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Chemical fluxes in time through forest ecosystems in the UK – Soil response to pollution recovery

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ABSTRACT

Long term trend analysis of bulk precipitation, throughfall and soil solution elemental fluxes from 12 years monitoring at 10 ICP Level II forest sites in the UK reveal coherent national chemical trends indicating recovery from sulphur deposition and acidification. Soil solution pH increased and sulphate and aluminium decreased at most sites. Trends in nitrogen were variable and dependant on its form. Dissolved organic nitrogen increased in bulk precipitation, throughfall and soil solution at most sites. Nitrate in soil solution declined at sites receiving high nitrogen deposition. Increase in soil dissolved organic carbon was detected – a response to pollution recovery, changes in soil temperature and/or increased microbial activity. An increase of sodium and chloride was evident – a possible result of more frequent storm events at exposed sites. The intensive and integrated nature of monitoring enables the relationships between climate/pollutant exposure and chemical/biological response in forestry to be explored.

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1. Introduction

During the last two decades, much attention has been devoted to the effects of acid rain. The main cause of acidification was the emission of sulphur and nitrogen compounds (SO_2, NO_x and NH_3) into the atmosphere. Detrimental changes to soil and water ecosystems due to acid deposition and acidification have led to the development of national and international policies aimed at reducing emissions of acidifying pollutants. For example, in Europe reductions were agreed as part of the Gothenburg Protocol in 1999, which targeted emissions reductions of sulphur dioxide, nitrogen oxides and ammonia of 80%, 50% and 12%, respectively, by 2010 when compared to the 1990 baseline (Jenkins and Cullen, 2001). Increasingly, policies have adopted an effects-based approach to proposing solutions for environmental problems and implementing emissions reductions in a targeted and cost-effective way. As a part of this process there is a need to provide policy makers with information highlighting the consequences of changing emissions on the environment and its constituent ecosystems.

Many environmental pollutants (particularly S and N compounds) can affect the functioning of forest ecosystems (Luttermann and Freedman, 2000). The availability of N compounds controls many biogeochemical processes and has a strong influence on net primary production in terrestrial ecosystems (Pussinen et al., 2002; Hyvonen et al., 2007). Deposition of N and S can also cause soil acidification, leaching of base cations and aluminium from the soil (Stoddard et al., 1999) and increased movement of nitrogen compounds, base cation and aluminium into surface waters (Beier et al., 2001). It has been suggested that more forest ecosystems will reach a state of nitrogen saturation and nitrogen leaching from soils may increase (Eichhorn et al., 2001; Emmett, 2007). Considerable changes occur in elemental concentrations as bulk precipitation passes through tree canopies due to canopy capture of aerosol-gaseous forms of elements, canopy

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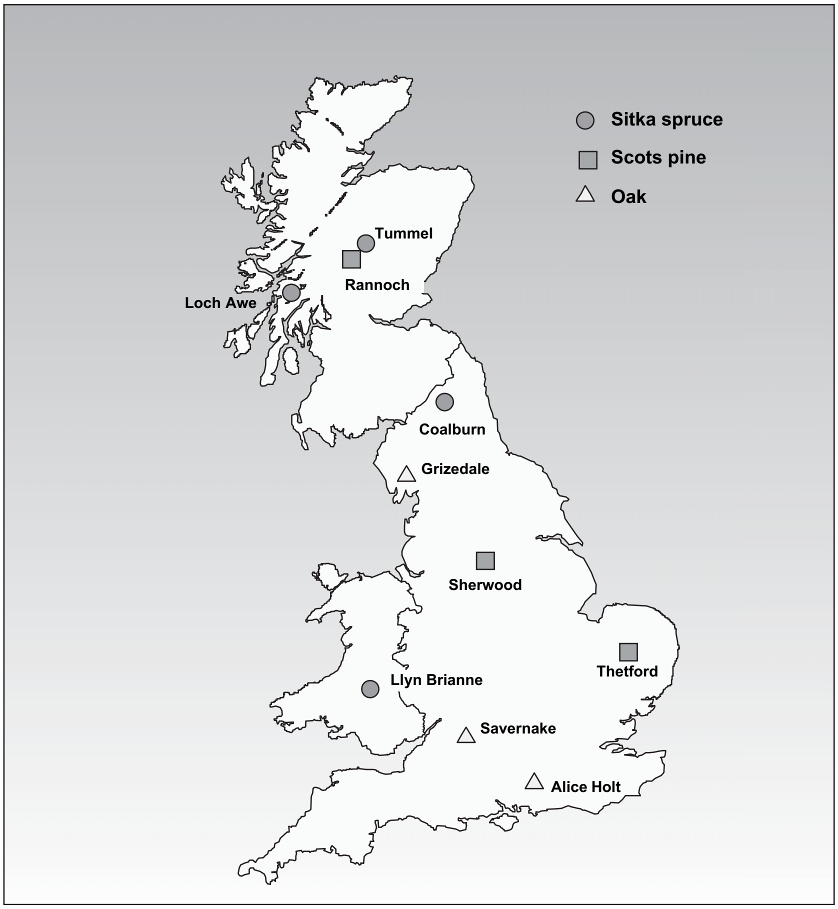

Fig. 1. Location and stand types of the ten UK Level II forest condition monitoring plots.

absorption of elements from the atmosphere such as ammonia and nitrate and canopy leaching and exchanging of various elements. Until now, studies on the concentrations and deposition of pollutants from the atmosphere and their possible impact on the forest ecosystem in the UK have relied mainly from data on the chemical composition of bulk precipitation and through the Critical Loads approach (Hall et al., 2004; Fowler et al., 2005, 2007). Nevertheless, within the Critical Loads approach, there are a number of uncertainties, which need validation for reliable assessment of the impacts of acid deposition on the forest ecosystems to be predicted on a national scale.

The European intensive forest monitoring (ICP Level II plots) sites were established in 1995. The monitoring was specifically designed to investigate the effects of acid deposition on forest ecosystems to evaluate the cause/effect relationships. The monitoring includes both chemical inputs and outputs of the forest ecosystems, and forest growth and health, and can thus evaluate the effectiveness of emission reduction policies. Recent evaluation of the European forest monitoring programme stressed the importance and need to stakeholders and policy makers of effective communication, analysis and evaluation of policy-relevant indicators (Moffat et al., 2008). Elemental and water flux budgets have already been calculated at Intensive Monitoring plots by several countries (Boyle et al., 2000; Farrell et al., 2001) and European wide assessments have been recently carried out by de Vries et al., 2003, de Vries et al., 2007 and van der Salm et al., 2007. There are several earlier studies, focusing on the behaviour of N in forest ecosystems (Dise et al., 1998a,b; Gundersen et al., 1998a,b; ; MacDonald et al., 2002), base cations (Armbruster et al., 2002) and Al (Dise et al., 2001). Temporal trends in throughfall and soil water chemistry have been evaluated for some Norwegian monitoring plots (Moffat et al., 2002), but assessment of the elemental fluxes and their temporal trends in the UK's Level II plots has not yet been attempted. The temporal record of chemistry in bulk precipitation, throughfall and soil solution at 10 Level II sites in the UK, using consistent sampling and analytical protocol, covers 12 years, which is long enough to address most of the inter-annual variability in weather.

The main objectives of this study were:

1) to evaluate the long term trends in bulk precipitation, throughfall and soil solution elemental fluxes from the Level II forest monitoring plots, between 1995 and 2006, in order to determine direction of trends, their magnitude and significance,
2) to understand the nature, sources and causes of the identified trends, and
3) to investigate the soil response to pollution change and recovery.

2. Methods and analysis

2.1. Level II intensive forest monitoring sites

Data from ten intensive forest monitoring Level II sites, established in 1995 in the UK were used for this study (see map in Fig. 1). The sites form part of a European network (ICP Forests), established to gain a better understanding of the effects of air pollution and other environmental factors on forest ecosystem structure and function. Table 1 shows climatic and site characteristics and Table 2 the soil

Table 1
Site and climatic characteristics of 10 Intensive Forest Monitoring Level II sites in the UK. Basal area was measured in 1995. Averaged annual temperature at the sites is reported.

Site name/number	Tree species	Planting year	Basal area ($m^2\ ha^{-1}$)	Elevation (m)	Slope (%)	Rain (mm)	T (°C)
Alice Holt/512	Oak	1935	22.0	80	0	800	11.6
Savernake/516	Oak	1950	20.0	107	1	750	11.3
Grizedale/517	Oak	1920	20.0	115	30	1800	9.5
Thetford/715	Scots pine	1967	36.6	20	1	600	11.3
Sherwood/716	Scots pine	1952	39.3	265	22	1200	9.8
Rannoch/717	Scots pine	1965	32.8	470	25–30	1400	8.5
Coalburn/919	Sitka spruce	1974	47.1	300	1	1400	9.0
Tummel/920	Sitka spruce	1969	59.2	400	6–10	1100	7.5
Loch Awe/921	Sitka spruce	1971	55.0	40	5	2300	7.5
Llyn Brianne/922	Sitka spruce	1973	47.3	450	20	2100	10.1

characteristics of the ten sites. Additional information about this monitoring network is available in Vanguelova et al. (2007a).

2.2. Measurements and analysis

Bulk precipitation, throughfall and soil solution samples have been collected from 10 Level II plots. In each site, samples from 2 bulk precipitation (installed in the open ground near the forest plots) and 10 throughfall collectors (installed under the stands canopy) were collected every two weeks from 1995 until 2006. Soil lysimeters have been used to sample soil solution every two weeks from 9 Level II sites. There are 12 lysimeters (PRENART SuperQuartz soil water samplers, Plenart Equipment Aps, Denmark) at each site, 6 located at 10 cm soil depth and the other 6 located at 50 cm soil depth. Bulk precipitation, throughfall and soil solution were collected and measured according to Level II protocols described in detail in the ICP forests manuals (Manual, 2002, 2004). Water samples were filtered through a 0.45 μm membrane filter and analysed for pH by pH meter; Al, Ca, Mg, K, Na, P, S, Mn and Fe by ICP-OES (Spectro flame, spectro Ltd.), NH_4–N colorimetrically, dissolved organic carbon (DOC) and total N by Carbon analyser (Shimadzu 5000, Osaka, Japan) and sulphate (SO_4^{2-}), phosphate (PO_4^{3-}), nitrate NO_3–N and chloride (Cl^-) by Ion Chromatography (Dionex DX-500). Dissolved organic nitrogen (DON) is calculated from measured total and inorganic nitrogen forms. Aluminium (Al) and manganese (Mn) in bulk precipitation and throughfall were not measured. Quality assurance and quality control on dissolved ion concentrations in bulk deposition, throughfall and soil solution are described by de Vries et al. (2001). The bulk precipitation and throughfall elemental fluxes were calculated using measured water volumes at the sites and measured elemental concentrations. Stemflow was calculated for broadleaves and conifers, based on measurements at one oak and one Scots pine site (0.6% and 0.4% of bulk precipitation respectively) by Arcangeli et al. (2007). The soil solution elemental fluxes were calculated by the climatic water balance model using bulk precipitation, throughfall and evapotranspiration, estimated by the Penman-Monteith semi-empirical model (Monteith and Unsworth, 1990; Hough and Jones, 1997). Input daily meteorological data for the Penman-Monteith model came from local meteorological stations at the sites and/or the nearest automated weather stations (AWS), where data were provided by the British Atmospheric Data Centre (BADC). Monthly elemental fluxes for bulk precipitation, throughfall and soil solution were calculated from monthly water fluxes and bimonthly water and chemistry measurements. Dry deposition, canopy nutrient and base cation uptake and leaching were calculated by the 'Canopy Budget Model' as proposed by Ulrich (1983) and implemented by Draaijers and Erisman (1995) and used also recently by Zhang et al. (2006). Only results on dry deposition of sulphur are discussed in this study. Soil solution sampling and analysis at Coalburn (for shallow soil) and the Rannoch sites started in 2002; soil solution sampling was not done at Loch Awe.

2.3. Statistical analysis

Twelve years (from 1995 to 2006) of monthly bulk precipitation, throughfall and soil solution elemental fluxes were quality checked according to quality criteria set in the ICP forests manuals (Manual, 2002, 2004). Data on DOC and DON in bulk precipitation, throughfall and soil solution have only been collected since 2002, so only five years of data were used in the analysis of these two variables. The Seasonal Mann-Kendall Test (SKT) (Mann, 1945; Kendall, 1975; Hirsch et al., 1982; Hirsch and Slack, 1984; Claudia, 2004), as described in detail by Evans et al. (2001) was used to determine statistically significant temporal trends in bulk precipitation, throughfall and soil solution chemistry at individual sites. The SKT is a non-parametric test for detecting monotonic but not necessarily linear change over the period of record. Non-parametric tests are more suitable for non-normally distributed data, missing and extreme values, which are frequently encountered in environmental time series (Yue and Pilon, 2002). Trend analyses were also undertaken to determine the significance of changes in the bulk precipitation, throughfall and soil solution water fluxes. Pearson's Product–Moment Correlation was used to reveal relationships between water quantity and ion concentrations in bulk precipitation, throughfall and soil solution over the whole monitoring period. The statistical package GenStat (GenStat, 2003) was used for these analysis.

Table 2
Soil type and soil pH, carbon, nitrogen, Cation Exchange Capacity (CEC by $BaCl_2$ extraction) and Base Saturation (BS) of 10 Intensive Forest Monitoring Level II sites in the UK. Soil characteristics are shown only for the two horizons for each plot where the soil solution samplers are situated.

Site name	Soil type (FAO)	Soil horizon	Soil pH (H_2O)	C%	N%	Soil CEC $cmol_c\ kg^{-1}$	Soil BS%
Alice Holt	Eutric vertisol	Ah	5.4	2.69	0.56	23.10	95
		BCg	6.2	1.08	0.027	25.83	96
Savernake	Eutric vertisol	E	4.7	3.47	0.138	15.73	22
		2BCtg	6.2	1.21	0.068	23.15	99
Grizedale	Cambic podzol	Ah	4.3	8.27	0.456	12.92	9
		Bs	5.1	5.01	0.279	6.71	7
Thetford	Ferralic arenosol	Ah	5.3	1.98	0.482	4.93	92
		Bw	7.0	0.31	0.285	3.23	99
Sherwood	Cabric podzol	Ah	4.1	2.69	0.161	6.51	4
		BC	4.5	1.37	0.064	2.58	7
Rannoch	Gleyic podzol	E	4.2	3.87	0.111	10.03	9
		Bs	4.8	3.42	0.082	2.35	13
Coalburn	Umbric gleysol	Ah(g)	4.0	6.52	0.357	17.46	6
		Bg	3.8	1.66	0.060	12.41	33
Tummel	Ferric podzol	Ah	5.1	2.5	0.185	6.3	52
		Bs	5.9	0.4	0.027	0.9	54
Loch Awe	Dystric gleysol	Ah	3.9	3.46	0.426	12.6	11
		Bs	4.8	1.21	0.178	4.2	4
Llyn Brianne	Umbric gleysol	A	4.0	4.44	0.29	16.36	3
		Bg	4.3	3.51	0.05	13.18	2

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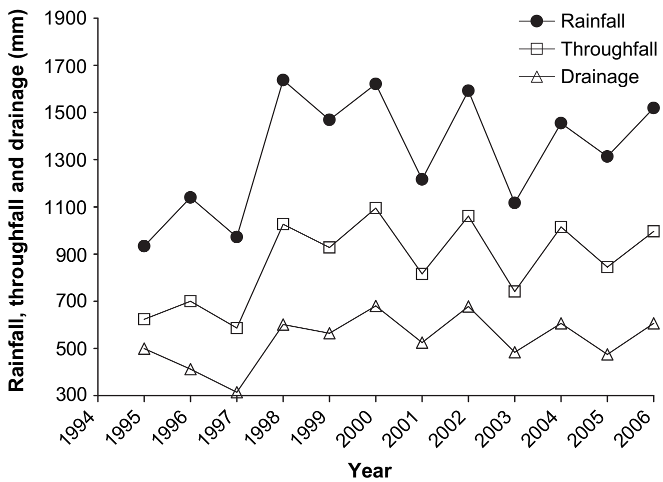

Fig. 2. Annual average of bulk precipitation, throughfall and drainage (soil water fluxes) for all sites.

Table 4
Correlations coefficients between monthly bulk precipitation and soil water and monthly throughfall and soil water flux at nine Level II sites in the UK. Values represents r^2 of the relationships and significant level is indicated at $p < 0.05$ (*) and at $p < 0.01$ (**).

Site	Bulk precipitation/ soil water	Throughfall/ soil water	Soil drainage
Alice Holt	0.499	0.703*	Poorly drained
Savernake	0.890**	0.901**	Poorly drained
Grizedale	0.815**	0.895**	Well drained
Thetford	0.753*	0.598*	Perfectly drained
Sherwood	0.715*	0.756*	Well drained
Rannoch	0.883**	0.884**	Well drained
Coalburn	0.243	0.462	Very poorly drained
Tummel	0.489	0.526*	Well drained
Llyn Brianne	0.575*	0.705*	Imperfectly drained

3. Results

3.1. Changes in water fluxes at the sites

The ten individual sites showed no significant trend in annual precipitation and throughfall and nine sites for soil water flux over the 12 year sampling period, although the year-to-year variability of averaged data from all sites was considerable as expected within precipitation data (Fig. 2). The years 1995, 1996 and 1997 were dry while 1998, 2000, 2002, 2004 and 2006 were wet. Throughfall ($p < 0.05$) and soil water fluxes ($p < 0.05$) significantly increased only at Coalburn in the north of England. Annual average site bulk precipitation, throughfall, interception, stemflow and drainage are shown in Table 3. As expected, the canopy interception is almost double in the coniferous sites (32–53% of bulk precipitation) compared to the broadleaved sites (16–21% of bulk precipitation). This is reflected in the soil water flux, which is almost double at the oak sites (52–66% of bulk precipitation) than that of the Scots pine and Sitka spruce sites (31–47% of bulk precipitation). Total water draining through the soil is very strongly positively related with the total throughfall ($r^2 = 0.98$, $p < 0.001$, $n = 9$ Level II sites), but less with total bulk precipitation amounts ($r^2 = 0.76$, $p < 0.01$, $n = 9$ Level II sites). These relationships varied amongst the different sites, depending on the species, the age of the stands and the soil properties (Table 4). In most sites ion concentrations declined as precipitation increased (data not shown). Statistically significant negative relationships between bulk precipitation amount and ion concentrations were found for K and Ca, nitrate, ammonium, dissolved organic nitrogen and sulphate at nine sites. The same relationships in throughfall were found for K, Ca, Mg, nitrate, ammonium, sulphate, DON and DOC concentrations at these nine sites. In contrast, precipitation and throughfall amounts were significantly positively related with Na and Cl concentrations in most upland sites. Soil water was generally not related with any of the ion concentrations with the exception of Alice Holt, Savernake and Tummel where water amounts were significantly correlated with soil solution Al. At Thetford and three of the four Sitka spruce sites soil water amounts were positively related with soil solution DOC concentrations.

Table 3
Averaged annual water fluxes in 10 Intensive Forest Monitoring Level II sites in the UK. The water fluxes are in mm. Bulk precipitation and throughfall are measured at the sites where interception is calculated. Stemflow calculations for broadleaved and conifers are based on measurements at one oak and one Scots pine site (annual averaged of 0.6% (se = 0.18%) and 0.4% (se = 0.11%) of bulk precipitation respectively; Arcangeli et al. (2007)). Soil drainage is modelled by the climatic water balance model using bulk precipitation, throughfall and evapotranspiration (ET), estimated by the Penman-Monteith semi-empirical model.

Site	Bulk precipitation	Throughfall	Interception	Stemflow	Drainage	ET
Alice Holt	800	670	130	4.8	325	350
Savernake	750	590	160	4.5	230	365
Grizedale	1800	1500	310	10.5	1130	380
Thetford	600	420	190	2.5	0	560
Sherwood	1200	810	380	5.0	365	450
Rannoch	1400	820	540	5.5	465	360
Coalburn	1400	830	550	5.5	420	415
Tummel	1100	740	370	4.5	385	360
Loch Awe	2300	1100	1200	9.0	–	–
Llyn Brianne	2100	1300	800	8.5	950	360

3.2. Changes in bulk precipitation, throughfall and soil solution chemistry

3.2.1. Acidity and sulphur

Significant decline in bulk precipitation and throughfall acidity was detected at most of the sites over time (Fig. 3). Significant ($p < 0.01$) recovery of soil pH was observed in two previously very polluted sites – Sherwood and Llyn Brianne, despite the low buffering capacity of the soils there (Table 2). The Acid Neutralising Capacity (ANC) at these sites increased significantly ($p < 0.01$) for the 12 years of monitoring, from −950 to −39 $\mu mol_c\ l^{-1}$ at Sherwood and from −70 to 63 $\mu mol_c\ l^{-1}$ at Llyn Brianne. In contrast, at Grizedale, Coalburn and Tummel, despite bulk precipitation and throughfall decline in acidity, the soil solution pH at 10 cm soil depth fell (($p < 0.05$), Fig. 3). Sulphate (SO_4) in bulk precipitation declined significantly only at the upland sites with high bulk precipitation (Grizedale, Coalburn, and Llyn Brianne) while sulphur in the throughfall declined significantly at all of the sites except the two pristine sites in Scotland, Rannoch and Loch Awe (Fig. 3). Annual dry deposition of SO_2 at the sites was relatively high, up to 47% of total S deposition in the lowlands and at sites previously heavy polluted such as Sherwood. The air concentration of SO_2 measured at the sites from 2002 to 2006 declined over the monitoring period (data not shown), and the dry deposition of S is the largest contributor to the change in the throughfall S in the lowland sites at Alice Holt, Savernake, Thetford. Significant decline in shallow (10 cm) and deep soil (50 cm) solution SO_4 was detected at sites where the magnitude of sulphate decline in throughfall is highest, and soils are of sandier texture, for example at Sherwood.

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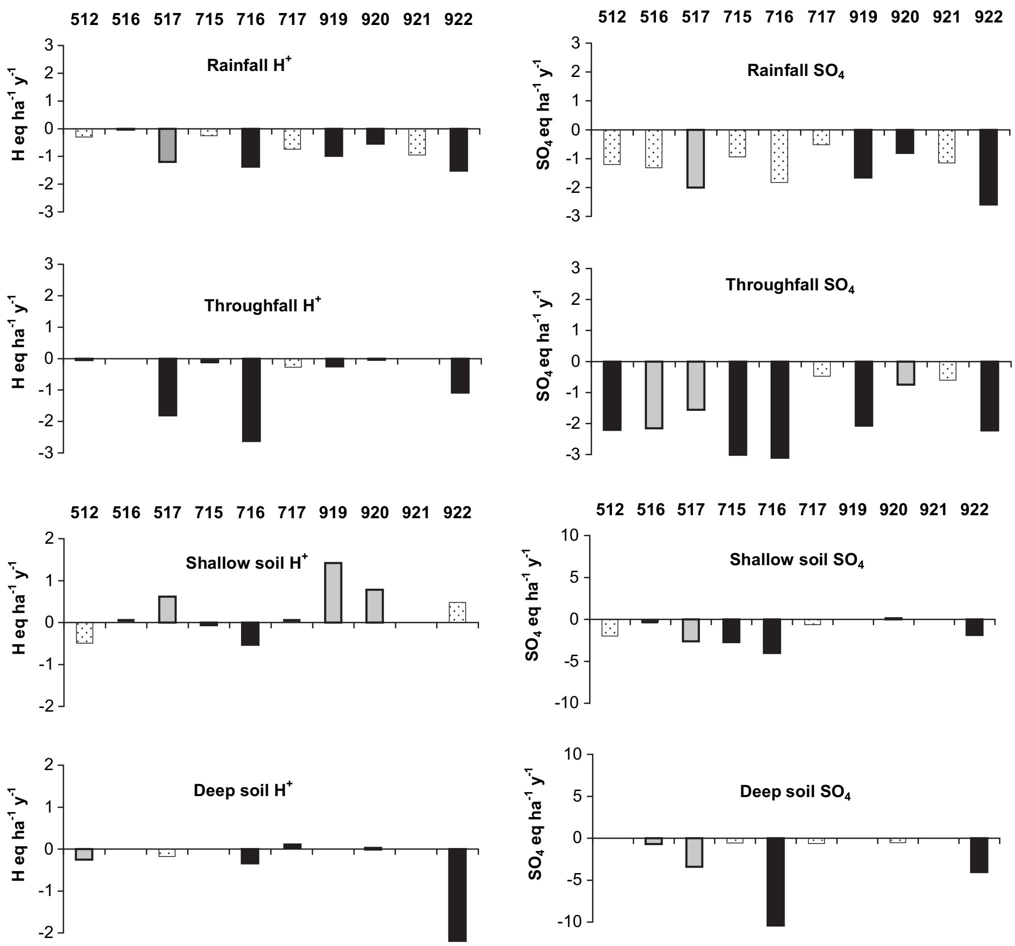

Fig. 3. Slopes and significance levels of trends from the Seasonal Mann-Kendall Test for acidity and sulphate in bulk precipitation, throughfall, shallow (10 cm depth) and deep (50 cm depth) soil solution at individual sites (sites numbers are as specified in Table 1). Black bars represent trends significant at $p < 0.01$, grey bars those significant at $p < 0.05$ and dotted bars are those not significant.

3.2.2. Ammonium, nitrate, dissolved organic nitrogen and dissolved organic carbon

Nitrate (NO_3–N) in bulk precipitation showed significant decline at only two upland sites – Loch Awe and Llyn Brianne and it was very variable in throughfall in all sites (Fig. 4). Ammonium (NH_4–N) in bulk precipitation and throughfall significantly declined in most of the upland sites and in the throughfall of the lowland oak site at Alice Holt (Fig. 4). The contribution of reduced nitrogen to the total N in bulk precipitation was high at all sites, from 33 to 55%, while oxidised nitrogen was between 26 and 38% of the total N in bulk precipitation. Nitrate concentrations (NO_3–N) in soil solution varied greatly between sites, reflecting the range of current atmospheric deposition (Fig. 4). For example, at the Scots pine sites, the nitrate concentration at 50 cm depth was negligible at Rannoch in highland Perthshire (annual average of 0.04 mg l^{-1}), relatively high at Sherwood in the Pennines (annual average of 3.6 mg l^{-1}), and very high at Thetford in East Anglia (annual average of 19.8 mg l^{-1}). Soil solution NO_3–N at 10 and 50 cm depth significantly declined at the latter sites which have been under declining SO_2, acidity pollution and high N loading respectively. However, at two other sites – Grizedale and Tummel, NO_3–N at both 10 and 50 cm depth soil solution increased significantly (Fig. 4).

The contribution of DON to total N in bulk precipitation was between 14 and 50% across the sites. In contrast to the general decline in oxidised and reduced N forms, dissolved organic nitrogen (DON) was found to significantly increase in bulk precipitation and throughfall ($p < 0.05$) at 5 out of the 10 sites (Fig. 5). A significant increase in DON was also detected in the soil solution at shallow soil depth at 4 sites ($p < 0.05$) and at deep soil depth at 3 sites ($p < 0.05$) (Fig. 5). A significant increase in throughfall dissolved organic carbon (DOC) is apparent only at Tummel ($p < 0.05$) (Fig. 5). Soil solution DOC at shallow soil depth increased significantly ($p < 0.05$) at 5 out of the 9 sites including the sites as for DON changes detected (Fig. 5).

3.2.3. Base cations – calcium, magnesium and potassium

Bulk precipitation and throughfall Ca declined at most Level II sites, being significant in the throughfall only at the Alice Holt site ($p < 0.05$) (Fig. 6). Significant decrease in soil solution Ca concentrations was evident at Thetford, a Ca rich site on sandy soil over chalk, and at Sherwood and Llyn Brianne, which are sites on acid, sandy soils with low initial soil Ca reserves (e.g. soil base saturation of 4–7% and 2–4% respectively) (Fig. 6). Bulk precipitation and throughfall Mg were very variable and declined significantly only in the throughfall under oak at the Alice Holt site (Fig. 6). Soil solution Mg decreased significantly only at the Thetford site. Bulk precipitation K changed little, but at Grizedale and Llyn Brianne, throughfall K increased significantly, which resulted in an increase of K in the soil solution (Fig. 6). Four of the other sites appeared to be losing K significantly from both their shallow and deep soils.

3.2.4. Sodium and chloride

Bulk precipitation and throughfall sodium (Na) and chloride (Cl) increased significantly at most upland sites and this increase was especially pronounced ($p < 0.01$) in the throughfall at two very exposed sites – Loch Awe in far West of Scotland and Llyn Brianne

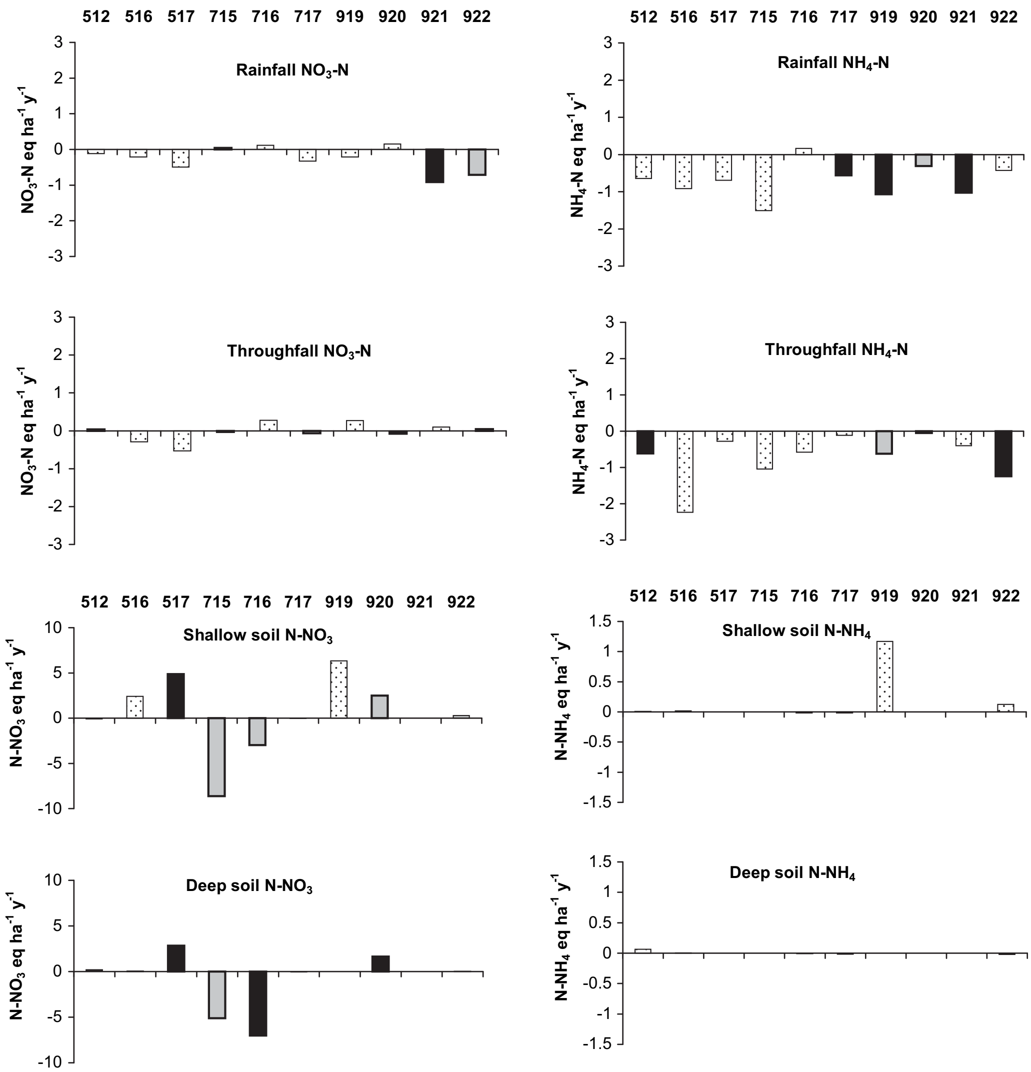

Fig. 4. Slopes and significance levels of trends from the Seasonal Mann-Kendall Test for NO_3-N and NH_4-N in bulk precipitation, throughfall, shallow (10 cm depth) and deep (50 cm depth) soil solution at individual sites (sites numbers are as specified in Table 1). Black bars represent trends significant at $p < 0.01$, grey bars those significant at $p < 0.05$ and dotted bars are those not significant.

in South-western Wales (Fig. 7). Soil solution Na and Cl were unchanged, with the exception of Coalburn where Na and Cl levels increased significantly ($p < 0.05$) at shallow depth (Fig. 7).

3.2.5. *Soil solution aluminium and manganese*

Soil solution total Al and Mn both declined significantly at 10 and 50 cm depth at Sherwood and Llyn Brianne, sites recovering from pollution (Fig. 8). In addition, Al declined significantly at 50 cm and Mn at both soil depths at the Thetford site. In contrast, Coalburn experienced a large increase in Al and in Grizedale and Tummel, Mn increased significantly at 10 cm soil depth (Fig. 8). These three sites experienced soil acidification for the last 12 years as shown in Fig. 3. The soil solution Ca/Al molar ratio decreased significantly at most sites with an exception of Alice Holt, a site on well-buffered clay soil (data not shown) (Vanguelova, 2004).

4. Discussion

4.1. *Changes in deposition – trends, nature and causes*

Trends in concentrations of SO_2 and NO_2, and the deposition of sulphur and nitrogen in bulk precipitation and throughfall are falling (Figs. 3 and 4) in line with both emission reductions (NEGTAP, 2001) and with the reduction of acidity in bulk precipitation, as monitored over the last 16 years in the 32 Acid Deposition Monitoring Network sites in the UK (Fowler et al., 2005, 2007). Forests are particularly efficient at scavenging air pollutants. For example, SO_4 in throughfall is two to three times higher compared to bulk precipitation as it combines the wash-off of previously dry-deposited sulphate particles and SO_2 and leaching of internal plant sulphur from foliage (Nyborg et al., 1977; Lindberg and Garten, 1988). This explains the steeper and significant decline in sulphate in throughfall compared with the more gradual and less significant decline of sulphate in bulk precipitation seen at the UK level II sites. The decline in bulk precipitation and throughfall Ca is expected to continue as a consequence of overall SO_4 decrease and pollution recovery. In general, the well-buffered sites may show the largest proportional decrease in base cation concentration in their soils, which is already evident at Thetford – a Ca rich site.

Level II data indicate large spatial variation in the levels of nitrogen in deposition and NH_3 concentrations and concern remains over the impacts of ammonia (NH_3) on forest ecosystems (Vanguelova et al., 2007a). Given the large decline in SO_4 and acidity, the scavenging of NH_4 would also be expected to change – in

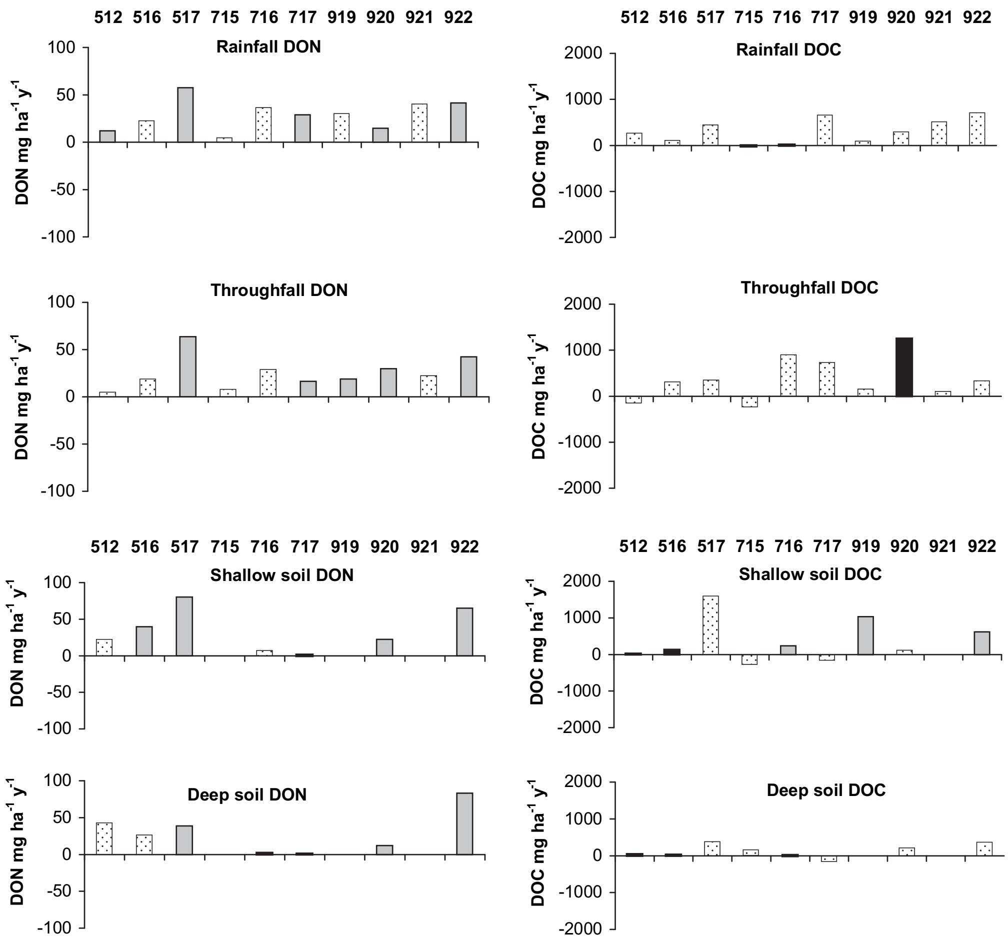

Fig. 5. Slopes and significance levels of trends from the Seasonal Mann-Kendall Test for DON and DOC in bulk precipitation, throughfall, shallow (10 cm depth) and deep (50 cm depth) soil solution at individual sites (sites numbers are as specified in Table 1). Black bars represent trends significant at $p < 0.01$, grey bars those significant at $p < 0.05$ and dotted bars are those not significant.

particular with increasing travel distance of NH_4 and the gradual change in the partitioning of NH_3/NH_4 (Fowler et al., 2005). Emissions of NO_x and NH_3 in the UK were reduced by 35% and 15% respectively over the monitoring period (Goodwin et al., 2004) and the reduction of NH_4 and NO_3 in deposition seen at some of our sites (Fig. 4) is broadly consistent with the reduction in bulk precipitation NH_4 and NO_3 detected from the UK Acid Deposition Monitoring network (Fowler et al., 2005). In some parts of Europe and North America reduction of emissions of oxidised N are contributing to a stabilisation or decline in deposition, but there is currently limited control of emissions of reduced N (Emmett, 2007). In addition, although total deposition is declining linearly with the decline in emissions, the partitioning between wet and dry deposition is expected to change (Fowler et al., 2005, 2007). This will ensure that N will continue to have a significant impact for some time to come in many regions (Galloway et al., 2003).

The significant increase in bulk precipitation and throughfall DON observed in the short period of between 2000 and 2006 (Fig. 5) at a number of forest monitoring sites is of concern and adds to the complex picture of nitrogen inputs, cycling and forest ecosystem response. The source of DON in bulk precipitation is uncertain. It has been assumed that it may be generated by agricultural practices, due to its high correlation to NH_4 (Ham and Tamiya, 2007), but also may be driven by changes in water, gas and aerosol circulation and deposition (Wedyan and Fandi, 2007). Rainwater amounts and DON concentrations were negatively correlated only at Alice Holt and the Llyn Brianne sites, which excludes water as a general driver for DON increase. Annual averaged bulk precipitation DON was positively related with NH_4 and NO_3 ($n = 9$, $r^2 = 0.672$ $p < 0.05$ and $r^2 = 0.677$ $p < 0.05$ respectively). However, monthly bulk precipitation DON was not or was very weakly related with NH_4 and NO_3, suggesting that although DON and NH_4 and NO_3 may share a similar source, their seasonal patterns are different. Despite the large number of reports considered in a global review by Cornell et al. (2003), evidence for long-term temporal changes in rainwater organic nitrogen concentrations is ambiguous. With regard to sources, the same review highlighted the likelihood that some of the DON and other organic material observed may not be locally generated, but undergo extensive or long-range atmospheric transport (Cornell et al., 2003), with a land-to-sea gradient in organic nitrogen concentration.

A detailed examination of the nature and causes for the significant increases in throughfall DON, DOC and K alone at some sites suggested that these trends are due to episodic peaks of DON, DOC and K which are not detected in the bulk precipitation but are detected in the soil (Pitman et al., 2008). These are seen particularly in the DOC increases at the Tummel site, which were linked with aphid infestation and the DON and K increase at the Grizedale site which were linked with caterpillar infestation (Pitman et al., 2008). The results from the UK's Forest Condition Survey for the period 1993–2003 clearly show two occasions when the crown density of Sitka spruce deteriorated markedly (at a national level) in 1996 and 1997, and between 2001 and 2002 (Hendry, 2005) which supports the evidence from the

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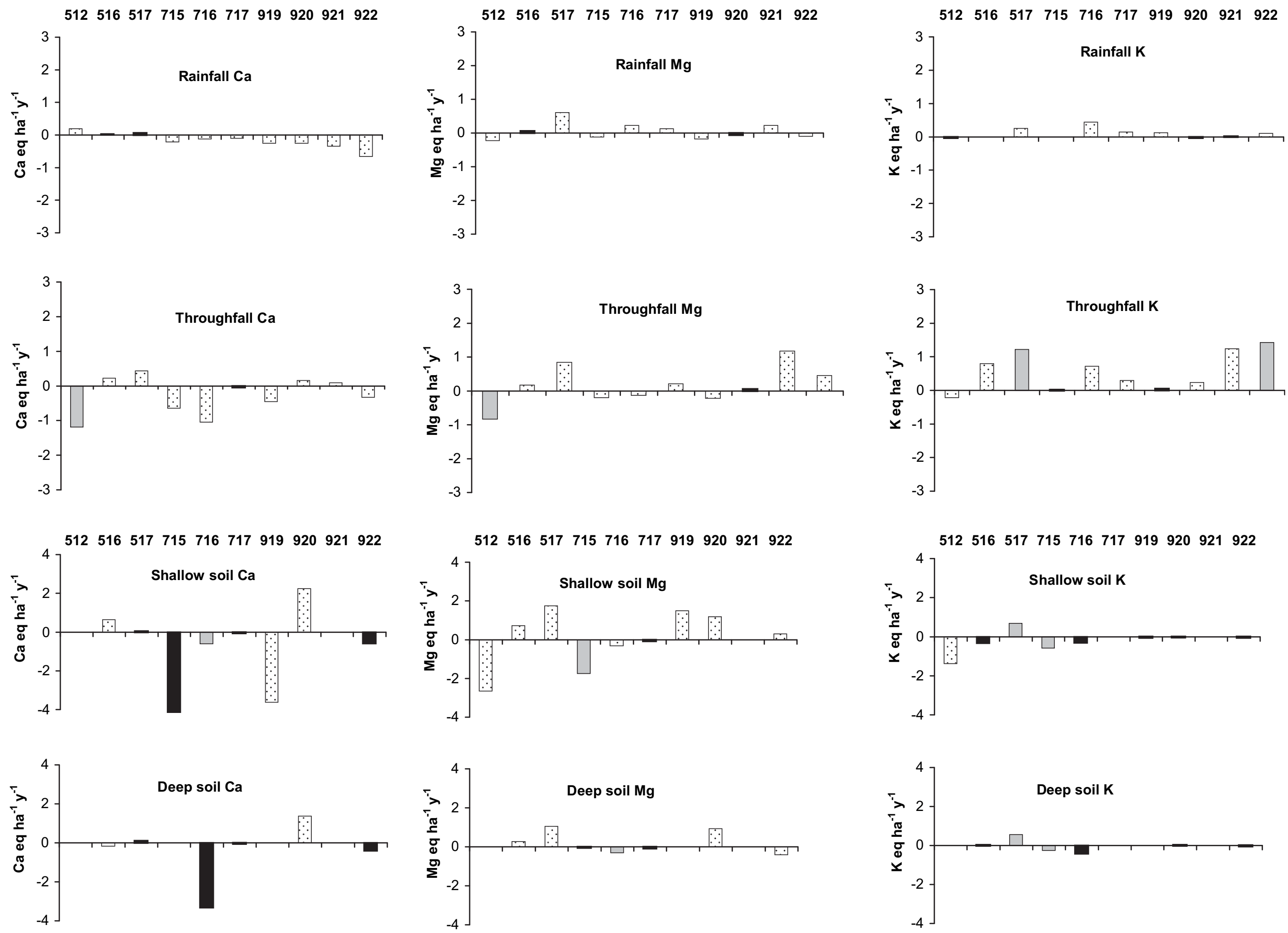

Fig. 6. Slopes and significance levels of trends from the Seasonal Mann-Kendall Test for Ca, Mg and K in bulk precipitation, throughfall, shallow (10 cm depth) and deep (50 cm depth) soil solution at individual sites (sites numbers are as specified in Table 1). Black bars represent trends significant at $p < 0.01$, grey bars those significant at $p < 0.05$ and dotted bars are those not significant.

intensive Level II monitoring (Vanguelova et al., 2007a; Pitman et al., 2008). It is suggested that some insect pests may become more damaging as a result of climate change, in part, driven by expectations that more frequent and severe summer droughts will make trees more susceptible to biotic agents (Broadmeadow, 2002). Thus, the biotic impacts on forest chemical fluxes cannot be neglected because these can be of similar magnitude to pollution impacts and also could become more significant in the future.

Another possible link between changing climate and chemical fluxes in forest is suggested through the increase in bulk precipitation and throughfall Na and Cl in the upland sites, especially in the western coastline sites (Llyn Brianne, Grizedale and Loch Awe, Fig. 7). These changes are most likely related to an increasing number of storm events as is also suggested by the significant positive relationships between Na and Cl in bulk precipitation and throughfall and water amounts only at these sites. An example of these are the number of windthrows of Sitka spruce which have occurred at the Loch Awe site during the monitoring period, which are the result of repeated storms in the past 5 years. Some of the changes in Na and Cl are detected only in throughfall but not in bulk precipitation, particularly at Sherwood and Rannoch and this could be due to the higher fog and mist interception by upland forests but also due to the sea salt particles which would also be higher in throughfall than in bulk deposition (Hultberg and Grennfelt, 1992; Chiwa et al., 2004).

4.2. Soil response to changes in deposition chemistry

Despite the decrease in atmospheric sulphur deposition, significant downward trends in sulphate in soil solution were only observed at the previously very polluted sites such as Sherwood and Llyn Brianne, or at sites with predominant sandy or sandy loam texture soils such as Thetford and Grizedale (Table 2). There was no detectable change in the sulphate in highly clay soils such as in the Alice Holt and Savernake and on the highly organic soils such as in the Coalburn site, where SO_4 is likely to be adsorbed onto clay minerals and organic matter respectively. Recovery of the soil pH at polluted sites such as Sherwood and Lynn Brianne is evident despite being slow because of the very low buffering capacity of the soils at these sites. The application of the dynamic biogeochemical model SAFE (Soil Acidification of Forest Ecosystems) predicts limited changes in the soil solution in the timescale of 10–40 years at the Level II sites, under current emission reductions (Langan et al., 2009). The application of the MAGIC dynamic model, however, predicts that in the long term, despite the observed recovery of the coniferous sites, there will be re-acidification, associated with predicted increases in NO_3 leaching at Sherwood, and base cation depletion (due to forest uptake) at Llyn Brianne (Evans et al., 2007). Soil acidification at the Coalburn, Grizedale and Tummel sites is not related to changes of deposition inputs but is a response to increased water or increased canopy generated

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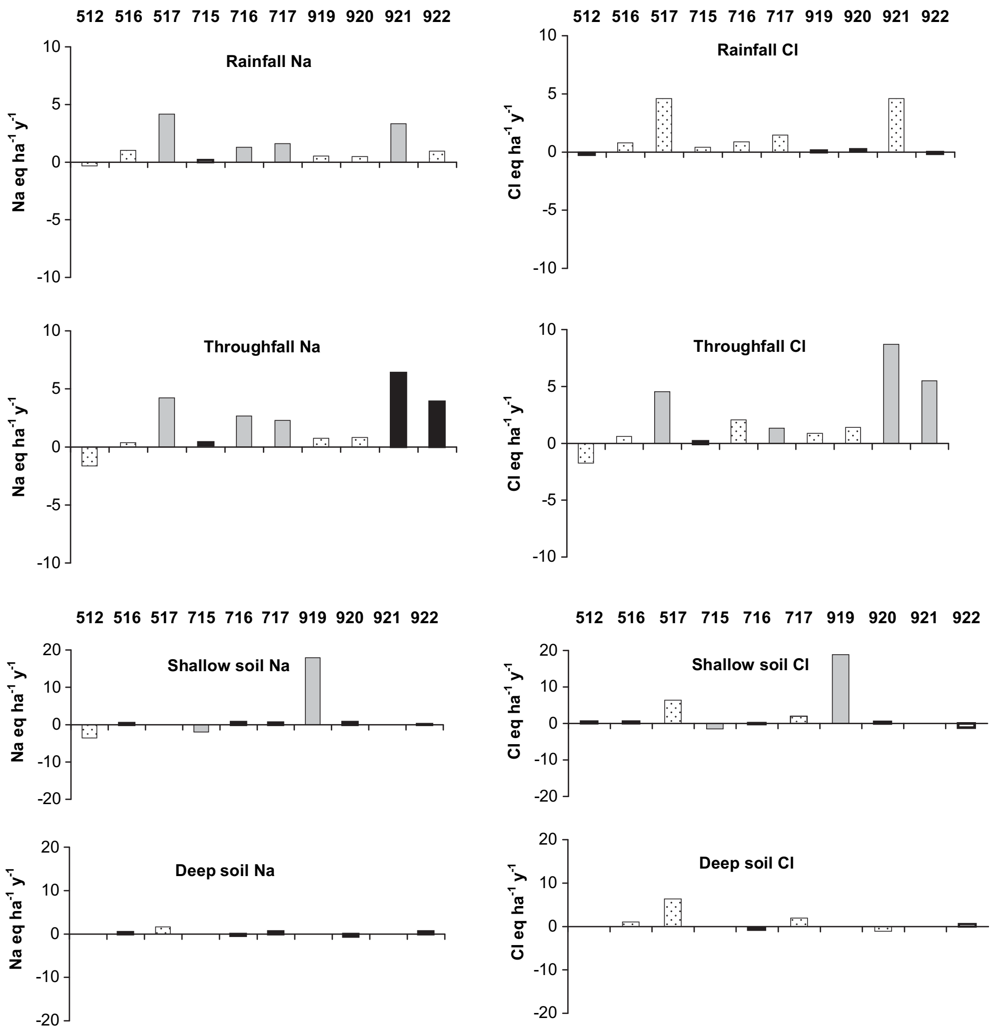

Fig. 7. Slopes and significance levels of trends from the Seasonal Mann-Kendall Test for Na and Cl in bulk precipitation, throughfall, shallow (10 cm depth) and deep (50 cm depth) soil solution at individual sites (sites numbers are as specified in Table 1). Black bars represent trends significant at $p < 0.01$, grey bars those significant at $p < 0.05$ and dotted bars are those not significant.

nitrogen input due to repeated insect infestations (Pitman et al., 2008). These results highlight the importance of drivers other than pollution. For example Waterlogging in the soil related to increased nitrification and acidification, was followed by an increase in Al in the soil solution in earlier studies of a Scots pine stand on a podzol (Vanguelova et al., 2005). The observed changes in soil solution chemistry were of similar magnitude to those induced by deposition (Vanguelova et al., 2007c).

Several soil chemical indicators suggest that the infertile soils at some Level II sites such as at Grizedale, Sherwood, and Llyn Brianne are vulnerable to loss of base cations as a result of acid deposition (Vanguelova et al., 2007a). The results from this study confirm that these sites have significantly lost Ca and in some intances K over the last decade (Fig. 6). This loss may be partly due to pollution recovery, but also due to demand from tree growth. These sites are mainly on podzolic and peaty podzolic gley soils, which are representative of a significant proportion of British forests. The soils at Thetford have significantly lost soil Ca, Mg and K. These changes may not be directly related to changes in atmospheric pollutant inputs. This may be explained by comparing water fluxes in dry years (1995, 1996, 1997) which lead to less leaching through the soil and consequently maintain high in cations, than the subsequent wetter years (1998–2006) giving rise to increased leaching and a concurrent fall in base cations (Table 2). Foliar Ca, Mg and K at the Level II sites have responded to the decline in base cations in soil solution. However, although declining, foliar base cation concentrations are still in the intermediate or optimal range for tree growth and there is no sign of nutrient deficiency at present at the sites. Llyn Brianne is the exception, where the very low Ca reserve in the soil and the long term decrease in Ca in soil solution have resulted in foliar Ca levels falling to the critical value of 0.12% dry matter as proposed by Van Den Burg (1985). The decline in soil base cations at Llyn Brianne and Thetford suggest that at coniferous acid sensitive sites this may become more of a management problem when decisions on forest harvesting practices need to be made – such as between stem only harvesting or whole tree harvesting. For example, whole tree harvesting in the Hubbard Brook Experimental Forest increased SO_4 adsorption in subsoil and reduced solution concentrations and watershed efflux of SO_4 (Fuller et al., 1987). However, increased mineralisation and nitrification led to substantial NO_3 loss, soil solution acidification and potentially toxic Al levels. Base cation budget research, applying different harvesting scenarios in Sweden has shown that these cation stores in the soils can be depleted by harvesting to rates that could lead to negative effects on trees and runoff water quality within one forest rotation (Akselsson et al., 2007).

The soil solution calcium to aluminium molar ratio is very variable across the Level II sites (Vanguelova, 2004), but ratios below the critical threshold of 1.0, which indicate a potential risk of

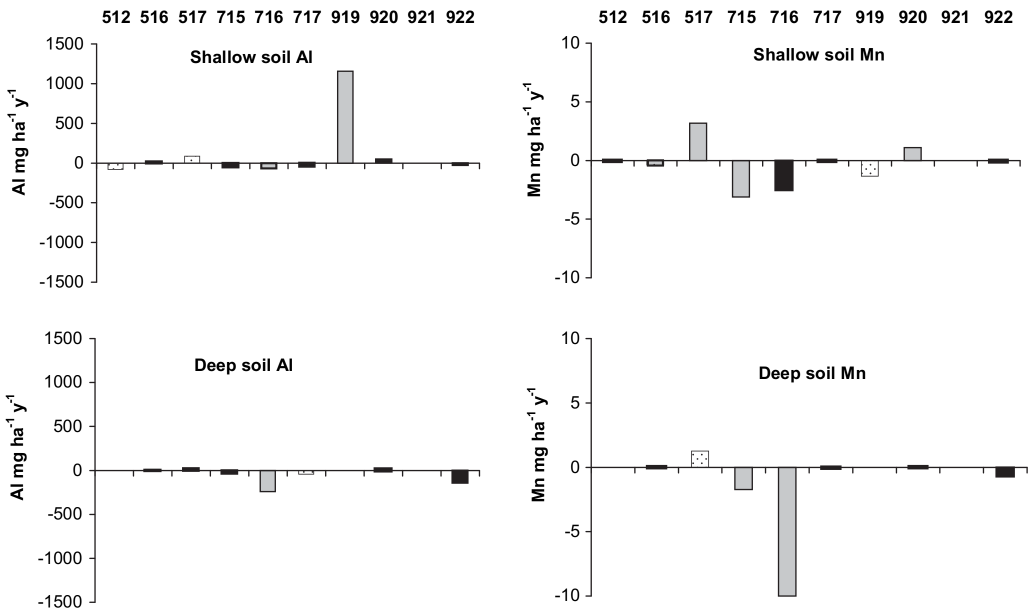

Fig. 8. Slopes and significance levels of trends from the Seasonal Mann-Kendall Test for Al and Mn in shallow (10 cm depth) and deep (50 cm depth) soil solution at individual sites (sites numbers are as specified in Table 1). Black bars represent trends significant at $p < 0.01$, grey bars those significant at $p < 0.05$ and dotted bars are those not significant.

aluminium toxicity to tree fine roots and tree nutrient uptake (Cronan and Grigal, 1995; Vanguelova et al., 2007b), have been observed at Grizedale, Sherwood and Llyn Brianne. These sites have received the highest atmospheric pollution inputs of acidity, sulphur and nitrogen (Vanguelova et al., 2007a) and represent the most sensitive soils (Table 2). Other Level II sites, such as Thetford (sand over chalky drift), Alice Holt and Savernake (both on heavy clay soils) (Table 2), are more resilient to soil acidification due to their high soil base status. The decline in Ca/Al molar ratio at most sites is due to Ca depletion at Sherwood, Llyn Brianne, Grizedale and Thetford and due to Al increase in Coalburn and Tummel sites. It has been shown that low Ca/Al ratios together with high free Al in the soil solution can affect fine root growth and increase root mortality in Scots pine (Vanguelova et al., 2007b,c). Nevertheless, studies have failed to show a relationship between soil solution Ca/Al molar ratio and forest increment rates, defoliation and/or foliar chemistry for either Norway spruce, Sitka spruce or Beech in Denmark (Hansen et al., 2007). Two soil surveys of the European Level I forest condition monitoring plots found no link between soil acidity and above-ground forest conditions and growth, and work by Freer-Smith and Read (1995) failed to link the crown condition with aluminium or base cations in soil solution in the UK. In contrast, numerous field research studies have established relationships between soil acidification and root functioning which were recently reviewed in Vanguelova et al. (2007b). This suggests a real difference in the sensitivity of the belowground tree response compared with that above ground and the likely time lag between the two responses.

Out of all ten Level II sites, the Thetford site is the only N saturated site according to the different "stage of N saturation" as described by Aber (1989, 1998). This site is in East Anglia, close to intensive animal units. Nitrogen enrichment due to high N deposition (ranging from 13 to 19 kg ha^{-1} a^{-1}) combined with low bulk precipitation (annual average of 600 mm) results in a very high NO_3–N concentration in the soil solution throughout the year. The drainage at this site is very limited (e.g. 190 mm annual average), and a concentration effect is observed in the soil with monthly peaks of NO_3 concentrations of up to 140 mg l^{-1} and mean annual concentrations of up to 40 mg l^{-1} – a concentration 3 times higher that the UK water drinking standard of 11.3 mg l^{-1}. These results suggest that forest soils with a low organic matter content and surrounded by intensive agriculture, are at risk from the effects of high nitrogen deposition (Pitcairn et al., 1998). This is clearly demonstrated by an extremely low soil carbon to nitrogen ratio of under 5 at Thetford, reflecting excess nitrogen mineralisation and leaching (Emmett, 2002). The Scots pine at Thetford already shows very high N concentrations in the needles, with values much above 1.7%, which has been quoted to indicate nutrient imbalance in conifers (Gundersen, 1999). This is confirmed by the consistent decline of foliar P, Mg and K over the last 12 years at this site (data not shown). On the positive side, soil solution NO_3 has significantly declined at Thetford over the last 12 years of record, which is likely to be a response to the overall decline in N emissions at high N deposition areas such as East Anglia (Fowler et al., 2005). Changes in ground flora at the site for the last 12 years have also confirmed the N recovery process (data not shown).

Nitrate concentrations in soil solution have increased dramatically at two of the Sitka spruce sites, Tummel and Coalburn, but not as a response to N deposition. At Tummel, N increase followed repeated severe defoliation by the green spruce aphid, which is confirmed by increases in throughfall DOC and by litter-fall analysis (Pitman et al., 2008). The increase in nitrate levels at Coalburn are likely to be a result of increased water flux and build up of nitrate in the soil due to the presence of subsoil heavy clay horizon and consequent very poor drainage (Tables 3 and 4). Therefore, increase in NO_3–N at these sites is not due to external inputs but was either canopy generated or driven by changes in soil water regime.

In contrast, the increase in soil solution DON at 5 out of 9 sites seems to be a direct response to increased bulk precipitation and throughfall DON deposition. However, indirect drivers such as decreased acidity and increased microbial activity in the soil organic layer might have also contributed to the increase in soil solution DON and should not be ruled out. The increase in DON could be also directly related to the increase in DOC.

Soil solution DOC has risen significantly at 10 cm soil depth at three Level II sites. The increase in Sherwood and Llyn Brianne is likely to be driven by the recovery from pollution. It has been suggested in numerous studies that high acidity and sulphate

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inhibit organic matter decomposition (Monteith et al., 2007; Chapman et al., 2008; Clark et al., 2006). Atmospheric deposition can affect soil organic matter solubility through at least two mechanisms – by changing either the acidity of soils or the ionic strength of the soil solution, or both. The soil solution pH increased and ionic strength of soil solutions decreased the most at Sherwood and Llyn Brianne due to the large decrease in SO_4, base cations and aluminium. Soil pH also determines the solubility of Al, as seen in the increase in pH and decrease in Al at Sherwood and Llyn Brianne and vice-versa at Coalburn. Higher Al release during the process of acidification can bind with organic molecules, neutralising high-affinity binding sites and thereby triggering SOM coagulation (Tipping and Woof, 1991). Thus, declining acid deposition may also affect DOC concentrations indirectly by reducing aluminium mobilisation. Reduced acidity in throughfall reaching the forest floor, on one hand will directly stimulate organic matter decomposition based on the chemical balance mechanism but also indirectly stimulate microbial activity in the soil organic layers.

Carbon loss might be also dependent on the high organic matter in the peaty gley soils, as in Coalburn where the peat layer is between 18 and 22 cm deep and at Llyn Brianne between 25 and 30 cm. In addition, changes in soil DOC could be driven by changes in soil water. This is suggested by the strong positive relationships between soil water flux and DOC concentrations at all Sitka spruce sites, but also at the Thetford site. The importance of soil temperature in stimulating microbial activity and release of carbon should also not be overlooked. Meteorological measurements for the last 20–30 years suggest that there has been an annual average soil temperature increase of 1–2 °C at 30 cm soil depth, measured near most of the Level II sites, which could have also stimulated a release of organic carbon from topsoil to soil solution.

Overall the soil carbon stocks at the 10 Level II sites are highly variable, with values of between 47 tC ha^{-1} and 500 tC ha^{-1} for the top 1 m of soil (Vanguelova et al., 2007a). This range of soil C stock is to be expected given that the monitoring sites are under both broadleaf (on soils with lower C content) and conifer forests (on soils with high soil C stock) where there is a distinct difference between humus layer development due to quality of litter (e.g. acidity, lignin content, etc.), the light reaching the forest floor, consequent understory vegetation development and different decomposition rates. Generally, the sites with higher soil C content; e.g. Lynn Brianne, Coalburn and Grizedale (Table 2) have higher DOC fluxes at shallow depth of soil, (e.g. annual DOC fluxes between 110 and 233 kg ha^{-1} a^{-1}) than the sites with lower soil C; e.g. Alice Holt, Savernake, Thetford (e.g. annual DOC fluxes between 1 and 60 kg ha^{-1} a^{-1}) (Morison et al., 2008). The magnitude of the soil carbon stock may be a factor determining the soil sensitivity to carbon release, however changes in environmental (climate and pollution) factors are much more important drivers for soil C dynamics, both in terms of magnitude and direction.

5. Conclusions

The evaluation of the long term trends in bulk precipitation and dry deposition at the Level II intensive forest monitoring sites provides evidence for changes in important deposition chemistry which confirm the successful implementation of the emission reduction policies in the UK. Long term trends in throughfall and soil solution chemical fluxes at these sites show the ecosystem response to changes in deposition and the rate of chemical recovery, particularly from acid and sulphur deposition. However, concerns over the local effects of excess nitrogen deposition pollution remain, alongside those of potential climate change, which is predicted to have both direct and indirect impacts on forest ecosystems. This study also reports important findings for the carbon and nitrogen cycling in forest ecosystems, with increasing trends of soil solution DOC and DON likely to be a direct response to pollution recovery, but also to monitored changes in soil temperature resulting in increased microbial activity. In addition, climate change driven changes have been detected by the significant increase of Na and Cl deposition over the period of monitoring, supporting a trend of increased storm events at some western and exposed forest sites. Declining base cations and specifically Ca in soils and tree uptake at some coniferous acid sensitive monitoring sites, highlights the need to carefully evaluate site conditions in terms of soil and geology when decisions on forest harvesting practices are made. Detailed environmental studies of some monitoring sites suggest significant importance of biological influence on the chemical cycling on both broadleaf and conifer systems. This has helped the evaluation of direct and indirect impacts of air pollution and climate change on forest ecosystem biogeochemisty and tree health and improved our understanding of the interrelationship between chemical and biological impacts.

The intensive monitoring programme is a unique forest surveillance network, providing continuous, detailed information on the condition of the forest ecosystem and its interaction with the wider environment at both local and regional scales. The integrated nature of monitoring across the Level II network enables the relationships between climate, pollutant exposure and chemical and biological response in forestry to be explored. The network also has important value in supporting international reporting commitments concerning sustainable forest management in the UK.

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