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# Effects of acid sulfate on DOC release in mineral soils: the influence of $SO_4^{2-}$ retention and Al release

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## Summary

DOC in acid-sensitive upland waters is dominated by allocthonous inputs from organic-rich soils, yet inter-site variability in soil DOC release to changes in acidity have received scant attention in spite of the reported differences between locations in surface water DOC trends over the last few decades. In a previous paper, we demonstrated that pH-related retention of DOC in O horizon soils was influenced by acid-base status, particularly the exchangeable Al content.  In this paper, we investigate the effect of $SO_4^{2-}$ additions (0-437 μeq $L^{-1}$) on DOC retention and release in the mineral B horizon soils from the same locations.

DOC release decreased with declining pH in all soils, although the shape of the pH-DOC relationships differed between locations, reflecting the multiple factors controlling DOC mobility.  DOC release decreased by 32-91% in the highest acid treatment (437 μeq $L^{-1}$), with the greatest decreases occurring in soils with very low %base saturation (BS<3%) and/or high capacity for $SO_4^{2-}$ retention (up to 35% of added $SO_4^{2-}$). The lowest DOC retention (i.e. greatest DOC release) occurred in the soil with the highest initial base status (12% BS).  These results support our earlier conclusions that differences in acid-base status between soils alter the sensitivity of DOC release to similar S deposition declines. However, superimposed on this is the capacity of mineral soils to sorb DOC and $SO_4^{2-}$, and more work is needed to determine the fate of sorbed DOC under conditions of increasing pH and decreasing $SO_4^{2-}$.

## Introduction

Increasing concentrations of surface water dissolved organic carbon (DOC) during the last two decades or more have been reported for sites in the UK, Europe, and North America (e.g.Driscoll *et al.*, 2003; Evans *et al.*, 2005; Skjelkvale *et al.*, 2005). A number of diverse drivers for this trend have been proposed, including climate-related effects (Evans *et al.*, 2006), but many studies reporting DOC increases across regions (e.g. Worrall *et al.*, 2008; Hruska *et al.*, 2009) and at the national scale and beyond (Evans *et al.*, 2006; De Wit *et al.*, 2007; Monteith *et al.*, 2007), have implicated the decline in atmospheric sulphur (S) deposition and subsequent recovery from acidification and/or decrease in ionic strength as at least partly responsible. However, despite the near-ubiquitous increase in DOC amongst monitoring networks, attributing widespread trends to recovery from acidification has been difficult, partly because there is considerable local variability in the strength and temporal pattern of the DOC response (e.g. Worrall *et al.*, 2003; Evans *et al.*, 2005). Considering that DOC in acid-sensitive upland waters is dominated by allocthonous inputs from organic-rich soils (Palmer *et al.*, 2005; Billett *et al.*, 2006), it is surprising that the recent debate on the site-to-site variability in surface water DOC trends has not focused on inter-site differences in soil sensitivity to changes in acidity. Recently Clark *et al.* (2011) demonstrated a decrease in DOC release from organic soils from six locations that are part of the UK Acid Waters Monitoring Network (UK AWMN), following laboratory addition of $H_2SO_4$. Clark *et al.* (2011) observed that O horizons of podzols and throughflow influenced basin peats were more sensitive to acid additions than were ombroptrophic blanket peats, and attributed this relative sensitivity to differences between soils in base saturation and exchangeable Al contents such that DOC retention was greatest in O horizon soils with highest exchangeable Al. Inter-site differences in mineral soil sensitivity to acid loading at UK acid-sensitive sites have not been investigated.

The effect of altered acidity on dissolved organic matter (DOM) mobility is primarily due to a change in net charge as DOM molecules become deprotonated, such that DOM mobility increases with pH (De Wit *et al.*, 2007). However, DOM binding to polyvalent cations (particularly $Al^{n+}$ species) depresses DOM charge and may counter any pH-related effect on DOM solubility (Tipping & Hurley, 1988; Kalbitz *et al.*, 2000) and hence any changes in activity of these ions, as a result of changes in acidity, also needs to be considered. Recent modeling analysis has highlighted the role of soil Al pools in mediating the effect of pH and ionic strength on mineral horizon DOC response to acid deposition (Löfgren et al., 2010).

Direct effects of pH on DOC charge and binding to polyvalent cations likely are ubiquitous in both organic and mineral horizons. However, in mineral soils the overall control on DOC retention-release in response to changes in $SO_4^{2-}$ deposition potentially is more complex because DOC has a high affinity to sorb to soil minerals, particularly to amorphous Al- and Fe- oxides (Kaiser & Zech, 1998a). An increase in DOM sorption with pH decrease has also been attributed to ligand exchange between mineral surfaces and functional groups of DOM (Tipping, 1981; Gu *et al.*, 1994). Hence, DOC retention could increase if high $SO_4^{2-}$ loading leads to pH-related increase in either positive surface charge on soil Al- and Fe-oxides or ligand exchange mechanisms. The presence of $Ca^{2+}$ and $Mg^{2+}$ may further enhance adsorption due to a co-adsorption or cation bridging effect (Tipping, 1981).

However, much depends on the soil's ability to buffer increased acidity. Mineral soils also have a capacity to sorb $SO_4^{2-}$ (Moore *et al.*, 1992; Kaiser & Zech, 1998b), thereby potentially buffering the effect of acid $SO_4^{2-}$ loading on solution pH and subsequent DOC protonation. Sorption of negatively charged species is pH dependent (e.g.Nodvin *et al.*, 1986) so that at lower pH a greater range of mineral surface sites will become available for sorption of DOC and/or $SO_4^{2-}$. Sulfate and DOC are competitive for sorption sites (Vance & David, 1992), and desorption of both has been observed when the other is present to excess in percolating solutions (Guggenberger & Zech, 1992; Kaiser & Zech, 1998b; 1999), although DOC has a higher affinity for soil minerals than $SO_4^{2-}$ (Kaiser & Zech, 1998b). Nevertheless, the very small increase in DOC retention with decreasing pH in spodic B horizon soils from Bear Brook watershed in Maine (David *et al.*, 1990) was attributed to pH-related $SO_4^{2-}$ retention (Vance & David, 1992). At very low pH, Vance and David (1992) found that DOC sorption decreased and attributed this to solubilization of metal-humic complexes.

Considering the variety of pH-dependent mechanisms for DOC retention and release in acidic mineral soils, a considerable inter-site variation in the soil DOC response to changes in acid loading might be expected. Of particular importance in acid sensitive soils with low base status are: i) differences in $SO_4^{2-}$ retention, leading to pH attenuation; ii) differential competitive effects between $SO_4^{2-}$ and DOC for adsorption sites; iii) differences in availability of $Al^{n+}$ leading to DOC coagulation and/or subsequent solubilization depending on pH. This paper presents an experimental investigation of DOC retention-release from mineral B horizon soils of selected upland sites (organic horizons 10-40 cm thick) within the UK AWMN in response to additions of acid sulfate ($H_2SO_4$), to determine whether the magnitude of DOC release varies between different soils in response to identical $SO_4^{2-}$ additions. Our focus in this study was to identify inter-site sensitivity of native DOC release rather than the specific mechanisms of DOC-$SO_4^{2-}$ interactions, which have been investigated by others (Vance & David, 1992; Gu *et al.*, 1994). Our objectives were to determine: 1) whether DOC decreased in all soils in response to $SO_4^{2-}$ additions; 2) whether the pH-DOC relationship was the same in all soils, indicating a common mechanistic driver; 3) whether differences between soils could be attributed to differences in solution or soil exchangeable Al, similar to the outcome observed for organic soils (Clark *et al.*, 2011). We used batch experiments to assess the influence of chemical controls on DOC release for different soil types, as this removed confounding interactions with biological and hydrological processes that also influence DOC in the field (Clark *et al.*, 2010).

## Materials and methods

### *Experimental approach*

Batch extractions were performed with eight different treatment levels to examine the effects of acid $SO_4^{2-}$ ($H_2SO_4$) in a fully replicated experiment on soils collected from five acid-sensitive UK upland sites. Summary details of site characteristics and soil properties are shown in Table 1. Samples were collected from the top 10 cm of the B horizon. For additional detail on sites, including grid reference, see (Clark *et al.*, 2011).

The pH of $H_2SO_4$ treatments ranged from 5.40 (level 1, zero $SO_4^{2-}$ added) to 3.37 (level 8, 437 μeq $SO_4^{2-}$ $L^{-1}$ added), with a conductivity range of 1 to 162 μS $cm^{-1}$. No solutes other than $H_2SO_4$ were added. Field moist samples of B horizon soils were sieved through 5.6 mm sieves and thoroughly homogenized before being re-wetted with deionized water until saturated, consistent with the method outlined in Clark *et al.* (2011). This approach to sample preparation is not uncommon for batch experiments (e.g. Kaiser *et al.*, 2001; Zysset & Berggren, 2001). For each soil and treatment level, triplicate 10 g samples were shaken for 20 hours with 100ml of acid $SO_4^{2-}$ treatment solution.

Following equilibration, the pH and conductivity of suspensions were determined on a 30–40ml subsample of the unfiltered sample. All other analyses were conducted on samples filtered to 0.45 μm using a syringe filter system fitted with Whatman WCN cellulose nitrate filters, after gravity pre-filtering through Whatman GF/C. Total C (TC) was measured on the filtered water with a combustion-infrared analyser (Thermalox TC/TN, Analytical Sciences, Cambridge, UK). Preliminary measurements showed that total inorganic carbon concentrations in these acidic soil waters were negligible, and therefore total carbon was assumed to be equivalent to DOC. Major anions ($SO_4^{2-}$, $Cl^-$ and nitrate ($NO_3^-$)) were measured by ion chromatography (Dionex); major cations, $Fe^{3+}$ and $Mn^{2+}$ were measured by inductively-coupled plasma mass spectromtery.  Total monomeric Al ($Al_m$) was determined following complexation with catechol violet and colorimetric analysis at 585nm wavelength using a UV-VIS spectrophotometer.  Potential interference by iron was overcome by the addition of hydroxylamine hydrochloride to reduce $Fe^{3+}$ to $Fe^{2+}$, followed by chelation with 1-10 phenanthroline (McAvoy *et al.*, 1992).  Colour was measured at 254 nm using a scanning spectrophotometer (V-630, Jasco, Great Dunmow, UK).

The speciation of $Al_m$ was calculated using the chemical equilibrium model Mineql+ v4.6, based on the equations in Schecher & Driscoll (1995).  This method of speciating $Al_o$ and $Al_i$ was preferred over direct measurement of $Al_o$ by cation exchange column (and subsequent subtraction of $Al_o$ from $Al_m$ to obtain $Al_i$) because of the potential for Al-DOM complexes to become dissociated and thereby underestimate $Al_o$ (Lawrence *et al.*, 2007; Tipping & Carter, 2011).  Specific ultra-violet absorbance ($SUVA_{254}$, L mg $C^{-1}$ $m^{-1}$) was calculated as the absorbance at 254 nm in units per m (au $m^{-1}$) divided by the concentration of DOC in mg $L^{-1}$ (Weishaar *et al.*, 2003).

### *Data handling and Statistical analysis*

The experiments were designed so that the variation in soil DOC release from different sites in response to additions of $H_2SO_4$ could be examined with respect to changes in pH using ANOVA (Clark *et al.*, 2011). Significant differences between sites in i) soil and ii) solution chemistries for a particular treatment level were assessed by one-way ANOVA and Tukey HSD post-hoc test.

## Results

### *Bulk soil properties and 'control' solution chemistries*

All soils had low % carbon (means 1.60 – 4.75%) and were acidic (mean pH 4.03 – 4.54) with very low base saturation (means 2.4 – 12.7%), highlighting their sensitivity to acidic deposition (Table 1). There were few significant differences between sites in terms of these key soil properties, except that ETH was characterized by significantly higher ECEC (11.40 $cmol_c\ kg^{-1}$; $p<0.05$) and % base saturation (12.7%; $p<0.05$) most likely due to liming in the 1970s.

The solution chemistries in treatment level 1 (zero $H_2SO_4$ added) were 'controls', and unlike bulk soil properties, solution chemistries differed markedly between sites (Table 2). For example, GWY was characterized by significantly higher equilibrated $SO_4^{2-}$ concentration (mean 29 μeq $L^{-1}$), lower pH (mean 4.58) and lower $Al_m$ (62 μg $L^{-1}$) compared to all other sites. ETH had significantly higher DOC concentration (mean 11.54 mg $L^{-1}$) compared to other sites (means 3.69 – 7.79 mg $L^{-1}$) despite having a very low soil C content, second only to LCNA (Table 1). When DOC concentrations were normalized to soil C contents (nDOC, mg DOC $g^{-1}$ soil C), there was no significant difference between ETH and LCNA, and both were significantly higher compared to other sites. Differences in DOC concentrations between sites other than ETH and LCNA were not statistically significant. AM had a significantly higher concentration of $Al_m$ (mean 233 μg $L^{-1}$). All soils released some $SO_4^{2-}$ (6-28 μeq $L^{-1}$), in the order GWY>ETH=DL>AM>LCNA.

*Effect of acid addition*

There were marked differences between sites in $SO_4^{2-}$ retention-release curves (Fig. 1). All soils released some native $SO_4^{2-}$ (6-28 μeq $L^{-1}$) when zero $SO_4^{2-}$ was added (treatment level one), and most continued to release $SO_4^{2-}$ up to treatment level four (42 μeq $L^{-1}$ added $SO_4^{2-}$; Fig.1). At higher treatment levels, DL, AM and ETH all retained added $SO_4^{2-}$, with maximum retentions of 28-35% for DL (42-437 μeq $L^{-1}$ added $SO_4^{2-}$), 20% for AM (437 μeq $L^{-1}$ added $SO_4^{2-}$) and 16% for ETH (291 μeq $L^{-1}$ added $SO_4^{2-}$). By contrast, GWY and LCNA exhibited little capacity to retain added $SO_4^{2-}$ and for most treatment levels released more $SO_4^{2-}$ than added. The higher concentrations of equilibrated $SO_4^{2-}$ in GWY and LCNA relative to other sites influenced the response of other variables, particularly at the highest treatment level (Table 2). In particular, GWY and LCNA recorded the lowest pH values of the experiment (Fig. 2a), greatest conductivity (Fig. 2c) and high $Al_m$ concentrations (Fig. 2d).

All soils exhibited non-linear trends of decreasing pH and DOC with increasing $SO_4^{2-}$ concentrations in solutions, although there were differences between soils in the slope and shape of the response curves (Fig 2a and 2b). Similarly, there were near linear increases in conductivity although the slope differed between soils (Fig. 2c). The trends for $\log_{10}(Al_m)$ were somewhat more complicated with all soils showing an initial decrease in $\log_{10}(\mathrm{Al}_m)$ at low treatment levels, and an increase in $\log_{10}(\mathrm{Al}_m)$ (except for ETH) as $SO_4^{2-}$ concentrations increased (Fig. 2d). Concentrations of $\log_{10}(\mathrm{Al}_m)$ in ETH solutions did not increase but showed a slight decrease across the range of treatments (Fig. 2d). The initial decrease in $\log_{10}(\mathrm{Al}_m)$ was particularly sharp for AM, dropping to 0.73 at treatment level five before increasing again. Soils other than AM and ETH (which showed no increase in in $\log_{10}(\mathrm{Al}_m)$), exhibited increased $\log_{10}(\mathrm{Al}_m)$ concentrations at treatment levels six and higher.

Considering that there were differences between soils in % C and in DOC released with $H_2SO_4$ treatment, DOC was normalised to soil C content (nDOC; mg DOC $g^{-1}$ soil C) for easier comparison between sites (Table 2; Fig. 3). Relationships between pH and nDOC were complex (Fig. 3) with most soils exhibiting an initial small increase in nDOC with decreasing pH, followed by a decrease in nDOC as pH decreased further. The greatest percentage decline in nDOC between 'control' and maximum $SO_4^{2-}$ treatment occurred for GWY (91% decrease) and the smallest decline occurred for ETH (32% decrease). However the steepest declines in nDOC occurred for LCNA, declining from 4.5 mg DOC $g^{-1}$ soil C with 42 μeq $L^{-1}$ of added $SO_4^{2-}$ (treatment level 4) to 1.2 mg DOC $g^{-1}$ soil C at the highest treatment level. The soil which had the lowest solution DOC concentrations in 'control' solutions (AM), demonstrated very little trend in nDOC with decreasing pH (Fig. 3).

## Discussion

This experiment showed that in all mineral soils DOC concentrations and pH decreased with added $SO_4^{2-}$ except for the lowest treatment levels, consistent with observations in organic soils at these sites (Clark *et al.*, 2011). However, variability between soils in both initial nDOC and the change in nDOC per unit change in pH is not consistent with a common mechanism for DOC loss with added $SO_4^{2-}$. The two soils with highest initial nDOC (ETH and LCNA) demonstrated remarkably different response to acid $SO_4^{2-}$ treatment. For LCNA, the large initial nDOC and subsequent sharp nDOC decrease with pH decline of 1.0 pH unit, likely are all indicative of poor anion sorption capacity and consequently poor pH buffering with added $SO_4^{2-}$ treatments. For LCNA, retention of nDOC with decreasing pH is therefore likely due to protonation and subsequent coagulation. By contrast, $SO_4^{2-}$ retention was not as marked in ETH, and this may partly explain the more modest declines in pH and nDOC. In addition, partial buffering of acid $SO_4^{2-}$ by base cation exchange for $H^+$ may have occurred in ETH, since both the ECEC and % base saturation were significantly higher for ETH compared to other soils. This suggests that the DOC response to similar amounts of acid $SO_4^{2-}$ is strongly dependent on the initial acid-base status of soil, as suggested by Clark *et al*. (2011) for O horizon soils. Regional differences in surface water DOC increases have also been linked to the acid sensitivity of catchment waters, as indicated by aquatic $Ca^{2+}$ plus $Mg^{2+}$ concentrations (Monteith *et al.*, 2007). Generally, mineral soils with base saturation <20% are considered acid-sensitive in terms of Al release and pH buffering (Cronan & Schofield, 1990). In this experiment, ETH with BS at 12.7% appears to be relatively robust to pH and DOC change, and insensitive to Al release, indicating that %BS is not a comprehensive indicator of acid-sensitivity for these soils. However, it is also worth noting that this soil was limed in the 1970s, and significant concentrations of $Ca^{2+}$ are still present in the O-horizon (Clark *et al.*, 2011).

Low initial nDOC and strong $SO_4^{2-}$ retention with added $SO_4^{2-}$ indicates a capacity for anion sorption in DL. The $SO_4^{2-}$ retention clearly attenuated pH change in DL compared to other soils, yet nDOC retention did occur with a maximum treatment effect (85% decrease in nDOC) that was similar to that observed for GWY and LCNA

(91% and 75% decrease in nDOC, respectively) which had little capacity to retain added $SO_4^{2-}$ and experienced large pH declines (Table 2). This suggests that at least part of the DOC change in DL was due to sorption rather than increased protonation and subsequent coagulation/precipitation, which are often used to explain changes in DOC in organic soils (e.g. Evans *et al.*, 2006; Clark *et al.*, 2011), and that there is little or no competition between $SO_4^{2-}$ and DOC for sorption sites. This is consistent with reports from other researchers that DOC sorption dominates over $SO_4^{2-}$ in mineral soils at pH>4 (Courchesne & Hendershot, 1989; Gobran *et al.*, 1998), presumably because DOC is protonated and therefore not available for sorption at lower pH values, whereas sulfate exhibits the opposite behaviour (Nodvin *et al.*, 1986). In this experiment, DL solutions measured pH≥4.2 in even the highest $SO_4^{2-}$ treatments, hence it is likely that solution DOC in DL remained deprotonated and available for sorption across all treatment levels.

A number of researchers have noted that a significant proportion (30-40%) of $SO_4^{2-}$ retained is irreversibly sorbed to soils and reduces the soil's capacity to further retain anions (Harrison *et al.*, 1989; Guggenberger & Zech, 1992; Gobran *et al.*, 1998). The implication is that soils with a history of enhanced S deposition will have a decreased capacity to sorb DOM and other anions compared to soils that have received less S loading. GWY and LCNA were the most westerly of the sites used for this study and in an area where atmospheric deposition rates during 1986-2001 did not decline as much as in other parts of the UK, possibly due to a combination of factors, such as: i) continued S emissions from shipping (Fowler *et al.*, 2005); ii) high seasalt deposition events that the UK experienced during the 1990s (Monteith *et al.*, 2007); or iii) lower proportion of dry deposition due to distance from terrestrial pollutant sources. High initial nDOC and poor $SO_4^{2-}$ retention are consistent with $SO_4^{2-}$

saturation in LCNA, but low initial nDOC in GWY suggests that a history of $SO_4^{2-}$ loading has not impacted DOM retention. The legacy of continued S deposition may therefore have impacted differently on these two soils, although further investigation is needed to determine the exact mechanisms involved and the extent to which this has occurred.

AM exhibited the lowest DOC concentration in ‘control’ solutions, and after an initial increase decreased to a modest 50% of initial nDOC and mean pH of 4.43 with 83 μeq $L^{-1}$ of added $SO_4^{2-}$. With higher $SO_4^{2-}$ treatments, the nDOC response was more or less static, suggesting that retention and release of DOC reached some equilibrium. That some $SO_4^{2-}$ retention occurs even with highest $SO_4^{2-}$ addition, and that the minimum pH was close to pH 4.0 suggests that neither limited anion sorption capacity nor DOM protonation is the reason for low nDOC. A similar pattern of initial decrease in DOC followed by a flattening of the DOC-pH curve across the pH range 4.9 to 4.4 was observed by Zysset & Berggren (2001). Zysset & Berggren (2001) attributed this pattern of DOM release to precipitation of metal-DOM complexes at higher pH and subsequent solubilization as pH decreased.

Scheel *et al*. (2008) also observed co-precipitation of Al and DOM that was greater at pH=4.5 than in more acid conditions (pH=3.8). However, in an experiment on the formation of Al-fulvate complexes Farmer & Lumsdon (2001) demonstrated that DOM loss was independent of pH across the pH range 4.2 to 5.1, but was related to Al:C ratio. Precipitation of DOM occurred when the molar C/Al was less than 50 (or when Al/C>0.045 g $g^{-1}$; Farmer & Lumdson (2001)). In this experiment, $Al_m$/DOC and $Al_o$/DOC at pH>4.3 were on average greater for AM than for any other soil studied. Indeed across all treatment levels, only AM consistently approached $Al_o$/DOC>0.04 g $g^{-1}$ (Fig. 4). This suggests that Al-DOM complexation, and subsequent solubilization as pH decreased, was a relatively important influence on DOC solubility for AM.

Recent field studies have observed a decline in DOC concentrations in soil solutions from mineral horizons over the last 10 years (Löfgren *et al.*, 2010; Wu *et al.*, 2010; Borken *et al.*, 2011), and have speculatively attributed these trends to a number of possible mechanisms related to declines in $SO_4^{2-}$ deposition, including: i) competitive sorption of DOC with decreasing $SO_4^{2-}$ concentrations (Wu *et al.*, 2010; Borken *et al.*, 2011); ii) increased aggregation with Al as a consequence of increased net charge on DOC with increasing pH (2010); and iii) increased biological consumption due to reduced Al activity (Borken *et al.*, 2011). Our data suggest that $SO_4^{2-}$ and DOM retention may be compromised by previously adsorbed $SO_4^{2-}$ and that Al-DOC precipitation may be an important mechanism of DOM retention/release for some soils. However, considering that $SO_4^{2-}$-driven DOM solubility mechanisms are unlikely to be fully reversible (Harrison *et al.*, 1989; Gobran *et al.*, 1998), considerable further work needs to be undertaken to determine whether recent DOC trends are attributable to $SO_4^{2-}$ declines.

## Conclusions

The results of this experiment showed that acid $SO_4^{2-}$ treatment to mineral soils caused a decrease in DOC that was primarily driven by a decrease in pH, although the pH-related response differed between soils, reflecting different controls on DOC solubility. All soils studied here can be considered base-poor and therefore acid-sensitive to a degree; even so the initial base status was extremely important in determining soil's capacity to buffer acid inputs and therefore to control the solubility of DOC and the solubility of Al-DOM complexes. This has implications for the interpretation of long-term DOC trends in recovering acid waters, and may partly explain why some apparently acid-sensitive catchments have seen declines in DOC whilst others have not (Clark *et al.*, 2011). The soil sorption capacity was equally important for two reasons: i) in determining initial DOC release and ii) in attenuating pH change through $SO_4^{2-}$ retention, with some evidence that soils have responded differently to a similar history of S deposition. If $SO_4^{2-}$ is partially irreversibly sorbed, as observed by some studies, a legacy of historic S deposition may have permanently reduced the capacity for both $SO_4^{2-}$ and DOC sorption in some soils, whilst others may be unaffected. Such inter-site differences in mineral soil sensitivity to experimental $SO_4^{2-}$ additions make it difficult to assess how DOC has responded to past changes in $SO_4^{2-}$ loading, or indeed to predict future change. The extent to which $SO_4^{2-}$ sorption is reversible under conditions of increasing pH and decreasing $SO_4^{2-}$ deserves further investigation.

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## FIGURE CAPTIONS

**Figure 1** Plot of $SO_4^{2-}$ retained or released expressed per unit mass of soil as a function of initial $SO_4^{2-}$ added as $H_2SO_4^{2-}$.  Mean of n=3 replicates.  Error bars for LCNA indicate ± one standard error.  Error bars for other data sets omitted for clarity.  For full details of site codes, see Table 1.

**Figure 2** Means (n=3) of (a) pH, (b) DOC, (c) conductivity and (d) $Log_{10}$ $Al_m$ in equilibrated solutions. Error bars omitted for clarity.  For full details of site codes, see Table 1.

**Figure 3** Mean (n=3) **of** nDOC as a function of pH for all sites and replicated treatments.  Error bars indicate ± one standard error. For details of site abbreviations, see Table 1.

**Figure 4** Boxplot of $Al_o$/DOC for all treatment levels, by site.

## TABLES

**Table 1** Summary site characteristics and key soil properties (mean with standard error in parentheses; n=5).

| | Allt A'Mharcaidh (AM) | Dargall Lane (DL) | Etherow (ETH) | GWY (GWY) | Loch Coire nan Arr (LCNA) |
|---|---|---|---|---|---|
| Site characteristics: | | | | | |
| Geology | Biotite-granite | Greywackes, shales & mudstones | Millstone grit | Mudstones, shales & grits | Torridonian sandstone |
| Soil type | Podzol | Peaty podzol | Podzol | Peaty podzol | Peaty Podzol |
| Depth of top of B horizon from top of O horizon, range | *15 to 30cm* | *15 to 29 cm* | *17 to 23 cm* | *15 to 25 cm* | *6 to 22 cm* |
| Vegetation | *Calluna vulgaris* | *Calluna vulgaris, Eriophorum spp., Molinia spp.* | *Agrostis spp.* | *Festuca spp., Agrostis spp.* | *Calluna vulgaris, Eriophorum spp., Molinia spp.* |

| | | | | | |
|---|---|---|---|---|---|
| Soil properties: | | | | | |
| %C | 4.15 (0.93) | 4.75 (0.66) | 2.02 (0.21) | 3.14 (0.41) | 1.60 (0.35) |
| $pH_{CaCl2}$ | 4.54 (0.07) | 4.44 (0.05) | 4.09 (0.07) | 4.03 (0.06) | 4.20 (0.02) |
| ECEC /$cmol_c\ kg^{-1}$ | 1.59 (0.36) | 4.54 (0.57) | 11.40 (1.56) | 5.43 (0.48) | 2.07 (0.16) |
| %Base saturation | 3.6 (0.5) | 2.4 (0.2) | 12.7 (3.9) | 2.6 (0.3) | 4.6 (0.6) |
| Exchangeable Al /$cmol_c\ kg^{-1}$ | 1.07 (0.27) | 2.45 (0.20) | 7.56 (1.23) | 4.02 (0.43) | 1.46 (0.12) |
| Exchangeable $H^+$ $cmol_c\ kg^{-1}$ | 0.46 (0.09) | 1.98 (0.43) | 2.54 (0.44) | 1.26 (0.08) | 0.51 (0.07) |
| %Al saturation | 65.4 (3.1) | 56.1 (5.2) | 65.3 (2.6) | 73.5 (2.0) | 70.6 (2.3) |
| %H saturation | 31.0 (2.6) | 41.3 (5.3) | 21.9 (1.9) | 23.8 (2.36) | 24.5 (2.3) |

**Table 2** Mean (with standard error in parentheses; n=3) of equilibrated $SO_4^{2-}$, pH, conductivity, DOC, $Al_m$ and $SUVA_{254}$ for ‘control’ solutions (level 1: zero $SO_4^{2-}$ added) and in level 8 treatments (437 μeq $L^{-1}$ $SO_4^{2-}$ added). The last column gives the maximum treatment effect on nDOC (differences between treatment level 1 and treatment level 8; 1:8).

| Site | Equilibrated $SO_4^{2-}$ μeq $L^{-1}$ | | pH | | Conductivity μS $cm^{-1}$ | | DOC mg $L^{-1}$ | | nDOC mg DOC $g^{-1}$ soil C | | $Al_m$ μg $L^{-1}$ | | $SUVA_{254}$ L $g^{-1}$ $cm^{-1}$ | | nDOC mgDOC $g^{-1}$ soil C |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Level | 1 | 8 | 1 | 8 | 1 | 8 | 1 | 8 | 1 | 8 | 1 | 8 | 1 | 8 | 1:8 |
| AM | 15 (1) | 378 (18) | 4.94 (0.01) | 4.09 (0.00) | 3 (0) | 48 (1) | 3.69 (0.26) | 1.76 (0.06) | 0.89 (0.06) | 0.42 (0.01) | 233 (19) | 1370 (117) | 2.99 (0.08) | 0.80 (0.09) | -0.47 (0.01) |
| DL | 23 (1) | 285 (15) | 4.79 (0.02) | 4.20 (0.01) | 7 (1) | 44 (2) | 5.55 (0.91) | 0.80 (0.02) | 1.17 (0.19) | 0.17 (0.00) | 155 (24) | 839 (328) | 2.57 (0.11) | 1.98 (0.15) | -1.00 (0.00) |

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ETH | 22 (1) | 406 (43) | 5.05 (0.01) | 4.34 (0.01) | 11 (0) | 57 (0) | 11.54 (0.41) | 7.86 (0.25) | 5.71 (0.20) | 3.89 (0.12) | 154 (11) | 94 (9) | 4.96 (0.26) | 4.49 (0.08) | -1.82 (0.12) |
| GWY | 29 (2) | 437 (61) | 4.58 (0.02) | 3.85 (0.00) | 10 (0) | 69 (3) | 6.03 (0.80) | 0.56 (0.04) | 1.92 (0.25) | 0.218 (0.01) | 62 (15) | 942 (96) | 5.38 (0.37) | 4.07 (0.56) | -1.74 (0.01) |
| LCNA | 6 (1) | 421 (17) | 4.94 (0.08) | 3.95 (0.02) | 8 (0) | 91 (4) | 7.79 (0.63) | 1.94 (0.62) | 4.87 (0.39) | 1.21 (0.39) | 132 (8) | 1512 (225) | 3.18 (0.21) | 1.79 (0.74) | -3.65 (0.39) |

Figure 1

Figure 2

Figure 3

Figure 4