271	0.560
	2013	0.273	0.336	0.185	0.230	0.297	0.396	0.430
	2014	0.196	0.286	0.169	0.283	0.178	0.241	0.356
	2015	0.288	0.234	0.203	0.353	0.138	0.210	0.294
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	<b>0.213</b>	0.154	0.209	0.183
	2015	0.158	0.127	0.141	0.151	0.077	0.191	0.127
Dry nitric acid-N	2012	<b>0.052</b>	<b>0.105</b>	<b>0.037</b>	<b>0.069</b>	<b>0.073</b>	<b>0.057</b>	<b>0.121</b>
	2013	<b>0.093</b>	<b>0.156</b>	<b>0.073</b>	<b>0.132</b>	<b>0.114</b>	<b>0.089</b>	<b>0.189</b>
	2014	<b>0.046</b>	<b>0.099</b>	<b>0.031</b>	<b>0.072</b>	<b>0.058</b>	<b>0.061</b>	<b>0.139</b>
	2015	0.036	0.084	0.028	0.065	0.049	0.044	0.094
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
	2015	0.010	0.019	0.009	0.020	0.014	0.012	0.022
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
	2015	0.016	0.035	0.015	0.033	0.026	0.020	0.038
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
	2015	0.180	0.277	0.096	0.086	0.094	0.188	0.240
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
	2015	0.158	0.158	0.024	0.053	0.109	0.127	0.163
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	<b>0.210</b>	0.187	0.204	0.163
	2015	0.153	0.181	0.165	0.166	0.120	0.174	0.124

<b>Bulk wet NH<sub>4</sub>-N</b>	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	<b>0.211</b>	0.177	0.193	0.097
	2015	0.220	0.232	0.131	0.128	0.054	0.215	0.127
<b>Non-seasalt bulk wet chloride</b>	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	<b>0.043</b>	-0.003	0.028	-0.008
	2015	0.011	0.012	0.072	0.023	0.021	-0.002	-0.014
<b>Dry HCl</b>	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
	2015	0.019	0.027	0.017	0.030	0.019	0.012	0.025
<b>TOTAL ACID DEPOSITION</b>	2012	1.347	1.461	0.908	1.332	1.048	1.459	1.980
	2013	1.304	1.706	0.963	1.310	1.157	1.441	1.697
	2014	1.219	1.641	0.839	1.284	1.055	1.331	1.500
	2015	1.254	1.395	0.906	1.118	0.728	1.196	1.250

### 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, 8.6 % 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**

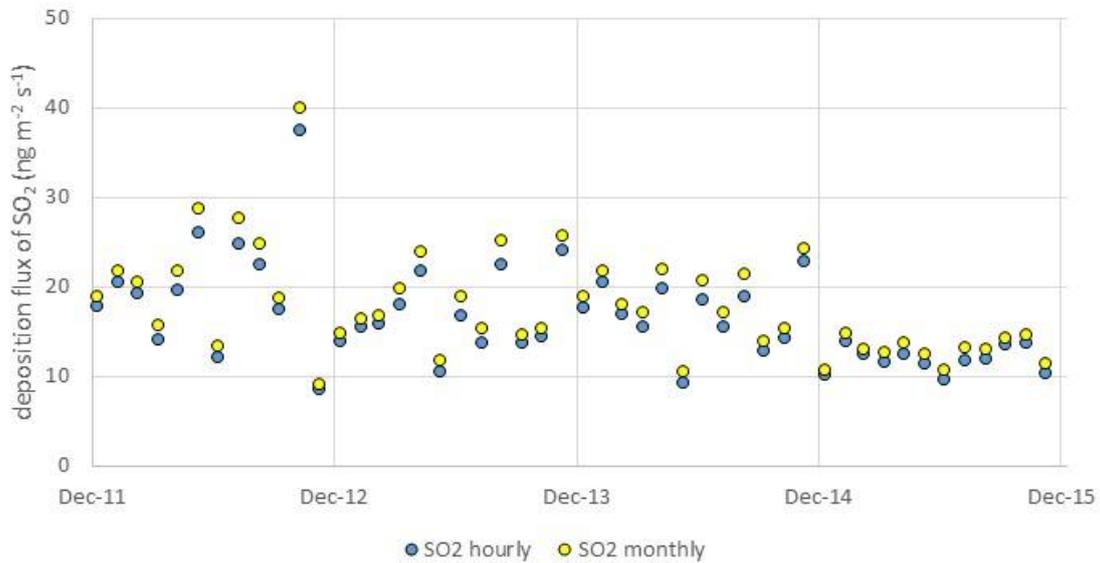


Figure 6.7.5 provides a comparable plot for NO<sub>2</sub> dry deposition. This shows less consistency in the direction of deviation, with monthly deposition estimates based on hourly gas concentrations higher than those based on monthly averages in some months and lower in others. On average, monthly estimates based on the monthly averaged concentration data were 6.5 % 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**

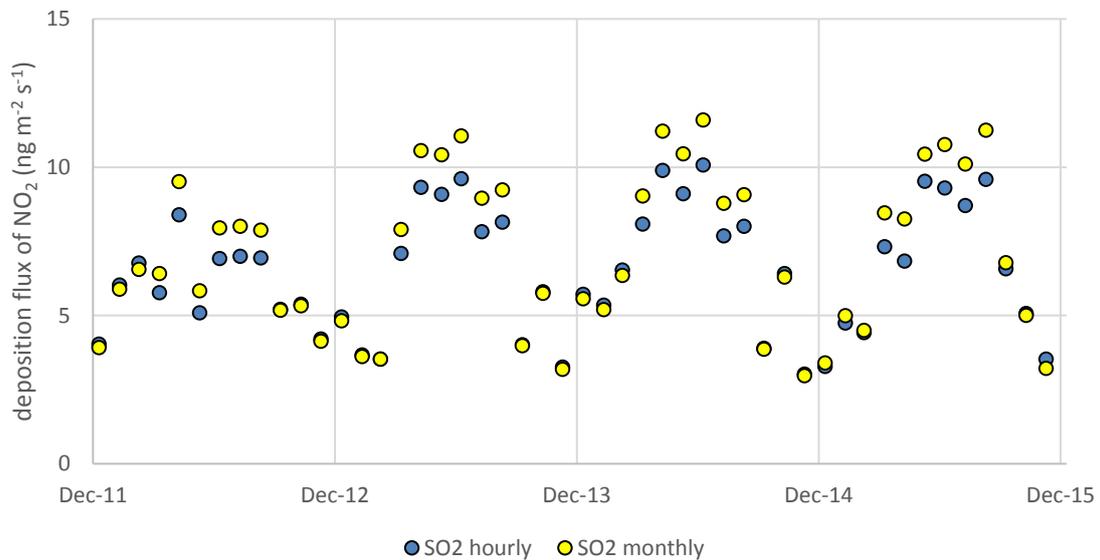


Table 6.7.2 summarises deposition flux estimates at an annual scale. This shows that annual SO<sub>2</sub> dry deposition estimates using averaged monthly data were between 8.1 and 8.9 % higher than those based on hourly data, while NO<sub>2</sub> dry deposition estimates using averaged monthly data were between 6.7 and 10.5 % 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.**

Method or comparator	species	kg ha <sup>-1</sup> yr <sup>-1</sup> (sulphur or nitrogen) or % difference between approaches			
		2012	2013	2014	2015
Hourly gas analyser	SO <sub>2</sub>	6.32	5.28	5.34	3.76
	NO <sub>2</sub>	1.89	2.01	2.21	2.08
Monthly gas analyser	SO <sub>2</sub>	6.86	5.74	5.81	4.06
	NO <sub>2</sub>	2.02	2.19	2.38	2.30
<b>% difference monthly/ hourly</b>	<b>SO<sub>2</sub></b>	<b>8.54</b>	<b>8.67</b>	<b>8.90</b>	<b>8.14</b>
	<b>NO<sub>2</sub></b>	<b>6.74</b>	<b>8.76</b>	<b>7.91</b>	<b>10.49</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.**

	ng m <sup>-2</sup> s <sup>-1</sup> (sulphur or nitrogen) or % difference between approaches			
	2012	2013	2014	2015
CBED SO <sub>2</sub> hourly	10.03	10.70	10.68	7.38
CBED SO <sub>2</sub> monthly	9.91	10.81	10.81	7.44
<b>% difference monthly/hourly</b>	<b>-1.26</b>	<b>1.01</b>	<b>1.20</b>	<b>0.89</b>
EMEP SO <sub>2</sub> hourly	23.83	25.24	25.53	18.06
EMEP SO <sub>2</sub> monthly	27.04	28.42	28.96	20.33
<b>% difference monthly/hourly</b>	<b>13.48</b>	<b>12.57</b>	<b>13.43</b>	<b>12.59</b>
CBED NO <sub>2</sub> hourly	6.34	6.83	7.75	7.78
CBED NO <sub>2</sub> monthly	7.24	8.24	9.02	8.68
<b>% difference monthly/hourly</b>	<b>14.32</b>	<b>20.54</b>	<b>16.43</b>	<b>11.67</b>
EMEP NO <sub>2</sub> hourly	1.71	1.76	2.04	3.58
EMEP NO <sub>2</sub> monthly	1.41	1.14	1.34	1.75
<b>% difference monthly/hourly</b>	<b>-17.39</b>	<b>-35.16</b>	<b>-34.16</b>	<b>-51.13</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 11.7 and 20.5 % higher than those based on hourly concentration whereas EMEP estimates based on monthly concentration data were between 17.4 and 51.1 %

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 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<sub>c</sub>) (see Section 5.2.1) determined by EMEP takes into account the influence of NH<sub>3</sub> in changing the pH of the surface film and its consequent effect on the rate of SO<sub>2</sub> uptake by the film, resulting in enhanced rates of deposition relative to CBED;
- In the EMEP routine, dry deposition of NO<sub>2</sub> falls to zero when ambient concentrations fall below 4 ppb.

In summary, relatively small differences in dry deposition estimates of both SO<sub>2</sub> and NO<sub>2</sub> 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 SO<sub>2</sub> 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 NO<sub>2</sub> deposition (based on the average of CBED and EMEP estimates) were of a similar level, reflecting a partial cancelling out of larger opposing differences between the monthly and hourly concentration based NO<sub>2</sub> 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 was in operation throughout the years 2012-2015 inclusive. Regular monthly measurements, covering meteorology, sulphur and nitrogen gaseous concentrations, bulk wet deposition chemistry and soil solution chemistry were made at all sites over this period. All samples were returned to the Environmental Change Network Coordination Unit (ECN CCU) at CEH offices in the Lancaster Environment Centre. Most samples were analysed by the CEH chemistry laboratories, while Gradko tubes, for the measurement of SO<sub>2</sub> and oxides of nitrogen, were processed by the UK Gradko laboratory. With the exception of the meteorological data, managed by Uniper, all data were compiled in a relational database at the ECN CCU. Raw data have been presented in a series of annual reports – this report covering the raw data from samples collected during 2015.

Initial problems concerning the over-estimation of precipitation and supply of power were largely overcome although 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, were 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 was 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. It has recently been identified that the Delta samplers operated by AGANET may have over-estimated HNO<sub>3</sub> concentrations and corrections have therefore been applied to pre-2015 summary data to allow for this.

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 substantially lower than those measured by gas analyser. Notably, a further year of data indicates that the difference between the measurements increased to a factor of 3 for 2014 and 2015 compared to a factor of 2 in 2012 and 2013. The increasing difference appears to be driven by the majority of SO<sub>2</sub> diffusion tube measurements being below the limit of detection from around the middle of 2014 to the end of the monitoring period. 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 there is likely to be a systematic bias to reporting of lower SO<sub>2</sub> concentrations by the diffusion tubes at this site. To allow for a possible underestimation of SO<sub>2</sub> concentrations by the diffusion tubes across the habitats monitoring network, 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 full four 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 this relatively short period of measurement.

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