

# Does elevated nitrogen deposition or ecosystem recovery from acidification drive increased dissolved organic carbon loss from upland soil? A review of evidence from field nitrogen addition experiments

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**Abstract** Dissolved organic carbon (DOC) concentrations have risen in upland waters across large areas of Europe and North America. Two proposed drivers

of these increases are (1) deposition of atmospheric pollutant nitrogen (N) with consequent effects on plant and decomposer carbon dynamics, and (2) soil recovery from acidification associated with decreasing sulphur deposition. Examination of 12 European and North American field N addition experiments showed inconsistent (positive, neutral, and negative) responses of DOC to N addition. However, responses were linked to the form of N added and to resulting changes in soil acidity. Sodium nitrate additions consistently increased DOC, whereas ammonium salts additions usually decreased DOC. Leachate chemistry was used to calculate an index of “ANC forcing” of the effect of fertilization on the acid-base balance, which showed that DOC increased in response to all de-acidifying N additions, and decreased in response to all but three acidifying N additions. Exceptions occurred at two sites where N additions caused tree mortality, and one experiment located on an older, unglaciated soil with high anion adsorption capacity. We conclude that collectively these experiments do not provide clear support for the role of N deposition as the sole driver of rising DOC, but are largely consistent with an acidity-change mechanism. It is however possible that the unintended effect of acidity change on DOC mobility masks genuine effects of experimental N enrichment on DOC production and degradation. We suggest that there is a need, more generally, for interpretation of N manipulation experiments to take account of the effects that experimentally-induced changes in

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acidity, rather than elevated N per se, may have on ecosystem biogeochemistry.

**Keywords** Nitrogen · Acidity · ANC Forcing · Atmospheric deposition · Dissolved organic carbon · Manipulation experiments

## Introduction

Dissolved organic carbon (DOC) is the major form in which carbon (C) is cycled within soils. Net ecosystem loss of DOC depends on the balance between processes releasing DOC into solution, such as microbial decomposition, root exudation, litter leaching and desorption; and those such as bacterial consumption and adsorption which remove it (e.g. Kalbitz et al. 2000; Neff and Asner 2001). In peaty soils, fluvial DOC export can represent a significant term in the ecosystem C budget, comparable to net ecosystem CO<sub>2</sub> exchange (Billett et al. 2004). In the last two decades, DOC concentrations have increased in many natural waters, with concentrations doubling in some lakes and rivers in the United Kingdom and United States since the late 1980s (Evans et al. 2005; Findlay 2005). The phenomenon of rising DOC appears to be extensive, with increases reported throughout most of the UK (e.g. Worrall et al. 2004a), parts of Central Europe (Hejzlar et al. 2003; Kopáček et al. 2006), Southern Scandinavia (Skjelkvåle et al. 2005; Vuorenmaa et al. 2006), and the northeastern United States (e.g. Driscoll et al. 2003; Stoddard et al. 2003; Findlay 2005).

Such large-scale changes have generated widespread speculation as to likely causes. Proposed mechanisms include increased decomposition rates in organic soils due to rising temperatures (Freeman et al. 2001); hydrological changes including increased flow through shallow organic horizons (Hongve et al. 2004); shorter lake residence times (Schindler et al. 1992; Curtis 1998); increased frequency and severity of droughts (Worrall et al. 2004b); fluctuations in solar radiation (Hudson et al. 2003); increased DOC production under elevated atmospheric CO<sub>2</sub> (Freeman et al. 2004); changes in ecosystem production and decomposition mediated by chronic N deposition (Pregitzer et al. 2004; Findlay 2005); and increased solubility of humic acids due to recovery from

acidification (Evans et al. 2006a). Although evidence exists to suggest that all these mechanisms can influence DOC, the spatial extent of increases favours a common, large-scale driver affecting DOC delivery to both lakes and streams. This argues against hydrological factors that do not operate consistently at these scales, and mechanisms only affecting lakes. Temperature and atmospheric CO<sub>2</sub> increases, whilst operating at large scales, may not be of sufficient magnitude to explain the bulk of observed DOC increases (Evans et al. 2006a).

Here, we address two mechanisms linked to the deposition of atmospheric pollutants: (1) ecosystem response to chronic nitrogen (N) deposition, and (2) recovery from declining sulphur (S) deposition. The first hypothesis proposes that N deposition could impact on DOC leaching through mechanisms affecting either its production or subsequent decomposition. Because N typically limits productivity in terrestrial ecosystems (Vitousek and Howarth 1991), increased net ecosystem productivity due to N deposition may simply increase the pool of ecosystem C available for leaching. However, effects of elevated N on decomposition are complex. Aber (1992) suggested that elevated N supply would increase demand for labile C as a substrate for N immobilisation, reducing DOC leaching. However, this hypothesis was not supported by results from forest N manipulation experiments (Gundersen et al. 1998; McDowell et al. 1998; Aber et al. 1998). The effect of N on decomposition appears to depend on substrate quality: increased N availability increases activity of cellulose-degrading enzymes such as  $\beta$ -glucosidase, but suppresses lignin-degrading enzymes such as phenol oxidase (Fog 1988; Berg and Matzner 1997; Waldrop et al. 2004). DOC losses will further depend on the balance of DOC production (from litter/soil organic matter decomposition or root exudates), and subsequent decomposition of that DOC to CO<sub>2</sub>. Zech et al. (1994) suggested that suppression of lignin-degrading enzymes by excess N could increase leaching of recalcitrant DOC compounds as intermediate decomposition products.

The hypothesis that N deposition will increase DOC leaching was supported by forest experiments in Michigan (Pregitzer et al. 2004) where DOC leaching increased markedly following sodium nitrate additions. Findlay (2005) suggested cumulative N deposition as a possible explanation for DOC increases in the Hudson River, New York. A study

of peat cores collected across a European N deposition gradient by [Bragazza et al. \(2006\)](#) also showed greater DOC release from high N-deposition sites, attributed to a combination of alleviation of N constraints on microbial activity and reduced production of inhibitory polyphenol compounds by *Sphagnum*. On the other hand, [Worrall et al. \(2006\)](#) concluded, based on analysis of monitoring data, that N inputs and DOC outputs appeared unrelated. Thus, there are several plausible mechanisms by which N may affect DOC availability in soils, but field observations do not uniformly support a simple linkage.

The second hypothesis suggests that declining S deposition has, by reducing soil solution acidity and ionic strength, increased the solubility of (weakly acidic) organic compounds in the soil ([Evans et al. 2006a](#); [Monteith et al. 2007](#)). This theory reprises a hypothesis by [Krug and Frink \(1983\)](#), who argued that increases in mineral acid inputs would be buffered by decreasing mobility of organic acids. Although this mechanism was insufficient to prevent surface water acidification in response to acid deposition, the fundamental mechanisms by which acidity and ionic strength influence organic acid solubility are well established, with laboratory studies showing consistently greater DOC leaching at higher pH ([Whitehead et al. 1981](#); [Hay et al. 1985](#); [Tipping and Hurley 1988](#); [Tipping and Woof 1990](#); [Kennedy et al. 1996](#)). Field studies are less consistent, although some experiments have shown reduced DOC in response to artificial acidification ([Cronan and Aiken 1985](#); [Schindler et al. 1997](#)). In the HUMEX catchment acidification experiment, Norway, DOC decreased in organic soil solution ([Vogt et al. 1994](#)), but not in the lake draining the site ([Hessen et al. 1997](#)). Experimental addition of aluminium chloride to a forest soil led to both acidification and strongly reduced soil solution DOC concentrations ([Mulder et al. 2001](#)), while [Clark et al. \(2005\)](#) showed reduced peat DOC leaching during natural acidic sulphate flushes. With atmospheric S deposition now declining across much of Europe and North America ([Fowler et al. 2007](#)), leading to reduced soil and water acidity ([Evans et al. 2001](#); [Skjelkvåle et al. 2005](#)), the reverse process (increasing DOC in response to declining acidity) would be predicted. A recent trend analysis by [Monteith et al. \(2007\)](#) showed that upward trends in DOC are spatially correlated with downward trends in sulphate ( $\text{SO}_4^{2-}$ ) concentrations across large areas of Europe and North America.

The influence of N deposition on DOC leaching is more difficult to assess from monitoring data alone because: (i) N deposition is not changing with the same magnitude or consistency as S deposition; (ii) most deposited N is retained within forest and moorland ecosystems (e.g., [Nadelhoffer et al. 1999](#); [MacDonald et al. 2002](#); [Aber et al. 2003](#)); (iii) nitrate ( $\text{NO}_3^-$ ) concentrations in soil and surface waters rarely demonstrate the upward trends expected in response to progressive N saturation (e.g. [Wright et al. 2001](#); [Goodale et al. 2003](#); [Stoddard et al. 2003](#)); and (iv) internal ecosystem N cycling generally far exceeds the magnitude of input and output fluxes, such that short-term relationships are difficult or impossible to discern ([Cooper 2005](#)). Nevertheless, N deposition levels are well above background levels in many regions, most ecosystems are accumulating N in the long term, and an N-related mechanism for DOC increases in those same regions thus appears plausible. Given widespread concern about the potential adverse effects of chronic N deposition on terrestrial ecosystems ([Aber et al. 1989, 1998](#); [Stoddard 1994](#)), multiple N manipulation experiments have been undertaken. Many of these studies also measured DOC, providing an opportunity to test of the role of N as a driver of increasing freshwater DOC. In general, the response of DOC to N additions has been a secondary focus of these studies, and in some cases not all DOC measurements have been published.

Here, we used published and some unpublished measurements from 12 long-term fertilisation studies to identify the roles of N amendment and acidification status as controls on ecosystem DOC loss. If N addition or ionic strength drive DOC loss, DOC should have increased in most fertilisation studies. If acidification status drives DOC loss, DOC should have increased or decreased depending on whether the form of N added increased or decreased soil acidity. We tested these alternative responses with measurements of changes in leachate DOC and an index of fertilisation-induced changes in acid neutralising capacity (ANC) across all studies.

## Methods

We reviewed data for 12 plot- or catchment-scale field N manipulation studies, spanning a range of soil and vegetation types across northern Europe and the

northeastern USA. Some of these experiments involve applications of more than one N form, or applications to more than one vegetation type, so in total 17 experiments were analysed (Table 1). Replicated N additions to four locations in Michigan (Pregitzer et al. 2004) have largely been reported in terms of mean response and were therefore treated as a single experiment. Other N fertilisation experiments at Fernow (Adams et al. 2006), Mt. Ascutney (McNulty et al. 2005), Catskill Mountains (Templer et al. 2005) and Niwot Ridge (Bowman et al. 2006) in America, and several NITREX experimental sites in Europe, could not be included as DOC was either not measured or not reported. Field N exclusion studies were also excluded, due to the difficulty of quantifying or controlling N inputs; uncertainty over the effects of removing inexact amounts of reduced and oxidised N (plus other ions in deposition) on acidity; and the impacts of roofs on internal C cycling (e.g. rapid leaching losses from fresh litter deposited on below-canopy roofs).

For each experiment considered, we collated information on (1) the form, level and duration of N additions; (2) ecosystem response in terms of N leaching; (3) changes, if any, in acidity; and (4) changes, if any, in DOC leaching. Unless otherwise stated, soil organic horizon soil solution was measured by zero-tension lysimeters, and mineral horizon soil solution by suction samplers. Chemical analysis methods are described in source references for each site (Table 1 and results section), and considered fully comparable between sites. Given variability in the type and availability of data from each experiment, it was not possible to undertake a systematic statistical analyses of experimental responses across all sites. Insofar as possible, interpretation has been based on previous published analyses for that site.

The net effects of the experimental treatments on soil solution ANC was defined by the charge balance of major base cations and acid anions in soil solution:

$$\text{ANC} = \text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+ + \text{NH}_4^+ - \text{SO}_4^{2-} - \text{Cl}^- - \text{NO}_3^- \quad (1)$$

The approximate acidifying/de-acidifying impact of each N addition depends on (1) the amount of added N leached as either  $\text{NO}_3^-$  or  $\text{NH}_4^+$ ; and (2) the amount of any (N-free) counter ion (variously  $\text{Na}^+$ ,

$\text{SO}_4^{2-}$  or  $\text{Cl}^-$ ) also leached. There may be no impact on acidity if all added N is retained and no other ions are applied. In most experiments that apply  $\text{NH}_4^+$  (as  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{NO}_3$ ),  $\text{NH}_4^+$  is either retained or nitrified to  $\text{NO}_3^-$ , a process which releases two moles  $\text{H}^+$  per mole  $\text{NH}_4^+$  nitrified and allows  $\text{NO}_3^-$  loss to leaching (exceptions can occur in peats, where  $\text{NH}_4$  may remain in solution). Leaching of added  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  or  $\text{NO}_3^-$  (added directly, or indirectly as nitrified  $\text{NH}_4^+$ ) will, according to the mobile anion concept (Reuss and Johnson 1985) also cause the leaching of some combination of base cations or acid cations (i.e.  $\text{H}^+$  and  $\text{Al}^{n+}$ ). Therefore, any  $\text{NH}_4^+$  addition to an ecosystem that is not fully N-retaining should be acidifying. In contrast, experiments where N has been added as  $\text{NO}_3^-$ , with  $\text{Na}^+$  as a counter-ion, are likely to be de-acidifying unless 100% of the  $\text{NO}_3^-$  is leached. This occurs because  $\text{Na}^+$  is normally mobile, whereas a large proportion of the  $\text{NO}_3^-$  is usually retained. This excess of base cation over acid anion leaching is likely (following the charge balance definition) to raise leachate ANC and reduce  $\text{H}^+$  and  $\text{Al}^{n+}$  concentrations. Gaseous ammonia ( $\text{NH}_3$ ) input will also tend to initially raise the pH, by consuming  $\text{H}^+$  ions to form  $\text{NH}_4^+$  (although this effect will be reversed if subsequent nitrification occurs).

As a simple, robust measure of the acidifying/de-acidifying impact of each N addition experiment, the charge balance definition of ANC (Eq. 1) was adapted to define ‘ANC forcing’, an indication of the base cation—acid anion imbalance in the system induced by the experimental treatment, which accounts for retention of the added ions within the system:

$$\text{ANC forcing} = \Delta\text{NH}_4^+ - \Delta\text{NO}_3^- + (\Delta\text{Na}^+) - (\Delta\text{SO}_4^{2-}) - (\Delta\text{Cl}^-) \quad (2)$$

‘ $\Delta X$ ’ represents the difference in the concentration of ion X (in  $\mu\text{eq l}^{-1}$ ) between the treatment and the control. Terms in parentheses are only included in the equation where those ions have been added in the experiment. A positive value indicates that the treatment is likely to have increased ANC and pH, a negative value that it is likely to have decreased them. The equation is best considered as an index of *potential* ANC change, in that it does not indicate what proportion of this experimentally-induced ion

**Table 1** Nitrogen addition experiments considered in this study

Experimental site	Country	Vegetation	Soil type (WRB 2006)	N form(s) added	N deposition (kg N ha <sup>-1</sup> year <sup>-1</sup> )	N treatments (kg N ha <sup>-1</sup> year <sup>-1</sup> )	Start/end (years)	Reference
Pwllpeiran	UK	Acid grassland	Histic podzol	NaNO <sub>3</sub> ,NH <sub>4</sub> NO <sub>3</sub>	11	10–20	1996	Emmett et al. (2001)
Ruabon	UK	Heather	Histic podzol	NH <sub>4</sub> NO <sub>3</sub>	16	10–120	1989	Pilkington et al. (2005a)
Aber	UK	Sitka spruce	Histic podzol	NaNO <sub>3</sub> ,NH <sub>4</sub> NO <sub>3</sub>	25	35–75	1990–1995	Emmett. et al (1998)
Whim	UK	Bog	Histosol	NaNO <sub>3</sub> ,NH <sub>4</sub> Cl,NH <sub>3</sub>	8	8–56	2002	Sheppard et al (2004)
Gårdsjön	Sweden	Spruce/pine	Podzol	NH <sub>4</sub> NO <sub>3</sub>	15	40	1991	Moldan et al. (1998)
Bear Brook	USA	Mixed hardwood	Haplic podzol	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	8	25	1989	Norton et al. (1999a)
IES	USA	Mixed hardwood	Dystric umbrisol	NH <sub>4</sub> NO <sub>3</sub>	10	50	1996	Wallace et al. (2007)
Solling	Germany	Beech	Dystric umbrisol	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	31	140	1982–1996	Meesenburg et al. (2004)
Harvard Forest (pine)	USA	Pine	Dystric umbrisol	NH <sub>4</sub> NO <sub>3</sub>	8	50–150	1988	Magill et al. (2004)
Harvard Forest (hardwood)	USA	Mixed hardwood	Dystric umbrisol	NH <sub>4</sub> NO <sub>3</sub>	8	50–151	1988	Magill et al. (2004)
Michigan (4 sites)	USA	Maple	Podzol	NaNO <sub>3</sub>	7–12	30	1994	Pregitzer et al. (2004)
Åmli	Norway	Scots pine	Podzol	NH <sub>4</sub> NO <sub>3</sub>	10	30–90	1990–1999	Vestgarden et al. (2001)
Experimental Lakes Area	Canada	Conifer, lichen	Leptosol	NaNO <sub>3</sub>	5	40	1995–1996	Lamontagne and Schiff (1999)

imbalance has subsequently been buffered by changes in base cations, versus changes in acid cations. As it is based on leachate/runoff chemistry, the equation implicitly takes account of any ecosystem N retention, N transformations, and also any retention of applied  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$  or  $\text{Cl}^-$ .

All experimental additions were assumed to have increased ionic strength, in approximate proportion to the total N addition. While this assumption could theoretically be violated, if addition of mono-valent ions were to cause a reduction in di- or tri-valent ion concentrations (e.g. reduction in  $\text{Al}^{3+}$  under less acid conditions), calculations for the Aber Forest dataset indicated that soil solution ionic strength consistently increased under both  $\text{NH}_4\text{NO}_3$  and  $\text{NaNO}_3$  additions (data not shown).

## Results

For eight field N-addition studies (Pwllpeiran, Ruabon, Aber, Whim, Gårdsjön, Bear Brook, IES and Solling), previously unpublished or re-analysed data are presented. For four studies (Harvard Forest, Michigan, Experimental Lakes Area, Åmli), data have been extracted from published literature. The 17 individual experiments span plot and catchment manipulations; a range of soils (peats to mineral soils); five vegetation types (bog, heathland, grassland, broadleaf and coniferous forest); different levels of N addition and duration; and five forms of N addition. Across this heterogeneous dataset, N addition invariably led to increased N leaching, at least at the highest dosage rate (Table 2). However DOC did not respond consistently: based on the best estimate of DOC leaving the system (streams in catchment experiments, lowest sampled horizon in plot experiments) and the highest rate of N addition applied, DOC concentrations increased in nine experiments, and decreased in eight (Table 2). Treatment effects on pH and ANC forcing varied predictably in relation to the form of N added:  $\text{NH}_4\text{NO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{Cl}$  additions were all acidifying,  $\text{NaNO}_3$  and gaseous  $\text{NH}_3$  additions were de-acidifying. We found no evidence that the chemical responses of streams in whole catchment manipulations differed substantively from those of soil solutions in plot experiments, so the two data types were analysed together.

Our initial observations suggest that N addition does not consistently affect DOC loss, but that there is a relationship between DOC changes, the form of N added, and the associated acidity change (Table 2). However, given the heterogeneity and complexity of the datasets collated, experimental responses are first examined in detail at individual sites, prior to a final synthesis of results.

### Pwllpeiran, Mid Wales, UK ( $\text{NaNO}_3$ , $\text{NH}_4\text{NO}_3$ )

Pwllpeiran, an acidic grassland on peaty podzolic soils, has received N in solution as  $\text{NaNO}_3$  (20 kg N  $\text{ha}^{-1}$  -  $\text{year}^{-1}$ ) and  $(\text{NH}_4)_2\text{SO}_4$  (10 and 20 kg N  $\text{ha}^{-1}$   $\text{year}^{-1}$ ) since 1997 (Emmett et al. 2001). The experiment is replicated for low- and high-intensity grazing regimes. The high-grazing treatment has substantially altered soil and vegetation C and N cycling (Emmett et al. 2001), and we therefore only consider observations from the low-grazing plots. Mineral soil solution was also strongly affected by lateral flow from above the treatment plots, so we analysed for the O horizon. Two full years of post-treatment data were available, 1998–1999.

Responses to the (relatively low) N doses are small but clear, and dependent on the form of N added (Fig. 1). Mean ANC forcing associated with  $\text{NaNO}_3$  treatment was  $+40 \mu\text{eq l}^{-1}$ , and mean pH for 1998–1999 in these plots was 4.48, versus 4.28 in the control plots. Because pH in pre-treatment samples was higher in the  $\text{NaNO}_3$ -amended plots than in the controls (4.31 vs. 4.15), it is uncertain to what extent later pH differences can be attributed to treatment, rather than between-plot heterogeneity. Mean DOC concentration in the  $\text{NaNO}_3$  plots was  $14.2 \text{ mg l}^{-1}$ , versus  $12.9 \text{ mg l}^{-1}$  in the control plots. DOC concentrations in the  $\text{NaNO}_3$  plots were actually slightly lower than controls in the pre-treatment samples, so this is considered a likely treatment response, albeit small. In the 20 kg N  $\text{ha}^{-1}$   $\text{year}^{-1}$   $(\text{NH}_4)_2\text{SO}_4$  treatment, mean ANC forcing was  $-32 \mu\text{eq l}^{-1}$ , pH was 0.1 unit lower than the controls (having started at similar values), and DOC was  $2 \text{ mg l}^{-1}$  lower at  $10.9 \text{ mg l}^{-1}$ .

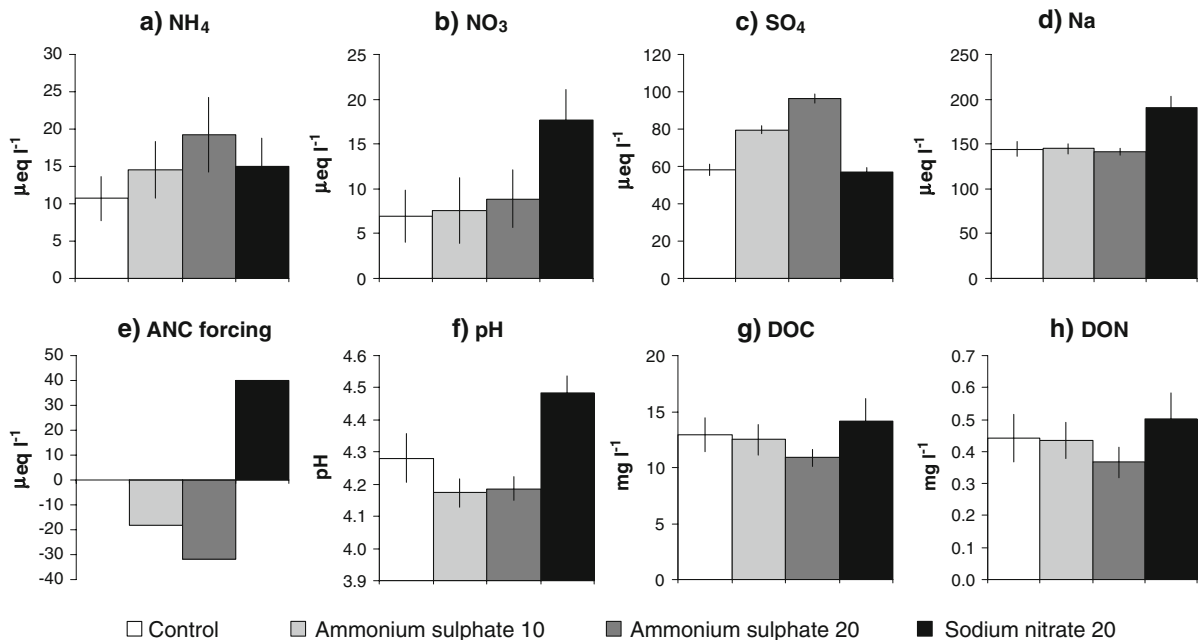
### Ruabon, North Wales, UK ( $\text{NH}_4\text{NO}_3$ )

At Ruabon, a managed *Calluna* heathland on peaty podzols,  $\text{NH}_4\text{NO}_3$  solution has been applied at 40, 80

**Table 2** Average concentrations of inorganic N ( $\mu\text{mol l}^{-1}$ ), DOC ( $\text{mg l}^{-1}$ ), pH and ANC forcing ( $\mu\text{eq l}^{-1}$ ) measured in the organic horizon (O), mineral horizon (M) and stream runoff (S) under ambient conditions (cont) and under the highest level of experimental treatment (treat)

Experiment	N addition ( $\text{kg N ha}^{-1}$ $\text{year}^{-1}$ )			N <sub>cont.</sub>			N <sub>treat.</sub>			DOC <sub>cont.</sub>			DOC <sub>treat.</sub>			pH <sub>cont.</sub>			pH <sub>treat.</sub>			ANC forcing		
	O	M/S	O	O	M/S	O	O	M/S	O	O	M/S	O	O	M/S	O	O	M/S	O	O	M/S	O	O	M/S	
Solling $(\text{NH}_4)_2\text{SO}_4$	82	2026	15	1063	24.0	24.8	3.9	10.9	4.14	3.54	4.50	4.09	–2,360											
Harvard Pine $\text{NH}_4\text{NO}_3$	60	2141	7	1143	53.5	67.4	15.0	17.0	2.94	2.55	3.64	2.94	–1,320											
Harvard Hardwood $\text{NH}_4\text{NO}_3$	23	1805	7	500	35.9	43.8	27.0	15.0	3.12	2.66	3.75	3.21	–550											
Whim $\text{NH}_4\text{Cl}$	10	79	9	39.5	37.1	37.6	3.76	–269																
Åmli $\text{NH}_4\text{NO}_3$	19	212	9	376	80.3	38.5	42.9	1.7	6.00	4.38	5.15	4.64	–171											
Aber $\text{NH}_4\text{NO}_3$	257	511	112	227	41.8	38.0	5.8	3.3	3.88	3.81	4.46	4.46	–145											
Bear Brook $(\text{NH}_4)_2\text{SO}_4$	25	43	2	2.4	2.0	5.47	4.87	–135																
IES $\text{NH}_4\text{NO}_3$	50	108	2	2.3	2.5	4.77	4.68	–106																
Gårdsjön $\text{NH}_4\text{NO}_3$	40	58	5	16.9	14.6	4.01	3.91	–50																
Pwllpeiran $(\text{NH}_4)_2\text{SO}_4$	18	28	2	12.9	10.9	4.28	4.19	–32																
Ruabon $\text{NH}_4\text{NO}_3$	31	87	2	23.3	17.7	4.19	4.10	–13																
Pwllpeiran $\text{NaNO}_3$	18	33	3	12.9	14.2	4.28	4.48	+40																
Aber $\text{NaNO}_3$	257	799	112	558	41.8	41.1	5.8	6.3	3.88	4.07	4.46	4.42	+51	+81										
ELA $\text{NaNO}_3$	40	141	5	18.8	43.2	4.35	4.73	+112																
Whim $\text{NaNO}_3$	10	83	3	39.5	54.4	3.76	4.14	+146																
Whim $\text{NH}_3$ (gas)	38	474	19	36.7	86.7	3.76	4.23	+345																
Michigan $\text{NaNO}_3$	30	373	17	7.4	20.4	–470																		

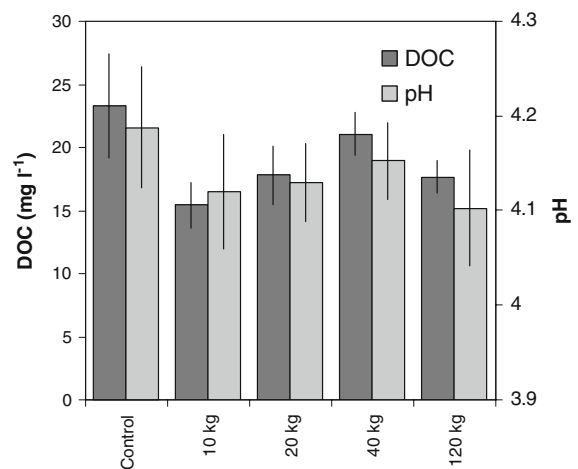
Sites are ranked by the estimated impact of N treatment in terms of ANC forcing. Horizontal line differentiates treatments having a negative ANC forcing (ammonium salts) from those with a positive ANC forcing (nitrate salts and ammonia gas). For Gårdsjön, control catchment pH and DOC estimates are based on comparison of standardised  $\text{H}^+$  and DOC concentrations (see text for further details of this, and data derivation and references for other sites). Note also that the IES plots received a higher level of N addition ( $100 \text{ kg N ha}^{-1} \text{ year}^{-1}$ ) from 1996–1999



**Fig. 1** Pwllpeiran experiment mean O horizon soil solution chemistry, by treatment, 1998–1999

and 120 kg N ha<sup>-1</sup> year<sup>-1</sup> since 1989. Analysis of O horizon leachate after 10 years (Pilkington et al. 2005a, b) showed high N retention, but NO<sub>3</sub><sup>-</sup> concentrations increased significantly from 3 μeq l<sup>-1</sup> in the controls to 37 μeq l<sup>-1</sup> under the highest treatment. Mineral (E) horizon leachate showed smaller, but still significant, increases in NO<sub>3</sub><sup>-</sup> (0.5–17 μeq l<sup>-1</sup>). N addition led to significant pH reductions in both horizons, and increased Al concentrations in the E horizon. ANC forcing, calculated from the data of Pilkington et al. (2005a), was negative but small in both horizons (O horizon -13 μeq l<sup>-1</sup>, E horizon -16 μeq l<sup>-1</sup> in the highest treatment).

DOC was not measured in the study above, but has been measured on O horizon samples in parallel treatment plots which have received NH<sub>4</sub>NO<sub>3</sub> additions of 10, 20, 40 and 120 kg N ha<sup>-1</sup> year<sup>-1</sup> since 1998. Although all treated plots are on average more acid than the controls, there is no clear relationship between treatment level and pH (Fig. 2). Similarly, DOC concentrations do not relate strongly to treatment level, but are on average lower in all treatments than in the control plots. Treatment mean DOC and pH are positively correlated (Fig. 2;  $R^2 = 0.80$ ,  $P = 0.042$ ), although this becomes non-significant if individual plot data are analysed.



**Fig. 2** Ruabon experiment mean O horizon soil solution DOC and pH, by treatment, in 'new' plots, 2007

Aber Forest, North Wales, UK (NaNO<sub>3</sub>, NH<sub>4</sub>NO<sub>3</sub>)

The Aber experiment was located in a Sitka spruce plantation on peaty podzols (Emmett et al. 1995, 1998). NH<sub>4</sub>NO<sub>3</sub> (35 kg N ha<sup>-1</sup> year<sup>-1</sup>) and NaNO<sub>3</sub> (35 and 75 kg N ha<sup>-1</sup> year<sup>-1</sup>) solutions were applied below-canopy from 1991 to 1995. NO<sub>3</sub><sup>-</sup> addition led to a rapid, near 1:1 increase in NO<sub>3</sub><sup>-</sup> leaching



whereas  $\text{NH}_4^+$  was largely retained, leading to soil acidification under the  $\text{NH}_4\text{NO}_3$  treatment (Emmett et al. 1998). No clear DOC responses were recorded.

We re-analysed soil solution data from the last two full years of measurement, for both O and B horizons (Fig. 3). The  $\text{NH}_4\text{NO}_3$  treatment was associated with a strong negative ANC forcing in both horizons, and lower O horizon pH. This pH response was absent in the B horizon, but mean Al concentrations were elevated (95 vs. 72  $\mu\text{g l}^{-1}$ ). Addition of  $\text{NaNO}_3$  had less effect on the acid-base balance than in other experiments due to the very low  $\text{NO}_3^-$  retention; ANC forcing was slightly positive at both dosage levels in the O horizon, but only positive in the B horizon under the larger (75  $\text{kg N ha}^{-1} \text{ year}^{-1}$ )  $\text{NaNO}_3$  treatment. The pH of O horizon leachate was elevated at both dosage levels, but again this difference was absent in the less acid B horizon.

DOC concentrations were much higher in the O than the B horizon (control plot means 42 and 6  $\text{mg l}^{-1}$  respectively), indicating strong DOC retention between horizons. DOC concentrations in the  $\text{NH}_4\text{NO}_3$  addition plots were 9% lower than controls in the O horizon, and 44% lower in the B horizon (Fig. 3f, l). This is consistent with an effect of acidity, and possibly Al, on DOC solubility during transit through the mineral soil (Kennedy et al. 1996).  $\text{NaNO}_3$  additions had no clear or consistent impact on DOC in either horizon, although the rank of mean DOC across all the three treatments and both horizons did correspond to that for ANC forcing.

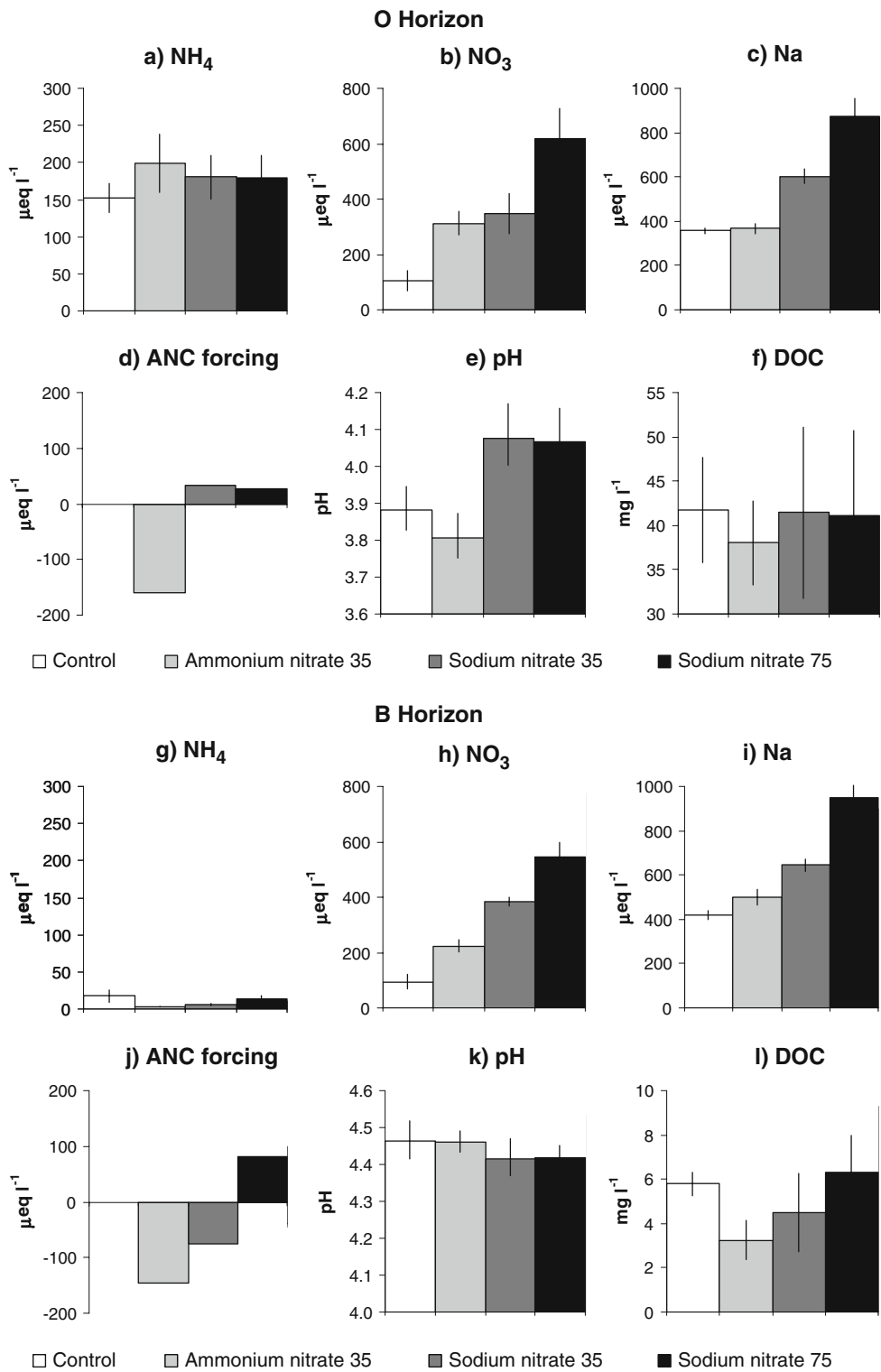
Whim Bog, Southeast Scotland, UK ( $\text{NaNO}_3$ ,  $\text{NH}_4\text{Cl}$ , gaseous  $\text{NH}_3$ )

Whim, a lowland raised bog with dwarf shrub species and *Eriophorum* over a *Sphagnum* layer (Sheppard et al., 2004), has received multiple treatments since 2002:  $\text{NaNO}_3$  solution at 8, 24 and 56  $\text{kg N ha}^{-1} \text{ year}^{-1}$ ;  $\text{NH}_4\text{Cl}$  solution at the same rates; and gaseous  $\text{NH}_3$  via a release system which exposes a downwind transect to dry  $\text{NH}_3$  deposition. Measured near-source deposition is 70  $\text{kg N ha}^{-1} \text{ year}^{-1}$ , decreasing towards ambient levels at a distance of 105 m. Close to the  $\text{NH}_3$  source, significant die-back of *Calluna vulgaris*, *Sphagnum* and other mosses has occurred, whilst other dwarf shrub species have increased in cover. Peat solution has been sampled with suction samplers at 5–10 cm since 2006.

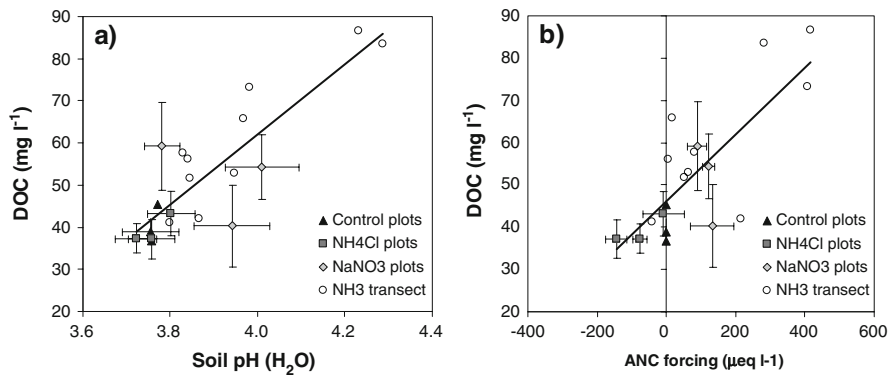
Results show divergent chemical responses to different N forms. Wet  $\text{NH}_4\text{Cl}$  additions have had little impact, with mean pH and DOC concentrations remaining similar to controls in all treatments (Fig. 4a). Wet  $\text{NaNO}_3$  addition has increased pH and DOC leaching at two treatment levels (8 and 56  $\text{kg N ha}^{-1} \text{ year}^{-1}$ ). Exposure to gaseous  $\text{NH}_3$  (effectively,  $\text{NH}_4\text{OH}$  deposition) has raised pH, and DOC concentrations have more than doubled close to the  $\text{NH}_3$  source, declining gradually to ambient concentrations along the transect. Combining all control and treatment plot data reveals a highly significant correlation ( $R^2 = 0.72$ ,  $p < 0.001$ ) between mean soil solution DOC and mean soil pH (measured in water) at the same location. ANC forcing values show a similar pattern (Fig. 4b), with positive mean values in eight out of ten samplers along the  $\text{NH}_3$  transect (highest value adjacent to source +410  $\mu\text{eq l}^{-1}$ ); positive values for all three  $\text{NaNO}_3$  treatment levels (+122  $\mu\text{eq l}^{-1}$  in the highest treatment); negative values in all three  $\text{NH}_4\text{Cl}$  treatments (−145  $\mu\text{eq l}^{-1}$  in the highest treatment); and a significant overall correlation ( $R^2 = 0.60$ ,  $p < 0.001$ ) between DOC and ANC forcing.

Gårdsjön, Southern Sweden ( $\text{NH}_4\text{NO}_3$ )

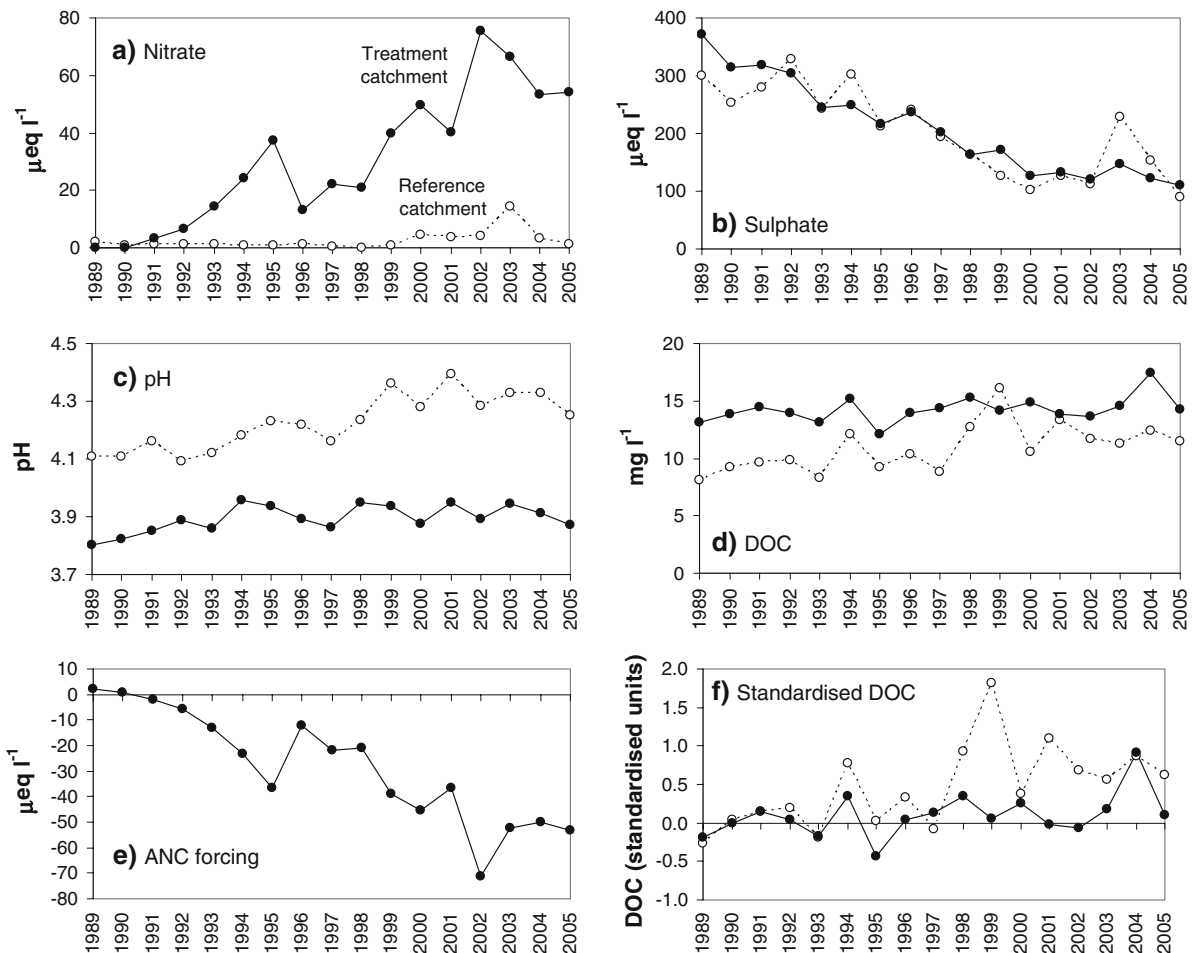
At Gårdsjön,  $\text{NH}_4\text{NO}_3$  solution has been added to a Norway spruce-dominated catchment at 40  $\text{kg N ha}^{-1} \text{ year}^{-1}$  since 1991 (Moldan et al. 2006). Stream  $\text{NO}_3^-$  concentrations were near-zero prior to the experiment, and remain low in the nearby reference catchment, but have risen progressively since N additions began in the treated catchment (Moldan et al. 2006; Fig. 5). Mineralisation and nitrification rates, and foliage and litter N content, have all increased (Kjønås et al. 1998). Interpretation of acidity responses to N additions at Gårdsjön is complicated by large decreases in ambient S deposition, which have led to recovery from acidification in both reference and treatment catchments. Furthermore, the treatment catchment was more acid than the reference even before N additions began (Fig. 5c). However, time series data suggest that pH recovery has been greater in the reference catchment, whereas recovery levelled off or even reversed at the treated catchment following the onset of  $\text{NO}_3^-$  leaching in the early 1990s. There has been a clear, increasingly negative ANC forcing associated with rising  $\text{NO}_3^-$  leaching.



**Fig. 3** Aber experiment mean soil solution chemistry, by treatment, 1994–1997



**Fig. 4** Whim experiment 2006–2007 mean peat soil solution DOC versus (a) mean soil pH and (b) mean ANC forcing, for wet N addition treatments and gaseous NH<sub>3</sub> transect



**Fig. 5** Gårdsjön experiment mean runoff chemistry in treatment and reference catchments, 1990–2005

After 15 years of treatment, DOC concentrations show some divergence between treatment and reference catchments (Fig. 5d). As mean DOC concentrations

also differed between catchments at the start of the experiment, they have been re-expressed in standardised form (subtracting the mean of the first 5 years, and

dividing by the standard deviation for the same period, Fig. 5f), which more clearly illustrates the relative DOC increase in the reference catchment. For 2001–2005, standardised DOC concentrations have been significantly higher in the reference catchment (two sample *t*-test,  $p < 0.001$ ), and we estimate that, due to  $\text{NH}_4\text{NO}_3$  addition, DOC concentrations are  $2.6 \text{ mg l}^{-1}$  (13%) lower than they would have been under ambient conditions. Applying the same approach to 2001–2005  $\text{H}^+$  concentrations suggest that mean treatment catchment runoff pH would have been 4.01 under ambient conditions, compared to an observed mean of 3.91.

#### Bear Brook, Maine, USA ( $(\text{NH}_4)_2\text{SO}_4$ )

The Bear Brook study comprises two adjacent broadleaf-dominated catchments, one of which has received  $25 \text{ kg N ha}^{-1} \text{ year}^{-1}$  as dry  $(\text{NH}_4)_2\text{SO}_4$  since 1989 (Norton et al. 1999a). Concentrations of  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{H}^+$  and Al have all increased, whilst pH and  $\text{HCO}_3^-$  have decreased (Norton et al. 1999b; Norton et al. 2004). Catchment retention of added N decreased from 96% to 81%, and retention of added S from 86% to 34%, by 1994 (Kahl et al. 1999). Internal N cycling has accelerated (Jefts et al. 2004), and tree foliar N concentrations have increased (Elvir et al. 2005).  $(\text{NH}_4)_2\text{SO}_4$  addition has thus led to both ecosystem N enrichment and acidification.

Bear Brook data to 2003 (Fig. 6) suggest pH has been fairly stable since the mid-1990s, consistent with calculated ANC forcing. DOC concentrations in the streams are fairly low ( $2.7 \text{ mg l}^{-1}$  in both catchments prior to treatment). David et al. (1999) reported no clear DOC changes up to 1994, but noted lower concentrations in the treated catchment in 1995, and a more pronounced decrease in organic acid concentrations. The longer dataset shows recent upward trends in DOC at both catchments, but a small, sustained relative reduction in DOC concentrations in the treated catchment. For the full treatment period, average DOC in the treated catchment was  $0.35 \text{ mg l}^{-1}$  (16%) lower than in the reference catchment.

#### Millbrook, New York, USA ( $\text{NH}_4\text{NO}_3$ )

The Millbrook (IES) experiments comprise six paired 20 m diameter plots in oak-dominated hardwood stands on silty loam with a thin O horizon (Wallace

et al. 2007). In each pair, one plot received  $100 \text{ kg N ha}^{-1} \text{ year}^{-1}$   $\text{NH}_4\text{NO}_3$  from 1996 to 1999, reducing to  $50 \text{ kg N ha}^{-1} \text{ year}^{-1}$  thereafter. In B horizon soil solution, sampled 2005–2006, treatment plot mean  $\text{NO}_3^-$  was  $106 \text{ } \mu\text{mol l}^{-1}$ , versus  $1 \text{ } \mu\text{mol l}^{-1}$  in the controls.  $\text{NH}_4^+$  was  $<2 \text{ } \mu\text{mol l}^{-1}$  in all plots. Mean pH was slightly lower in the treatment plots (4.68) compared to controls (4.77), mean ANC forcing across all plots was  $-105 \text{ } \mu\text{mol l}^{-1}$ . Mean DOC was  $2.3 \text{ mg l}^{-1}$  in the controls and  $2.5 \text{ mg l}^{-1}$  in the treated plots, but responses were highly variable, ranging from a 25% DOC decrease versus control in one of the paired plots to a 71% DOC increase in another pair.

At the IES experiments, N addition has led to tree mortality (Wallace et al. 2007). It appears that elevated N inputs led to slightly increased growth of some trees (fertilisation effect) but killed others (N saturation effect), with overall mortality of 35% of trees in treatment plots, compared to 2% in control plots. Mortality rates were highly variable among treatment plots, and examination of % DOC change for each treatment-control pair against % dead basal area shows a strong relationship (Fig. 7,  $R^2 = 0.79$ ,  $p = 0.019$ ). In plots with little mortality, DOC decreased in response to  $\text{NH}_4\text{NO}_3$  addition, and DOC only increased in plots where  $>20\%$  mortality occurred.

#### Solling, Northwest Germany ( $(\text{NH}_4)_2\text{SO}_4$ )

At Solling,  $140 \text{ kg N ha}^{-1} \text{ year}^{-1}$   $(\text{NH}_4)_2\text{SO}_4$  were applied to a mature beech stand on acid brown mineral soils from 1983 to 1993 (Meesenburg et al. 2004). Unlike all the other experiments described, soils at Solling were not glaciated and have a high anion adsorption capacity. In the first 3 years of addition, 100% of added S was retained in the soil, declining to 12% in 1992, after which the soils became a net  $\text{SO}_4^{2-}$  source (Meesenburg et al. 2004). N leaching, already high before the experiment, rose further (Fig. 8), and over 1983–1996 around half of all N additions were exported, predominantly as  $\text{NO}_3^-$ . ANC forcing associated with the elevated  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  leaching averaged  $-3,300 \text{ } \mu\text{eq l}^{-1}$  at 10 cm during 1990–1993, and  $-2,400 \text{ } \mu\text{eq l}^{-1}$  at 100 cm. Soil water pH decreased from 4.1 to 3.5 at 10 cm, and from 4.5 to 4.1 at 100 cm. Foliar % N increased significantly with treatment, while  $\text{NH}_4^+$

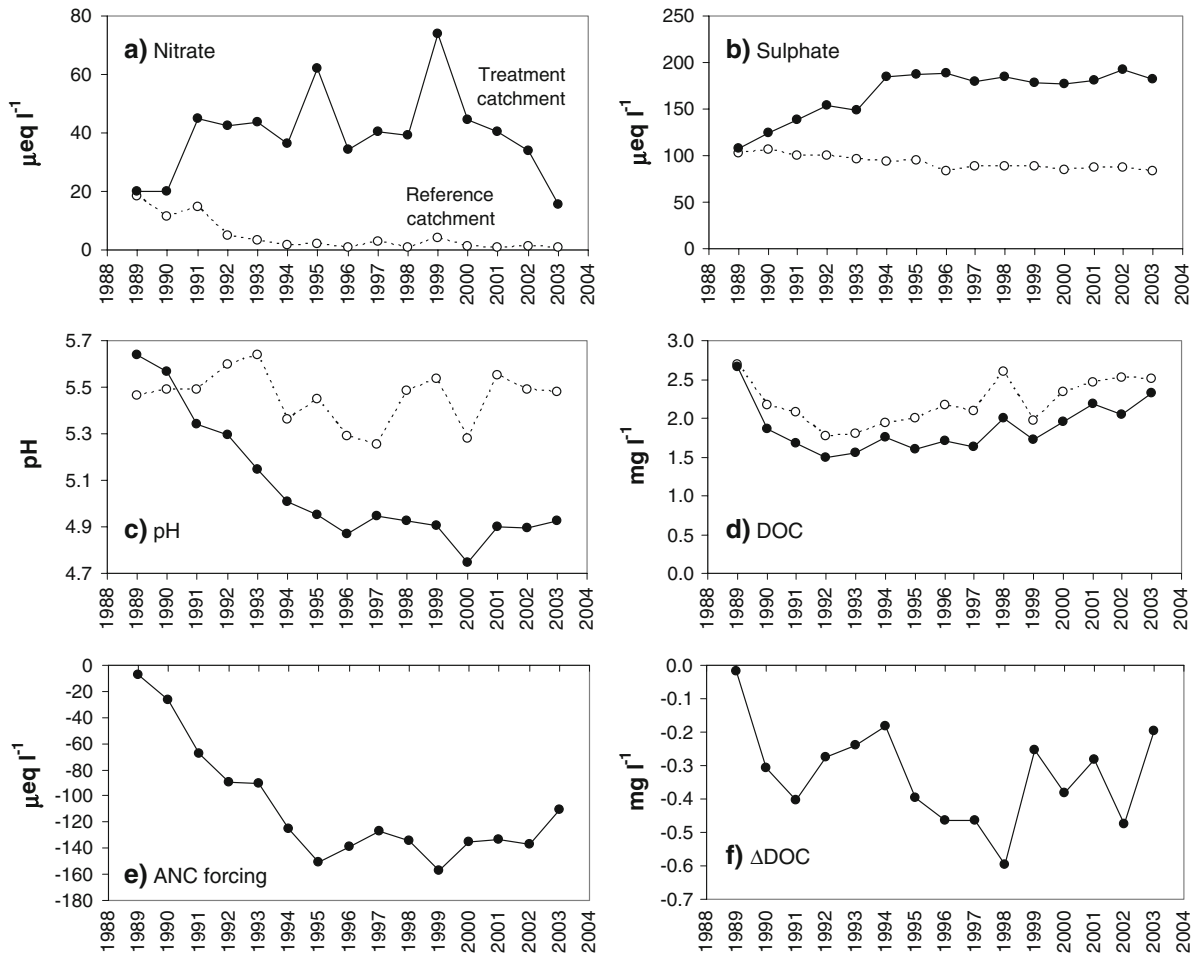


Fig. 6 Bear Brook experiment mean runoff chemistry in treatment and reference catchments, 1989–2003

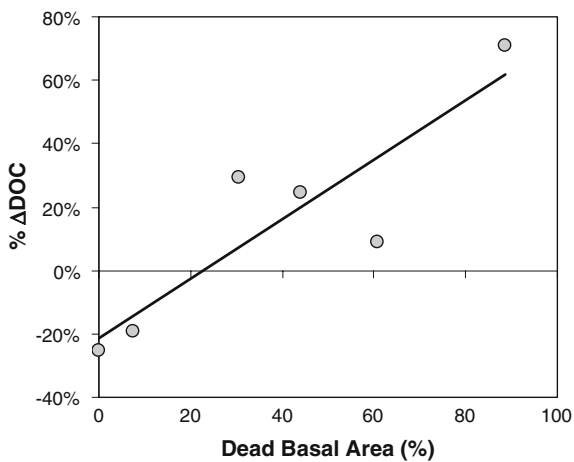


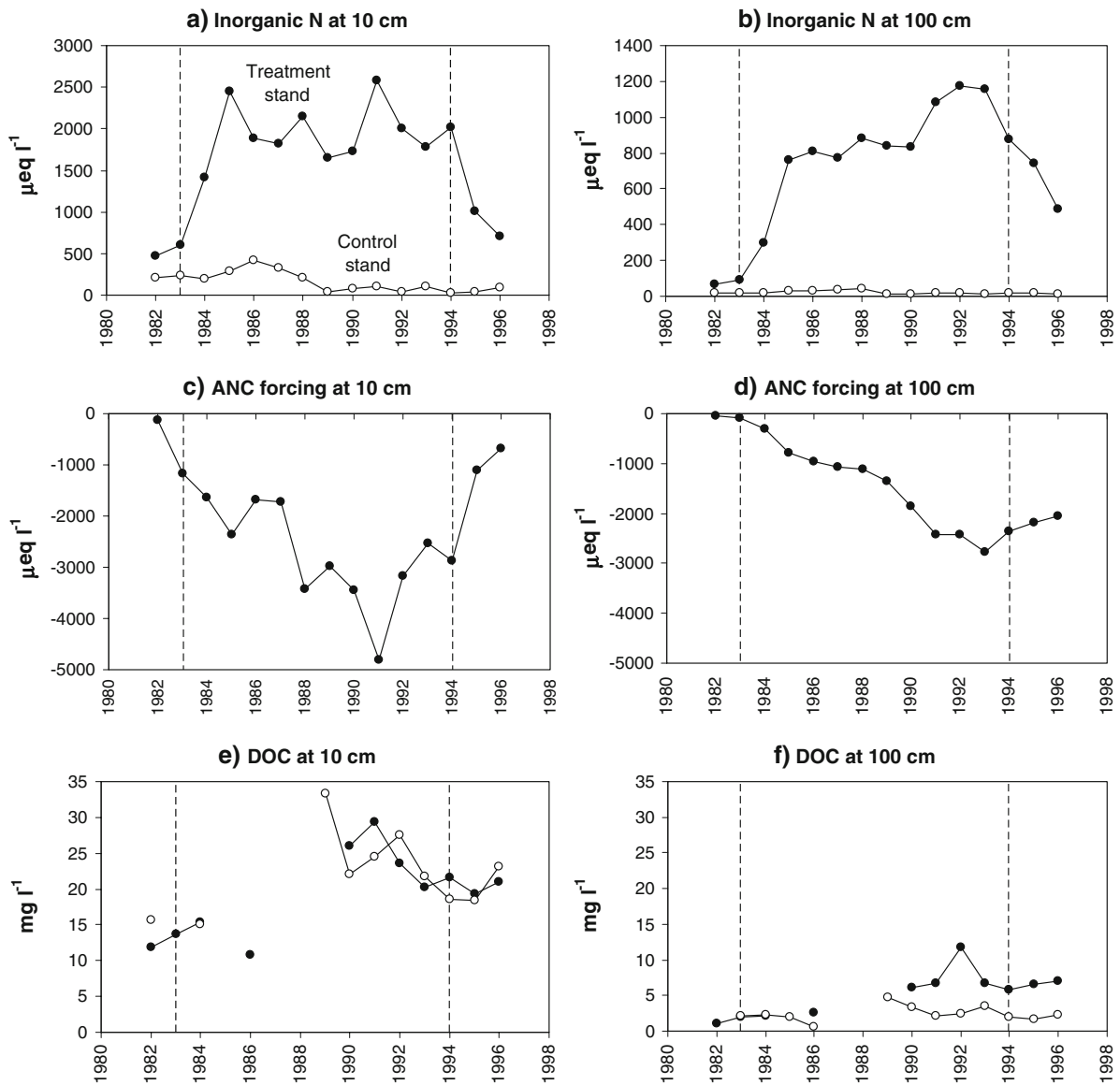
Fig. 7 Institute of Ecosystem Studies experiment, percentage change in DOC concentration versus percentage dead basal area in the treatment plots, for each treatment-control pair

and NO<sub>3</sub><sup>-</sup> immobilisation rates decreased (Meiwes et al. 1998; Corre et al. 2003).

At 10 cm, DOC in soil solution was unchanged after a decade of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> addition (1990–1993 treatment mean 24.8 mg l<sup>-1</sup>, control mean 24.0 mg l<sup>-1</sup>). At 100 cm, however, large DOC increases were recorded (1990–1993 treatment mean 7.8 mg l<sup>-1</sup>, control mean 2.9 mg l<sup>-1</sup>). This increase, coincident with a large pH decrease, contrasts strongly with results from the other experiments presented.

Harvard Forest, Massachusetts, USA (NH<sub>4</sub>NO<sub>3</sub>)

The Harvard Forest experiment comprises 50 and 150 kg N ha<sup>-1</sup> year<sup>-1</sup> additions of NH<sub>4</sub>NO<sub>3</sub>, since 1988, to a mixed hardwood stand and a red pine



**Fig. 8** Solling experiment annual mean inorganic N concentration, ANC forcing and DOC at two depths, 1982–1996

stand. Magill et al. (2004) report rapid increases in dissolved inorganic N (predominantly  $\text{NO}_3^-$ ) leaching in the high-N pine stand; smaller, delayed increases at the high-N hardwood and low-N pine stands; and near-zero concentrations in both control stands and the low-N hardwood stand. Venterea et al. (2003) measured significant, and very large, treatment-induced soil pH decreases in both hardwood and pine stands ( $\text{H}^+$  increase  $>1,400 \mu\text{eq l}^{-1}$  in both O horizons). Based on data reported by McDowell et al (2004) and Magill et al. (2004), ANC forcing is

approximately  $-300 \mu\text{eq l}^{-1}$  beneath the litter layer in both high-N plots and in the mineral soil of the high-N hardwood plots, and  $-1,000 \mu\text{eq l}^{-1}$  in the mineral soil in the pine high-N plot (Table 2). Biomass and litter N content increased and, as at the IES experiment, tree mortality increased with both high-N treatments and was particularly severe in the high-N pine plots (Magill et al. 2004).

McDowell et al. (2004) report no change in DOC leaching below from the forest floor and a substantial (but non-significant) DOC increase beneath the pine

high-N plots. Increases were also recorded in the biodegradable fraction of DOC (Yano et al. 2000). Frey et al. (2004) observed a decrease in phenol oxidase enzyme production. McDowell et al. (2004) suggest that this, together with tree mortality in the pine stand, should have decreased DOC production, and that other processes must counterbalance these decreases. Both they and Yano et al. (2000) suggest that abiotic controls may influence DOC loss. Magill et al. (2004) reported unchanged DOC in mineral soil solution, although the data presented (their Fig. 2) do suggest a decrease in DOC with N addition beyond the error range shown in the hardwood stand, from around  $21 \text{ mg l}^{-1}$  in the control plots to around  $15 \text{ mg l}^{-1}$  in the high-N plots. This would represent a 29% reduction in DOC leaching from the hardwood ecosystem, consistent with observed acidification. The lack of a DOC response in the pine stand cannot be directly explained by either an N-enrichment or an acidification mechanism.

#### Michigan experiments, USA ( $\text{NaNO}_3$ )

$\text{NaNO}_3$  has been applied at  $30 \text{ kg N ha}^{-1} \text{ year}^{-1}$  to replicated plots in four sugar maple-dominated hardwood stands (A, B, C, D) in Michigan since 1994 (Pregitzer et al. 2004; Zak et al. 2006). After 9 years of treatment, Pregitzer et al. (2004) reported a twenty-fold increase in soil solution  $\text{NO}_3^-$  concentrations relative to controls, while DOC increased by a factor of 2.3. By 2004, DOC in the  $\text{NaNO}_3$  plots averaged  $18.5 \text{ mg l}^{-1}$  versus  $6.6 \text{ mg l}^{-1}$  in the controls (Smemo et al. 2007). Interpretation has focused on biological responses, including inhibition of lignolytic activity (Pregitzer et al. 2004; Waldrop and Zak 2006; Smemo et al. 2007). Smemo et al. (2007) found increased polyphenolic and aromatic content of DOC leached from the  $\text{NaNO}_3$  plots relative to controls. Pregitzer et al. (2004), based on column leaching experiments, concluded that increased DOC losses were not due to ionic strength effects on DOC desorption, but Smemo et al. (2006), finding no change in DOC production from fresh litter, suggested that  $\text{NaNO}_3$  addition has reduced the abiotic sink for DOC in the mineral soil.

Data presented by Pregitzer et al. (2004) indicate mean  $\text{NO}_3^-$  for the last 5 years was around  $370 \text{ } \mu\text{eq l}^{-1}$  versus  $10 \text{ } \mu\text{eq l}^{-1}$  in the controls (their Fig. 2).  $\text{NH}_4^+$  concentrations were unchanged. Leaching of  $\text{Na}^+$

was not reported, but given the importance of N as a nutrient, retention of  $\text{NO}_3^-$  is likely to greatly exceed retention of  $\text{Na}^+$ , which is biologically and chemically unreactive. If no  $\text{Na}^+$  were retained, concentrations would increase by  $1,000 \text{ } \mu\text{eq l}^{-1}$ , giving an ANC forcing of  $+630 \text{ } \mu\text{eq l}^{-1}$ . This estimate is obviously uncertain in the absence of reported  $\text{Na}^+$  data, and may well be an overestimate, but nonetheless it seems probable that  $\text{NaNO}_3$  additions have had a substantial positive impact on ANC. Smemo et al. (2007) report a small overall increase in the mean pH of mineral horizon soil water in the  $\text{NaNO}_3$  plots (6.07) relative to controls (5.93), consistent with a pH effect on DOC sorption. They do not report complete pH data, but indicate that the stand with the largest DOC difference (stand B) had higher pH in the control (6.30) than the paired  $\text{NaNO}_3$  plot (5.77), concluding therefore that changing pH could not be responsible for the DOC increase at this site. Pregitzer et al. (2007) report that this same stand had almost double the organic C content in the top 10 cm of the  $\text{NaNO}_3$  plot, relative to the control (differences in other stands were much smaller), thus differences in DOC production between treatment and control plots at this stand (whether due to treatment or inherent plot variability) appear to outweigh any effects of  $\text{NaNO}_3$ -induced acidity change on subsequent DOC retention.

#### Åmli, Southern Norway ( $\text{NH}_4\text{NO}_3$ )

Åmli, a Scots pine forest, received 30 and  $90 \text{ kg N ha}^{-1} \text{ year}^{-1}$  as  $\text{NH}_4\text{NO}_3$  from 1990. Soil solution measurements from 1997–1999 (Vestgarden et al. 2001) showed significant increases in mean  $\text{NO}_3^-$  between control and high-N treatment plots, from 1 to  $136 \text{ } \mu\text{mol l}^{-1}$  in the O horizon, and 1 to  $270 \text{ } \mu\text{mol l}^{-1}$  in the B horizon. Changes in  $\text{NH}_4^+$  were smaller (O horizon  $18\text{--}76 \text{ } \mu\text{mol l}^{-1}$ , B horizon  $8\text{--}106 \text{ } \mu\text{mol l}^{-1}$ ). Overall, treatment reduced N retention from  $>90$  to 63%; tree growth and litterfall doubled; soil C/N decreased in both horizons; B horizon  $\text{H}^+$  and Al concentrations increased; and pH reduced by 0.5–1 units (Vestgarden et al. 2001, 2004).

DOC concentrations were significantly, and dramatically, lower in the B horizon under both levels of N addition ( $<4$  vs.  $43 \text{ mg l}^{-1}$  in controls). O horizon concentrations were also much lower ( $<40$  vs.

80 mg l<sup>-1</sup>), but differences were reported non-significant (Vestgarden et al. 2001). The authors attributed DOC reductions to increased microbial DOC consumption, although down-profile decreases in DOC (in both control and treated plots) were attributed primarily to abiotic factors.

Experimental Lakes Area, Northwest Ontario, Canada (NaNO<sub>3</sub>)

An ephemeral stream catchment in the Experimental Lakes Area, comprising bedrock outcrops and conifer 'forest islands' with up to 50 cm soil, was fertilised from April 1995 to August 1996 with 40 kg N ha<sup>-1</sup> year<sup>-1</sup> as NaNO<sub>3</sub> (Lamontagne and Schiff 1999). NO<sub>3</sub><sup>-</sup> concentrations increased rapidly from 1 μmol l<sup>-1</sup> (pre-treatment, and in two reference catchments) to around 100 μmol l<sup>-1</sup>. Stream pH increased from approximately 4.35–4.75, and DOC from approximately 19–43 mg l<sup>-1</sup> (estimated from 1996 data, Table 3 of Lamontagne and Schiff 1999). After treatment ceased, NO<sub>3</sub><sup>-</sup> rapidly returned to pre-treatment levels, whereas pH and DOC remained elevated. Lamontagne and Schiff (1999) noted the positive impact of NaNO<sub>3</sub> addition on pH, and considered that organic acid dissociation may have buffered this change. Stimulation of decomposition by N addition was considered minor, because DOC increases were similar from high-C/N forest soils and low-C/N lichen patches.

## Synthesis and discussion

DOC concentrations increased in nine and decreased in eight of the experiments analysed (Table 2). Including individual soil horizons and treatment levels for each experiment, there was no consistent DOC response to either the rate of N addition (Fig. 9a) or the resultant increase in soil solution inorganic N concentration (Fig. 9b). Based on these N-addition experiments, therefore, we are unable to support the hypothesis that increased N input generally leads to increased DOC loss.

On the other hand, there does appear to be a relationship between DOC response and the *form* of N added: DOC concentrations increased with treatment in all 5 NaNO<sub>3</sub> addition experiments, and in one experiment with elevated gaseous NH<sub>3</sub>. DOC

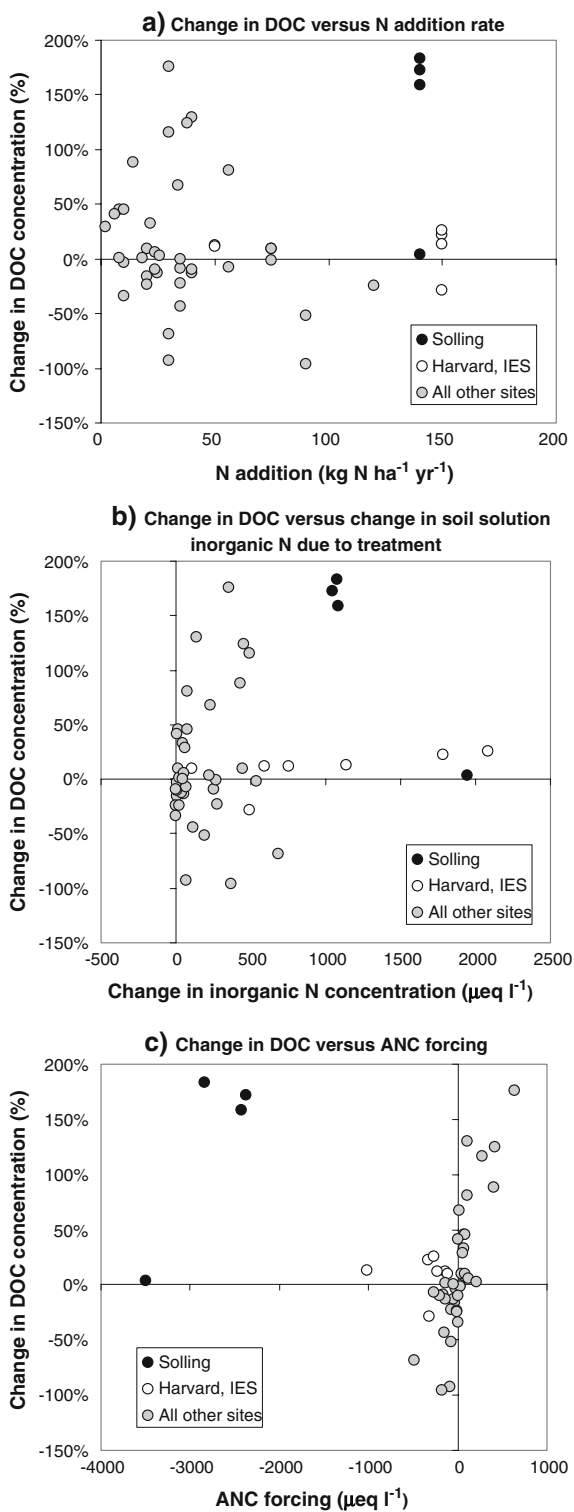
**Fig. 9** DOC response to all individual experimental treatments versus N addition rate (a), treatment-related increase in soil solution inorganic N concentration (b) and ANC forcing (c). Footnote: Data presented for all treatments at each site, and for both organic and mineral horizons where available

decreased with treatment in 8 out of 11 experiments where an NH<sub>4</sub> salt ('NH<sub>4</sub>X') was added, and increased in the remaining three. This form-dependent DOC response to N addition apparently corresponds to the effects of N form on soil acidity, namely a general decrease in acidity with NaNO<sub>3</sub> or NH<sub>3</sub> addition, and an increase in acidity with NH<sub>4</sub>X addition. The treatment-induced cation-anion imbalance, or ANC forcing, associated with the different N additions appears to be a reasonable predictor of DOC response (Fig. 9c), but with outliers for the three NH<sub>4</sub>X addition experiments where DOC increased or did not change: Solling in particular, and to a lesser extent the Harvard Forest and IES experiments.

We propose that atypical DOC responses at these sites may be explained by several factors. First, the Solling and Harvard experiments received larger N doses (140 and 150 kg N ha<sup>-1</sup> year<sup>-1</sup> respectively) than any other experiment studied. The IES experiments also received 100 kg N ha<sup>-1</sup> year<sup>-1</sup> during 1996–1999; of the remaining experiments, only the high-N treatment at Ruabon exceeded 100 kg N ha<sup>-1</sup> year<sup>-1</sup>, and at this site N retention remains very high. It is possible that, with the higher N loadings at Solling and Harvard Forest, there was indeed an N-induced increase in DOC production, outweighing any acidification-induced decrease. Such an interpretation is perhaps supported by the greater overall consistency of DOC increases in response to de-acidifying N treatments (in which N and acidity effects would be reinforcing), compared to acidifying N treatments (in which N and acidity effects would be offsetting). On the other hand, the Solling and Harvard experiments were also (by far) the most acidifying, with a maximum ANC forcing of -1,000 μeq l<sup>-1</sup> at Harvard and -3,500 μeq l<sup>-1</sup> at Solling, compared to -500 μeq l<sup>-1</sup> in the other experiments. At very low pH, the DOC-pH solubility relationship can reverse, as organic molecules become positively charged and therefore more soluble (Mulder et al. 1994).

Two other mechanisms may be relevant. Solling is the only site not to have undergone glaciation, and



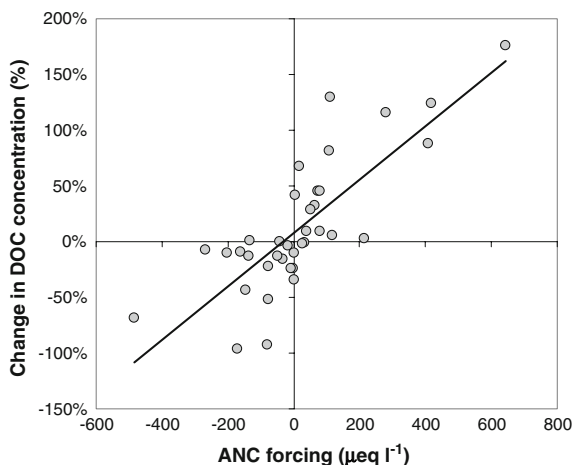


consequently has a much higher anion adsorption capacity. In such soils,  $\text{SO}_4^{2-}$  and organic anions compete for adsorption sites (Kalbitz et al. 2000). In a study of three similar German forests, Zech et al. (1994) found dramatically increased mineral soil solution DOC concentration with increased acidification, which was attributed to decreased DOC sorption. The lack of DOC change at 10 cm at Solling, with large increases at depth, is consistent with this mechanism. Zech et al. (1994) also proposed that at their most S- and N-polluted site, crown thinning could have increased forest floor DOC production, as elevated radiation intensity and temperature (together with elevated N) enhanced microbial activity. This mechanism is not applicable to Solling, where vegetation changes did not occur, but appears relevant to the Harvard and IES sites, where significant treatment-induced tree mortality was observed. At the IES sites (Fig. 6), DOC *did* decrease with acidifying  $\text{NH}_4\text{NO}_3$  addition in plots with low tree mortality, but increased in proportion to percentage dead basal area in the remaining plots. At Harvard, maximum mortality in the pine high-N stand coincided with DOC increases, despite a large decrease in soil pH. It seems likely that, in addition to any effect of increased forest floor light levels, a pulse of DOC will be released following tree mortality due to death of fine roots, mycorrhizae and other microbial biomass formerly supported by root exudation.

Based on these observations, we argue that the Solling, Harvard and IES experiments can reasonably be treated as having complicating factors from anion exchange or tree mortality, at least regarding the direct relationship between (experimentally N-induced) acidity change and DOC response in glaciated soils. The only other location with potentially similar concerns is the Whim  $\text{NH}_3$  experiment, where partial vegetation dieback near the  $\text{NH}_3$  source could have enhanced DOC loss. However, in biomass terms this dieback is much smaller than for the forest sites, and there was no deviation from linear DOC-pH and DOC-ANC forcing relationships at samplers beneath areas of vegetation dieback (Fig. 4). Therefore, we excluded the Solling, Harvard and IES experiments from the final analysis, but retained the

Whim  $\text{NH}_3$  experiment. The resulting plot of DOC change against ANC forcing (Fig. 10) reveals a highly significant correlation between percentage DOC change and ANC forcing ( $R^2 = 0.63$ ,  $p < 0.001$ ). The constant was not significantly different to zero, implying no residual effect of N fertilisation. Most strikingly, of the 37 total treatment/compartments combinations comprising this dataset, 14 fall in the bottom left quadrant of Fig. 10 (ANC forcing and DOC change both negative), and 16 fall in the top right quadrant (ANC forcing and DOC change both positive). The remaining seven sites all lie on the axes (four with  $\Delta\text{DOC} \leq 2\%$ , three with  $\Delta\text{ANC} \leq 2 \mu\text{eq l}^{-1}$ ). In almost all cases, therefore, a positive ANC forcing coincided with a DOC increase, and a negative ANC forcing coincided with a DOC decrease. The field N addition experiments studied thus support the hypothesis that DOC increases in surface waters are linked to changes in acidic deposition (Evans et al. 2006a; Monteith et al. 2007).

With regard to the specific mechanism through which such a link might operate, Monteith et al. (2007) suggest that soil solution acidity and/or ionic strength may control DOC mobility. They were unable to distinguish between these mechanisms on the basis of monitoring data, as decreasing atmospheric deposition has simultaneously reduced both acidity and ionic strength. In our experimental



**Fig. 10** DOC response to all individual experimental treatments versus ANC, excluding data from experiments with increased tree mortality (Harvard, IES) or soils with high anion adsorption capacity (Solling)

dataset, however, the different N forms added have differing impacts on soil pH, but all increase ionic strength. Different DOC responses to  $\text{NaNO}_3$  versus  $\text{NH}_4\text{X}$  addition thus appear more supportive of an acidity control. Kennedy et al. (1996) suggested that pH-dependent solubility of DOM might be more important in mineral (B) horizons than in organic horizons, but our assessment suggests that the proportional response of DOC to acidity change in organic and mineral soils is similar. However, the Aber Forest experiment, where DOC response to treatment was clearer in the B horizon than in the O horizon, lends some support to this hypothesis.

## Conclusions

Across a large experimental dataset, with few exceptions, DOC concentrations responded predictably to the form of N used for manipulation, increasing with  $\text{NaNO}_3$  additions or gaseous  $\text{NH}_3$  exposure, and decreasing with most  $\text{NH}_4$  salt additions. The consistency of DOC response across a wide range of soils, soil horizons and vegetation types argues for a fundamental, and relatively simple, controlling mechanism. The effect of treatment-induced changes in acidity on DOM solubility provides one plausible mechanism. This finding is consistent with the hypothesis, based on long-term monitoring data, that DOC increases in Northern European and North American surface waters are substantially attributable to regional decreases in acidifying, primarily S, deposition (Evans et al. 2006a; Monteith et al. 2007).

Several caveats apply to this conclusion. Firstly, ecosystem changes affecting rates of biotic DOC production may confound a generalised acidity-DOC relationship affecting subsequent mobility. Pulses of decomposition following forest dieback provide an example of this, but other environmental (e.g. climatic) factors may also be important. Secondly, soils with high anion adsorption capacities may show very different DOC responses to changes in acidic deposition. The large-scale DOC trend analysis by Monteith et al. (2007) specifically excluded data from unglaciated regions due to the complicating influence of S adsorption. Data from Solling suggest that observed DOC increases in high-latitude surface waters are unlikely to have been replicated in

lower-latitude, unglaciated regions of continental Europe or the Southeastern United States. Indeed, it seems possible that decreasing S deposition in these areas could have led to a DOC decrease.

The influence of atmospheric N deposition on DOC loss in non-experimental settings remains uncertain, but can by no means be discounted on the basis of this study. Given the role of N as a limiting nutrient; evidence that N deposition leads to soil C accumulation (e.g. de Vries et al. 2006; Evans et al. 2006b; Pregitzer et al. 2007);  $^{14}\text{C}$  studies showing the importance of recent NPP as a source of DOC (e.g. Palmer et al. 2001; Neff et al. 2006; Evans et al. 2007; Smemo et al. 2007); and studies showing a correspondence between ambient N deposition and DOC release (Bragazza et al. 2006), a relationship between N deposition and DOC release may still be anticipated, particularly over the longer timescales at which soil N and C accumulate. N addition experiments typically involve adding N at high concentrations and doses relative to chronic N deposition, potentially overloading ecosystem assimilation capacity such that more is leached, rather than accumulated in organic matter. The artificial application of N also, almost inevitably, leads to changes in acidity, and it is thus problematic to infer relationships between N input and DOC output on the basis of manipulation experiments alone. In this regard, we also note that this conclusion is not uniquely applicable to studies of N effects on DOC: acidity change may influence other processes commonly studied through N addition experiments, such as mineralisation, nitrification and denitrification; vegetation uptake; and biodiversity change. Measurement and evaluation of the effects of acidity change on these processes should therefore form a key element of all N manipulation experiments, which remain a vital tool for improving our understanding the environmental impacts of anthropogenic perturbation of the N cycle.

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