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Nitrogen cycle disruption through the application of de-icing salts on upland highways.

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Abstract

It is hypothesized that episodic introductions of road salt severely disrupt the soil nitrogen cycle at a range of spatial and temporal scales. A field-scale study has confirmed impacts on the nitrogen cycle in soil, soil solution and river samples. There is evidence that ammonium-N retention on cation exchange sites has been reduced by the presence of sodium ions, and that ammonium-N has been flushed from the exchange sites. Increases in soil pH have been caused in naturally acidic uplands. These have enhanced mineralization of organic-N, especially nitrification, leading to a reduction in the mineralizable-N pool of roadside soils. There is evidence to support the hypothesis that organic matter content has been lowered over decades either through desorption or dispersal processes. Multiple drivers are identified that contribute to the disruption of nitrogen cycling processes, but their relative importance is difficult to quantify unequivocally. The influence of road salt on soil and soil solution declines with distance from the highway, but impacts on water chemistry in a local stream are still strongly evident at some distance from the road.

Keywords: Cationic displacement, nitrogen cycle, road salt, sodium chloride.

1 Introduction

Episodic introductions of road salt have the potential to severely disrupt the soil nitrogen cycle. Road salting is utilized to minimize the risk of accidents under icy

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and snowy conditions. In the UK the preferred de-icing agent is sodium chloride (pure or mixed with grits and sands, often with an anti-caking agent), applied in solid or liquid form at a rate of 10-40 g m^{-2}, depending on conditions. Although high impacts of Na^+ and Cl^- on N cycling may be envisaged, there have been few studies to date that focus on such impacts (Green *et al*., 2007).

It may be hypothesized that high sodium inputs will flush ammonium ions from exchange sites and also reduce the extent of ammonium retention from atmospheric inputs, as reported for sea-salt deposition (Duckworth & Cresser, 1991), and this could conceivably lead to shortages of available N for some distance down slope of salted roads, and ammonium enhancement further down slope.

Road salts also may increase organic colloid mobility (Amrhein *et al*., 1992; Grolimund *et al*., 1996; Norrström & Bergstedt, 2001; Shainberg & Letey, 1984) and alter the structure of the soil (Bäckström *et al*., 2004; Norrström & Bergstedt, 2001). High exchangeable sodium percentage and low salt solution concentration lead to enhanced dispersal of soil colloids (Shainberg & Letey, 1984). Thus it may be further hypothesized that salting will lead to a reduction in the organic matter content of soil adjacent to roads, and thus to a decline in the pool of mineralizable soil N. Such an effect may be modified by salting effects on the mineralization of soil organic matter, however. Soil aggregate stability deteriorates through the accelerated leaching of calcium and magnesium ions from the soil exchange sites as a result of enhanced competition with sodium ions (Bäckström *et al*., 2004; Norrström & Bergstedt, 2001), reducing the bonding with the organic matter that aids flocculation and soil structural stability.

It is plausible that ammonification may increase as a result of the weakened tendency for organic matter and mineral structures to bind, as desorption reduces the physico-chemical protection of the organic matter. Moreover, increases in soil pH induced by cationic exchange with sodium may facilitate mineralization of organic N, and especially nitrification (Green *et al*., 2007). Green *et al*. (2007) assessed the fates of low-level ammonium-N and nitrate-N inputs to roadside soils impacted by salting over an extended period (decades) in the field using spiking equilibration experiments. They discovered that the use of road salts disrupted the proportional contributions of nitrate-N and ammonium-N to the mineral inorganic fraction of roadside soils; they suggested that is was highly probable that that the degree of salt exposure of the soil, in the longer term, controlled the rate of key microbial N transformation processes, primarily by increasing soil pH.

In addition, increases in sodium dominance of the CEC potentially increase dispersal of organic colloids when soils are first exposed to high salinity. Such an increase is unlikely to be evident in roadside soils exposed for decades to road salt, as once the organic matter has dispersed and leached from the soil it's gone from the system forever (Green *et al.*, under revision). Green *et al.* (under revision) applied salt at concentrations recorded in soil solution in the field (0, 10, 1000, 10 000 mg l^{-1}), simulating a road salting flush, to quantify the extent that dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) are still being mobilized from soils that have experienced varying degrees of road salt exposure in the field. A balance occurs between the effects on organic matter of long-term soil pH increase (which enhances organic matter solubility and mineralization), short-term pH suppression via a mobile anion effect (which reduces organic matter solubility), and short- and long-term sodium-induced dispersion, which now determines the influence of road salt on organic matter leaching from roadside soils and into associated drainage waters.

Spatial and temporal pH shifts will also influence microbial activity and thereafter transformation rates of inorganic N species. Green *et al.* (2007) concluded from their series of laboratory equilibration experiments that road salt-induced pH shifts may lead to enhanced nitrification of influxes of ammonium-N to salt impacted soils, thereby increasing leaching of nitrate-N to the local waterways, even at 4 ^{o}C. If nitrification is enhanced, leaching of nitrate-N into soil solution and freshwater bodies is likely (Green *et al.*, 2007). Hence, it is hypothesized that freshwaters below roadside soils should show evidence of disruption of N cycling. In summary we predict:

- High sodium inputs flushing ammonium from soils and a reduction in the extent of ammonium retention on exchange sites close to a highway;
- Ammonium retention increasing with down slope distance from a highway;
- Lowered organic matter content in soils close to roads and possible accumulation in soil down slope, and hence a decline in the pool of mineralizable-N;
- Increased mineralisation of organic-N;

- Increased nitrate concentrations in soil solution, rivers, and streams adjacent to the highway.

Therefore, this paper examines and assesses spatial and temporal variations in soil, soil solution and freshwater down slope of a highway in upland Cumbria, UK, to determine the affects road salt has on N-processes and test the above hypothesis.

2 Materials and methods

2.1 Field site

The study site was an upland area adjacent to the A6 at Selside, Cumbria, UK (NY 554 046 GB Grid), with altitudes up to 458 m above sea level (Fig. 1). Soil types consist of podzols with variable degrees of development and depths of organic-rich surface horizons (organic-rich leached horizon, iron-rich mottled gley B horizon (in places with signs of gley development), gravel layer C horizon with shale/slate), derived from Upper Ludlow, Ludlow series, Upper Silurian bedrock. The vegetation consists mainly of grasses, Juncus and bryophytes and the land is used for grazing cattle and sheep. This site presents an unusual opportunity as the road drainage is piped directly onto the soil surface at regular intervals. Hence the site presents three possible transect scenarios (a) impacted by direct (channelled from a pipe) drainage and by spray, (b) impacted by indirect drainage and spray and (c) an un-impacted control within the catchment on an adjacent hillside with the same altitude, aspect and land use. A dry stone wall ca. 1.5 m high down slope separates the road from the salt-affected sampling sites. For further details refer to Green *et al.* (2007).

2.2 Sample collection

2.2.1 Soil sampling

Transects for each transect-type scenario were marked out in duplicate, at a spacing of at least 10 m to ensure that pseudoreplication was avoided, perpendicular to the road; direct (drain-affected) transects (T1/T2) were immediately down slope of drainage pipe outlets; indirect transects (T3/ T4) were to the north of T1 and T2, respectively. The un-impacted control transects are referred to as T5 and T6. Soil samples from 0-10 cm were collected with a stainless steel trowel at 2, 4, 8, 16, 32 and 64 m from the wall, and thus 4 to 68 m from the road itself, for transects T1 to T4, and from corresponding distances on control transects T5 and T6, on the 7th April 2005. Further soil sampling was completed at 2, 8 and 32 m from the wall on the 12th October 2005, when residual salting impacts should be minimal, to provide an inter-seasonal comparison.

The samples were stored field moist in polyethylene bags at 2-4 °C in preparation for chemical analysis. Stones and residual identifiable vegetation fragments and roots were removed by rapid careful hand sorting immediately prior to use.

2.2.2 Soil solution sampling

Soil solutions at 2, 4, 8, 16, 32 and 64 m from the wall for each transect scenario were sampled using sets of three *in situ* MOM 0.1 μm pore Eijkelkamp MOM rhizon soil solution samplers (Rhizon SSS; Eijkelkamp Agrisearch Equipment, Giesbeek, The Netherlands). MOM rhizon samplers 10 cm long and 2.5 mm in external diameter were inserted at a depth of 5-10 cm, and evacuated with 60 ml syringes. Soil solution sampling was completed on 8 occasions between 12/10/2005 and 08/07/2006 (Table 1). Thus sampling was conducted prior to, during and after road salt application (Table 1). Sampling was more frequent over the salt application period. The air was purged from the sample syringes, which were then stored at 2-4 °C prior to chemical analysis. These samples were not filtered, as the rhizon sampler acts as a membrane filter.

2.2.3 Freshwater sampling

Runoff from the investigated 1500-m section of the A6 road drains eventually into Crookdale Brook (Fig. 1). A water sampling survey was completed on the Crookdale Brook during the period from 12/10/2005 to 08/07/2006. Six locations were sampled (S1 – S5 and S7) along the course of the Brook parallel to the A6, at intervals of approximately 200 m (Fig. 1). S6 was a tributary between S5 and S7. The water at each point was sampled in duplicate to confirm reproducibility of analytical procedures; 125-ml polyethylene bottles were rinsed several times with the sample water before a final collection was made. Samples were stored at 2-4 ^{o}C prior to chemical analysis.

Chemical analyses for soil, soil solution and freshwater samples were conducted as soon as possible after returning to the laboratory, with appropriate prioritization.

2.2.4 Bulk precipitation and drainage chemistry

Bulk precipitation samplers were used to assess spray inputs to the soil. Four samplers were installed at the study site (4, 8, 16 and 32 m from the wall), and one at the control site. Duplicate precipation samples were collected on the sampling dates outlined in Table 1.

Drainage water samples were obtained when flow was occuring from T1 and T2 (12/10//2005 and 08/07/2006). The samples were stored at 2-4 ^{o}C, prior to analysis these samples were filtered through Whatman no. 42 filter papers.

2.3 Soil analysis

Soils were analysed for pH (H_2O), loss-on-ignition (ashing at 800 ^{o}C), potassium chloride-extractable ammonium and nitrate, exchangeable base cations (1 M ammonium-acetate) and cation exchange capacity (CEC – 1 M acidified NaCl after ammonium saturation and 80 % ethanol washing) as previously described by Green *et al*. (2007). All extractions were completed on field moist, un-sieved semi-structured soil. Performance of all instrumental methods was checked using synthetic reference standard materials.

2.4 Freshwater, precipitation, road drainage and soil solution analysis

Water samples were analyzed for base cations, ammonium-N, nitrate-N, chloride, and sulphate using ICP-OES (base cations), ion chromatography (Dionex, anions) and a Bran and Luebbe AutoAnalyser 3 (N-species). Prior to analysis freshwater samples were filtered using Whatman no. 42 filter papers, whilst soil solutions were filtered by the 0.1 μm Rhizon membrane. Performance of all instrumental methods was checked using synthetic standard reference materials. Nitrate concentrations obtained by ion chromatography and automated colorimetry did not differ significantly.

2.5 Statistical analysis

For soil data, an one-way ANOVA non-parametric alternative test was utilised, the Kruskal-Wallis test, as there is debate and scepticism about whether two-way ANOVA extension of the identically named test is valid (Dytham, 2003 p.145). The non-parametric test will not indicate whether there is an interaction between site and distance, as this portion is not computed. For all statistical tests, significance was accepted at $\alpha \leq 0.05$. Statistical analyses were performed using SPPS version 11.0.1 (2001).

3 Results

3.1 Road drainage and bulk precipitation chemistry

Sodium ion concentration in the control site bulk precipitation ranged between 1.21 and 4.37 mg l^{-1}, in comparison to bulk precipitation at 4 m from the wall where concentrations ranged from 0.03 and 40.51 mg l^{-1}. The lowest sodium and chloride concentrations being detected before the winter maintenance season had commenced (02/11/2005). Sodium and chloride concentrations were significantly higher (at the 1% level) at 4 m than those of the controls after the salting-runs had been initiated. Spray data from the bulk precipitators is incomplete as a proportion of the samples were lost (i.e. bags dislodged, ripped or removed by on-site sheep/cattle), especially for the 27/01/2006. 9/12/2005 and 03/01/2006 are the only dates for which a complete set of data for the five bulk precipitators is available, both indicate a reduction in sodium and chloride concentration as the distance from the road is increased. There was no significant difference between water from the control and that from the salt-affected bulk precipitation collections for ammonium-N and nitrate-N, and no apparent distance affect for these N species.

All heavy metals (Ba, Cd, Cu, Mn, Pb, Zn) concentrations were below the detection limits of ICP-OES (< 0.02 mg l^{-1}) for both bulk precipitation and drainage water (T1 & T2) samples.

Road drain water samples contained higher concentrations of sodium and chloride in July (31.2 and 45.8 mg l^{-1}, respectively) as compared to October (1.5 and 0.93 mg l^{-1}, respectively). The ammonium and nitrate concentrations observed in the drainage water were 0.76 and 0.44 mg l^{-1}, respectively. The samples are not from the salt application period.

3.2 Base cation and hydrogen ion occupation of the CEC

Table 2 shows mean values of ammonium acetate-extractable base cations and KCl-extractable ammonium as a percentage occupation of CEC for T1/T2, T3/T4 and T5/T6 transects. These means are across all 6 distances. Table 3 shows the data disaggregated by distance (2, 4, 8, 16, 32 and 64 m) and transect type. The mean Na % occupancy of CEC (across all distances: Table 2) for T1/T2, T3/T4 and T5/T6 transects differ significantly at the 1% level (direct > indirect > control). Percentage occupation by sodium on the CEC never exceeds 0.65 % for T5/ T6, compared to maximum values of 3.5 and 34 % for T3/T4 and T1/T2, respectively. The percentage contribution for T1/T2 of sodium to the CEC declines to 16 m, and converges towards the control values thereafter. The spray-affected transects (T3/T4) do not follow a significant spatial pattern (Table 3) but always exceed the control soil values.

In October (data not shown) there was a reduction in Na % of CEC close to the road on the salt-affected transects, especially for the T1/T2 (34 to 5% at 2 m). Below 32 m there was no significant difference between the two sampling dates.

Ca % occupation of CEC for both sets of salt-affected transects is significantly above that for the control (1% level, Table 2). The Ca % of CEC for all salt-affected transects declines consistently with distance from the highway (Table 3), but results for T3/T4 again show a irregular spatial trend.

The Mg % of CEC at 2 m follows the order T3/T4 > T5/T6 > T1/T2 (Table 3). Differences between transect types are much smaller at 4 m, and Mg % of CEC generally increases further down slope for T1/T2 and T3/T4. Spatial variation is much less for T5/T6 than for salt-impacted transects, as would be expected where there is no salt impact.

For Ca and Mg % of CEC (data not shown) there was a general decline between April and October for all three transect scenarios at 2 and 8 m. However, Ca % of CEC for T1/T2 increases from less than 5% in April to more than 10% in October.

The H^+ % of CEC values, calculated by subtracting Σ base cations from CEC for the three scenarios show significant differences, with T5/T6 > T3/T4 = T1/T2 (1%

level). At 2 m the H^+ % of CEC for T1/T2 falls to 49%, compared to 72 and 89% for T3/T4 and T5/T6, respectively. Acidity increases down the salt-affected transects from 2 to 16 m, to ~ 88%. T5/T6 maintain a constant acidity at ~ 92% (Table 3). Below 16 m T1/T2 give values approaching control levels (64 m = 91%), while H^+ % of CEC for T3/T4 declines to 67% at 64 m reflecting the higher Ca % and Mg % values. H^+ % of CEC generally showed an increase for all transects in October (data not shown), indicating partial reversibility of the neutralizing effect of high sodium inputs over winter.

The CEC % occupation by base cations and hydrogen ions are also reflected in the soil pH (H_2O).

3.3 Soil pH

Soil pH (H_2O) at 2-4 m during April 2005 for the T1/T2 transects was higher by more than two units than that for the T3/T4 transects, and two and a half to three units higher than that for the T5/T6 transects (Fig. 2, 1% level). This corresponds to the high sodium dominance and low hydrogen occupancy of the CEC in the soils of the T1/T2 transect (Tables 2 & 3).

The T1/T2 soils at 2 m maintain a pH above 7 in October (Fig. 2), whilst for the T3/T4 soils pH has increased by over half a unit compared with the April value, almost certainly due to a lower mobile anion (Cl^-) effect in October. At 8 m all the soils still have a pH after summer at ~ 4.5 units, but the T5/T6 soils are still most acidic in October. Over time, the T5/T6 soil pH remains constant at ~ 4. All three scenarios are statistically significantly different from each other, in both April and October at the 1% level with T1/T2 > T3/T4 > T5/T6.

3.4 Soil extractable ammonium-N

Figure 3 shows KCl-extractable ammonium in April, at the end of the salting period, as a percentage occupation of CEC at 2, 4, 8, 16, 32 and 64 m for each transect type. It is immediately obvious that the T5/T6 transects contain significantly more extractable ammonium (on average 0.99%, Table 2) than either of the transects for other pollution scenarios (0.25 and 0.36% on average for T1/T2 and T3/T4, respectively) (1% level). In the most salt-impacted soils (T1/T2) the proportion of

CEC occupied by ammonium declines from 2 m through to 16 m (0.62 to 0.11%) and thereafter increases as the distance from the highway increases to 0.18% at 64 m (5% level). This initial decline also was seen for T3/T4 but only to 4 m, and the rate of increase in the proportional occupation of the CEC by ammonium with down slope distance was greater. The control appears to demonstrate a similar rate of increase as the transect is descended, but this was not significant (as expected). The T3/T4 soils display intermediate behaviour from 8 to 64 m.

The percentage occupancy of the CEC by ammonium for all pollution scenarios was significantly lower in October (0.23, 0.24 and 0.14 % for T1/T2, T3/T4 and T5/T6, respectively) than in April (0.25, 0.36 and 0.99% for T1/T2, T3/T4 and T5/T6, respectively), and the % ammonium on the CEC for the three scenarios converged to similar values. Plant uptake would be lower in April than in October, and more nitrification would occur over the summer prior to October, hence, reducing the ammonium concentration.

3.5 Soil extractable nitrate-N

Figure 4 shows the concentrations of KCl-extractable nitrate-N for T1/T2, T3/T4, and T5/T6 soils at 2, 4, 8, 16, 32 and 64 m in April 2005. The nitrate-N concentrations for T5/T6 (mean of 0.58 mg kg^{-1}) are significantly lower than those of either type of salt-affected transect (means of 2.34 and 3.34 mg kg^{-1} for T1/T2 and T3/T4, respectively). The T3/T4 soils contained the highest concentrations (1% level) but nitrate concentration did not differ significantly between the two salt impact scenarios (Fig. 4). Nitrate-N peaks on the salt-affected soils between 8 and16 m, which coincides with the decline in soil pH (Fig. 2) for T1/T2. Nitrate-N concentration on the T1/T2 transects is significantly higher at 16 m than at all other distances. However neither the T3/T4 nor the T5/T6 transects show a significant difference in mean nitrate-N concentration with distance from the wall. By October 2005 nitrate-N concentration was higher (results not shown) for salt impacted transects (7.27 and 5.19 mg kg^{-1} for T1/T2 and T3/T4, respectively) than for T5/T6 (3.35 mg kg^{-1}), but there was no significant difference between the three scenarios.

Seasonally, soil nitrate-N concentration for T5/T6 was overall statistically significantly higher in October (3.35 mg kg^{-1}) than in April (0.01 mg kg^{-1}) (1% level).

However, there was no significant difference between October and April for either of the salt-affected transects.

3.6 Soil loss-on-ignition and C:N

Table 4 shows soil loss of ignition for T1/T2, T3/T4, and T5/T6 from 2-16 m from the wall. It clearly shows a significant difference between T1/T2, T3/T4 and T5/T6 at 2, 4 and 8 m (5% level). At 2 m, LOI (%) is significantly lower for the T1/T2 and T3/T4 than for T5/T6. Further from the road LOI% in T3/T4 soils converges to the T5/T6 soil LOI (%) content, with the T3/T4 soils differing significantly from the T1/T2 soils up to 8 m. By 16 m the difference is not significant.

Figure 5 shows the C:N disaggregated by pollution exposure scenario and distance from the wall for April 2005. It is immediately obvious that the C:N is consistently and significantly lower across all distances for the control transects (T5/ T6) than either salt-impacted scenarios (1% level). Ratios for T1/T2 significantly change with distance (1% level). As the distance from the highway increases the C:N declines from 24.3 at 2 m to 14.4 at 64 m. Neither T3/ T4 nor T5/ T6 show significant changes in soil C:N ratio down slope from the road.

3.7 Soil solution sodium

Soil solutions from impacted soils from 12th October 2005 to the 8th July 2006 highlighted high concentrations of sodium ions, declining with distance from the road. Concentrations as high as 5800 mg Na l^{-1} were observed 2 m from the road for T1/T2. In comparison, soil solutions for T3/T4 contained < 200 mg Na l^{-1} at 2 m, declining to 21-48 mg Na l^{-1} at 64 m; the controls had background concentrations of 2-2.5 mg Na l^{-1} across all distances on the 03/01/2006. The trends in sodium ion concentration in the soil solution were reflected in chloride data, although chloride concentrations were higher due to the nature of the two elements, with some sodium tending to be retained within the soil due to its cationic properties. The large episodic increases in both sodium and chloride concentrations were closely associated with road salt application dates throughout the winter period, while data from 12/10/2005 and 03/11/2006 provide background soil solution concentrations prior to initiation of salt application for winter maintenance.

3.8 Soil solution nitrate-N

Figure 6 shows the soil solution nitrate-N concentrations for T1-T6 at distances 2, 4, 8, 16, 32 and 64 m from the wall on eight sampling occasions. The T5/T6 soil solutions very consistently contain minimal (< 0.14 mg l^{-1}) amounts of nitrate-N (note change of scale Fig. 6), whilst the salt-affected transects have dramatically increased, but spatially and temporally variable, concentrations. Nitrate-N concentrations for T1/T2 below the drains were consistently relatively low from 2 to 8 m, peaking at 16 to 32 m (with a maximum concentration of 25 mg l^{-1} on 09/12/2005), and thereafter declining (but still much higher than control concentrations) by 64 m. In T3/T4, nitrate-N concentration declined from 2 to 4 m, and thereafter peaked at 8-32 m, before declining at 64 m. Nitrate concentrations in salt-impacted soils were greatest generally in December and January.

3.9 Soil solution ammonium-N

If ammonium starts to accumulate slowly in soil during autumn months as a result of reduction in utilization by microbes and vegetation, high ammonium-N concentrations in soil solution would be expected where chloride concentration rises sharply in response to road salting (the mobile anion effect). Such an effect would be particularly great close to the road, and this can be clearly seen for T1, T2 and T4 (Fig. 7). It was noted that T4 had higher Cl^- concentrations than T3, so the mobile anion effect would be less for T3. However high ammonium-N occupancy of exchange sites was seen on salt impacted sites at 32 m (Fig. 1) and this is also reflected in soil solution ammonium-N concentration at these distances in Fig. 7. The apparently anomalously high ammonium-N concentration down much of the T6 transect in July 2006 could possibly reflect a localized high input from animal defecation during a wet (10.6 mm of rainfall over 24-h) sampling period, as on the other sampling dates T5 and T6 displayed generally similar values (note differences in scales for T5 and T6).

3.10 Crookdale Brook

Water pH and concentrations of the base cations Ca, Mg and Na in the river increased as the road (Fig. 8) and Crookdale Brook converged (Fig. 1). However base cation concentrations varied over time too, and were especially high during periods when winter maintenance was prominent (22/11/2005- 27/01/2006). This suggests relationships between the quantities of base cations observed in Crookdale Brook and road salt application.

The sampling sites ranged over 1.5 km of the water course from S1, where there was no road salt effect, to S7, with a progressive increase in the road effect (Fig. 1). Site S7 might be expected to have the greatest potential affect as it is closest to the road, with a drainage pipe entering the system up slope, just prior to the river sampling point. However, the concentration of sodium ions at S7 is diluted by the introduction of additional unpolluted water (S6) from the Borrowdale Brook tributary prior to the sampling point. Up stream of S1, the catchment area spans over ca. 7 km^2; hence, the enhancements in base cation concentrations depicted in Fig. 8 are very significant, bearing in mind the relative area of unaffected catchment upstream of S2. A considerable road impact occurs within a few hundred metres. This trend is also apparent in chloride concentration, and there were positive significant relationships between the concentrations of base cations (Na, Mg and Ca) and chloride (all at the 1% level). S7 data was excluded in drawing up the correlation matrix for reasons discussed earlier.

Figure 8 shows that nitrate-N in the river increased as the road and Crookdale Brook converged, especially during periods when winter maintenance was prominent (22/11/2005- 27/01/2006). There is a relationship between the concentrations of nitrate and sodium observed (5% level). There does not appear to be a spatial trend with respect to the river ammonium concentrations (Fig. 8), although the high ammonium concentrations in autumn reflect temporal trends also observed in October/November in upland streams in Scotland (Clark *et al.*, 2004).

4 Discussion

Organic matter is mobilized as a result of a high pH desorption process as well as via a loss of soil aggregate stability following displacement of calcium and magnesium ions from soil organic matter cation exchange sites by sodium ions. From Table 4 it is clear that organic matter loss from salt-impacted soils has occurred between 2 and 8 m, which correspond to dominance of the base cations by sodium (Tables 2 & 3), but also higher pH (Fig. 2). Organic matter within 2-8 m has probably shifted down slope due to the sodium dispersal effects on organic matter. This mobilization would be facilitated by the higher soil pH in the salt-effected soils (Fig. 2), especially at 2-4 m, which would also favour loss of organic matter by mineralization. There would be less organic matter input near drain-affected areas too which, coupled to past heavy leaching losses, could lead to the apparent accumulation down slope. Lower organic matter input is a likely result of lower root density and/or faunal activity (Peinemann *et al*., 2005). Visual examination of the soil profiles clearly showed reduced organic horizon depths at salt-affected sites at 2-8 m, which is indicative of a degenerative long-term process. This would make less organic N available for mineralization. The reduced organic matter depth is unlikely to be a result of pedological processes as the trend depicted between the salt-exposure scenarios close to the road has been consistently replicated in several studies completed by the authors at 4 m from the wall (Green *et al*., 2007, under revision). In addition the C:N ratio for the control transect (2-32 m) is significantly and consistently lower than ratios for either of the salt-impacted transects (Fig. 5). The C:N ratio provides some evidence towards a greater mineralization as a result of a higher pH at salt-impacted transects (Fig. 2), although this is not unequivocally proven here.

A high negative charge is essential in the bonding of soil organic matter to the layered clay minerals by cation bridges (calcium and magnesium ions) and to iron and aluminium oxides. Steric changes of the organic matter associated with this bonding and the formation of the cross linkages between polymers by polyvalent cations stabilize the organic molecules against both chemical and biological attack (Peinemann *et al*., 2005). If the calcium and magnesium ions are displaced from the organic matter cation exchange sites, the organic fraction becomes vulnerable to mobilization. However, it is clear from Tables 3 & 4 that there are elevated calcium contents in salt-affected transects close to the highway over and above the control values. This is a product of the road salt itself containing a portion of calcium ions, as well as sparing soluble residues (i.e.7.5% by mass, which includes gypsum) (Kay Monoghan, Salt Union, Pers. Comm). Hence, the organic matter loss at this site is more likely to be controlled by pH.

It must be noted that most of the organic matter that was potentially mobile has already been dispersed close to the road (Green *et al.*, under revision), so evidence of such facilitated movement of organic matter in soil solution now is unlikely as road salting has been conducted in this region for several decades. The freshwater data (Fig. 8) illustrate a sudden increase in both calcium and magnesium concentrations for the first salting event sampled (22/11/2006). However, this was not reflected in the soil solution data for the soils upslope where no sudden increase in concentration of either cation was detected (results not shown). The effect is due to the higher chloride input acting as a mobile anion on soils further down slope, with calcium and magnesium being displaced from soils in the riparian zone.

Ammonium will be competitively displaced through cationic exchange processes. Duckworth & Cresser (1991) noted that environments receiving salt inputs from marine sources (although episodic in nature) may experience greater mobility of NH_4^+ in the soil system, due to competitive ion-exchange effects from the weak neutral soluble salts. The proportion of ammonium on the CEC is also markedly lower than that of the control for both T1/T2 and T3/T4 (Fig. 3); this is as hypothesised. Such displacement may lead to ammonium limitation, which may also generate plant stress and growth suppression. It could be made worse by faster nitrification (Fig. 4) at the higher pH in salt-effected soils, coupled to nitrate leaching.

The interpretation of the possible influence of road salting on the nitrogen cycle is complex due to the number of possible drivers involved which may be affected by salting. Soil pH (Fig. 2), salinity and the displacement of organic matter (including organic-N) and cation exchange effects all influence key processes in the nitrogen cycle such as ammonification and nitrification. It is very clear though that ammonium % occupancy of the soil CEC has been reduced over time in the salt-affected transects, by displacement and/or enhanced nitrification at higher soil pH. Therefore no major displacement flush would necessarily be expected in the soil solution data in this study. However, there is an initial increase in ammonium-N in soil solution at 2 m after December; thus some displacement may be occurring at very high mobile anion concentrations or a direct road runoff influence is present (Fig. 7, T1/T2). The ammonium and nitrate concentrations observed in the drainage water (0.76 and 0.44 mg l^{-1}, respectively) and road salt analysis (0.02 and 0.05 mg l^{-1} per 200 mg NaCl l^{-1}, respectively) could explain a portion of this observation, but is a small contribution compared to concentrations in soil solution detected at 2 m from the highway for T1/T2.

The sodium and chloride concentrations observed at the A6 are likely to be typical of A roads in the UK. The heavier traffic loads tend to be on trunk routes and motorways, which will tend to have a greater number of applications within the winter maintenance period.

The reduction in CEC (Table 2) has a knock-on effect on bioavailability of ammonium for further microbial transformation processes or direct plant uptake. What also needs to be considered is the role of salinity and pH shifts on the microbial population as well as effects upon soil structure stability and the enhanced organic matter mobility; these together ultimately affect microbial functioning. Heavy metal contamination from spray or road drainage, and hence interfering with microbial processes in the soil are unlikely due to the concentrations of manganese, copper, lead, cadmium, zinc and barium all being below < 0.02 mg l^{-1}.

There are clear spatial variations between and within transects with respect to pH (Fig. 2) which will enhance or suppress nitrification within the study area. Elevated nitrate-N concentrations above control levels are evident in both drainage- and spray-affected soils, suggesting that nitrification has been enhanced by the elevated pH. The decline in KCl-extractable nitrate-N below 32 m (Fig. 4) corresponds with the start of ammonium-N build up in soil solution (Fig. 7) in salt-affected soils, probably as a result of less nitrification due to more acidic conditions at 16-32 m and beyond, and increasingly organic soils as the distance from the highway increases. The elevated nitrate-N concentrations in soil solution along polluted transects also indicate an enhanced potential for leaching to surface waters (Fig. 7).

Green *et al*. (2007) showed that the concentration of ammonium-N was much greater in unpolluted control soils. As well as the ammonium leaching from salt-impacted soils, this probably reflects the lower organic matter content, and hence lower CEC (Tables 2 & 3), that has evolved in impacted soils, leading to a reduced pool of mineralizable N and lower content of stored ammonium. However, it can only be speculated about the extent to which this reflects enhanced leaching losses of organic C and N over many years, enhanced decomposition of organic matter at the higher soil pH that is a consequence of the salting impact over several decades, or reduced input of plant litter as a consequence of salt impacts upon vegetation growth.

There is clearly potential for enhanced nitrate loading of waterways due to leaching, which has particular relevance to the Water Framework Directive. This is especially true in the UK uplands where major trunk roads often run parallel to rivers that supply a substantial portion of UK potable waters (Smart *et al.*, 2001). However, it is in these areas where de-icing salts are most likely to be needed to maintain the flow of traffic through the winter months on roads.

5 Conclusion

There is clear evidence that a number of effects on the nitrogen cycle are induced by highway winter maintenance activities. There is evidence indicative of high sodium inputs flushing ammonium from soils and a reduction in the extent of ammonium retention on exchange sites close to the highway (Fig. 3 and Table 2), while with increasing distance from the highway down slope ammonium retention increases (Fig. 3). In addition there is evidence to support the hypothesis that organic matter content, and hence the pool of mineralizable-N, of roadside soils is lowered, with a possible increase down slope. Evidence to support the theory that enhanced mineralization of organic-N, especially nitrification, is promoted by the increase in soil pH on soil processes is provided in this paper, along with evidence of increased soil solution nitrate-N in rivers and soil solutions.

Multiple drivers are involved in the processes, but their relative importance is difficult to establish unequivocally. The experiments performed by Green *et al.* (2007; under revision) complement the field study discussed above. The influence of road salt declines as the distance from the highway increases; however, the impacts on the Crookdale Brook, many tens of metres from the road, are still prominent.

Acknowledgements

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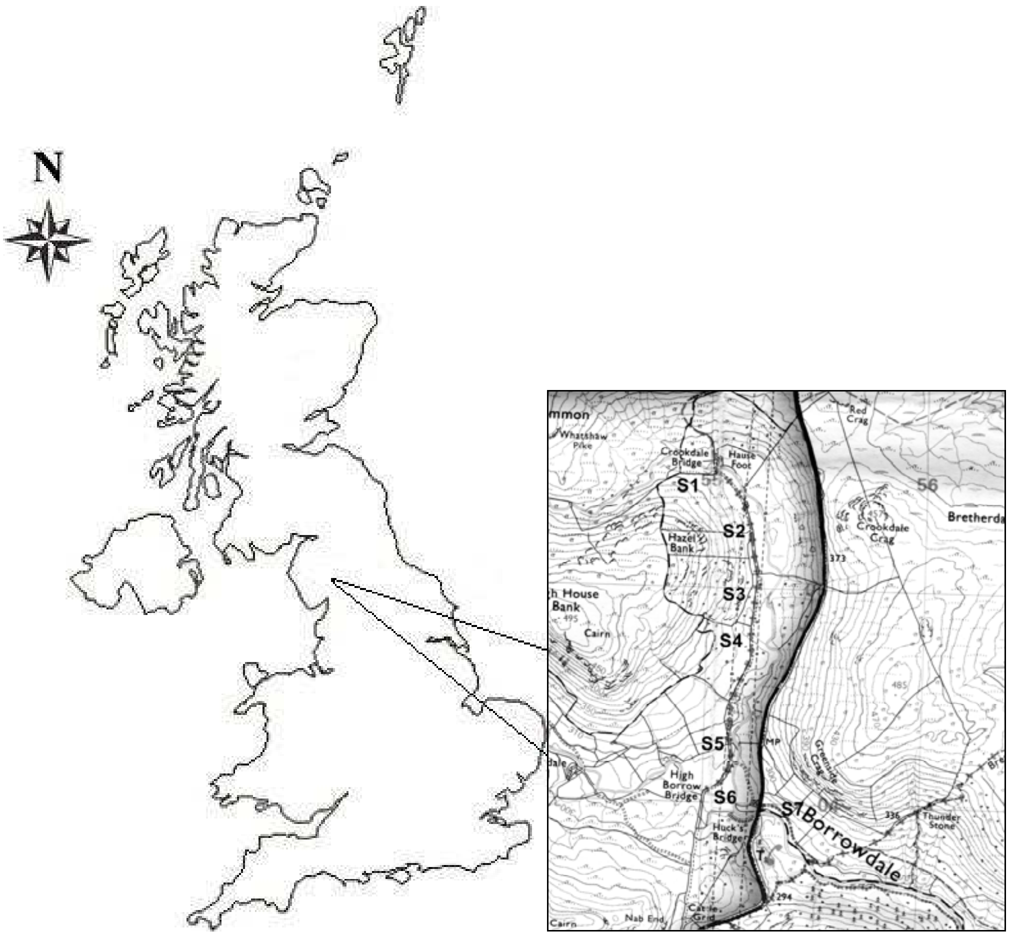

Figure 1: Map showing the location of the field Site, UK. The A6 road runs due north across the centre of the insert map; S1 – S7 indicate the river sampling points. (C) Crown Copyright Ordnance Survey. All rights reserved.

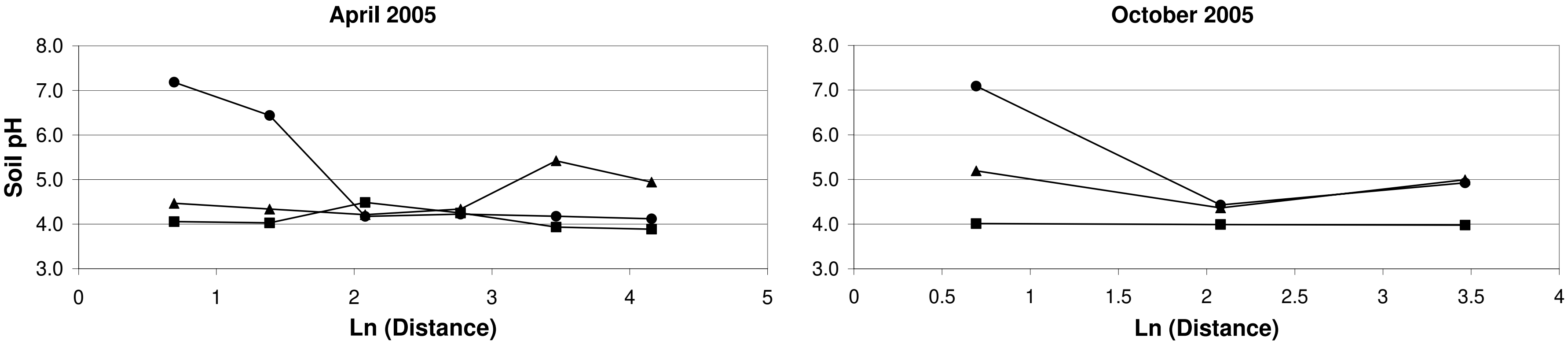

Figure 2: Soil pH (H_2O) for April and October 2005 for soil samples at 2, 4, 8, 16, 32 and 64 m from the wall for the controls (T5 & T6: squares), drain-impacted soils (T1 & T2: circles) and indirectly affected soils (T3 & T4: triangles).

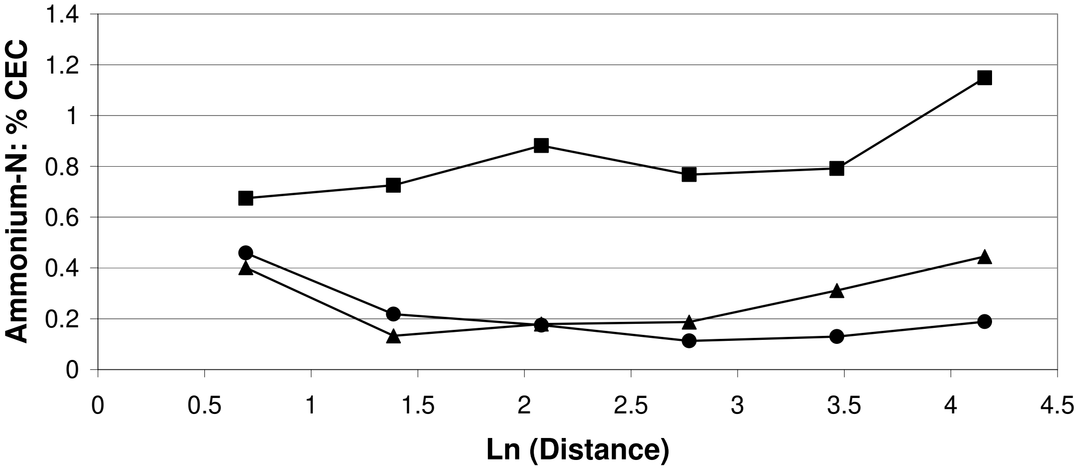

Figure 3: Mean percentage ammonium-N occupation of the CEC for April 2005 for 2, 4, 8, 16, 32 and 64 m from the wall for the controls (T5 & T6: squares), drain-impacted soils (T1 & T2: circles) and indirectly affected soils (T3 & T4: triangles).

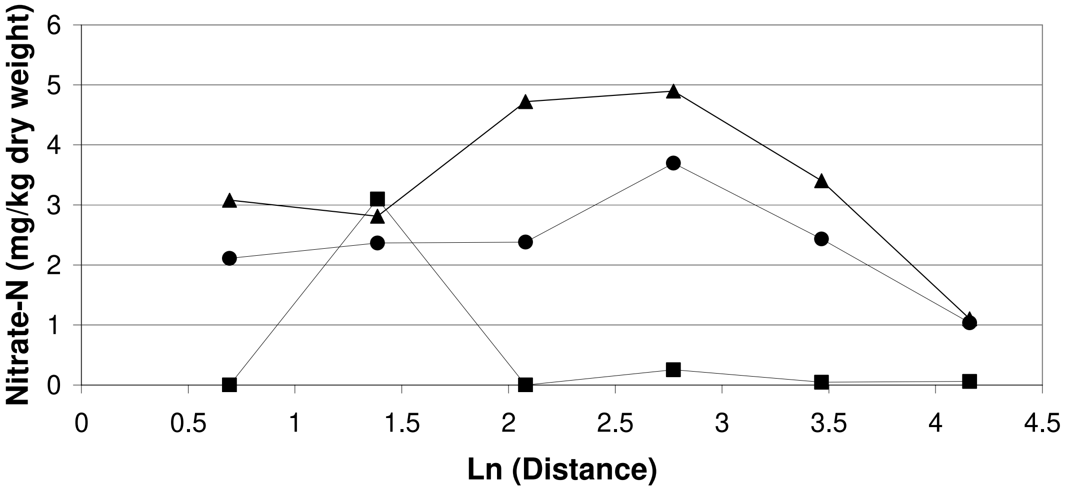

Figure 4: KCl-extractable nitrate-N concentration (mg/kg) for April 2005 for soils sampled at 2, 4, 8, 16, 32 and 64 m from the wall for the controls (T5 & T6: squares), drain-impacted soils (T1 & T2: circles) and indirectly affected soils (T3 & T4: triangles).

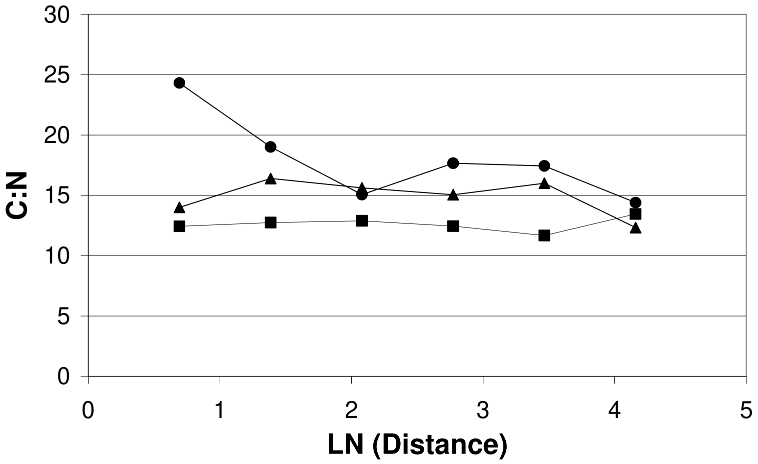

Figure 5: C:N for April 2005 for soil samples at 2, 4, 8, 16, 32 and 64 m from the wall for the controls (T5 & T6: squares), drain-impacted soils (T1 & T2: circles) and indirectly affected soils (T3 & T4: triangles).

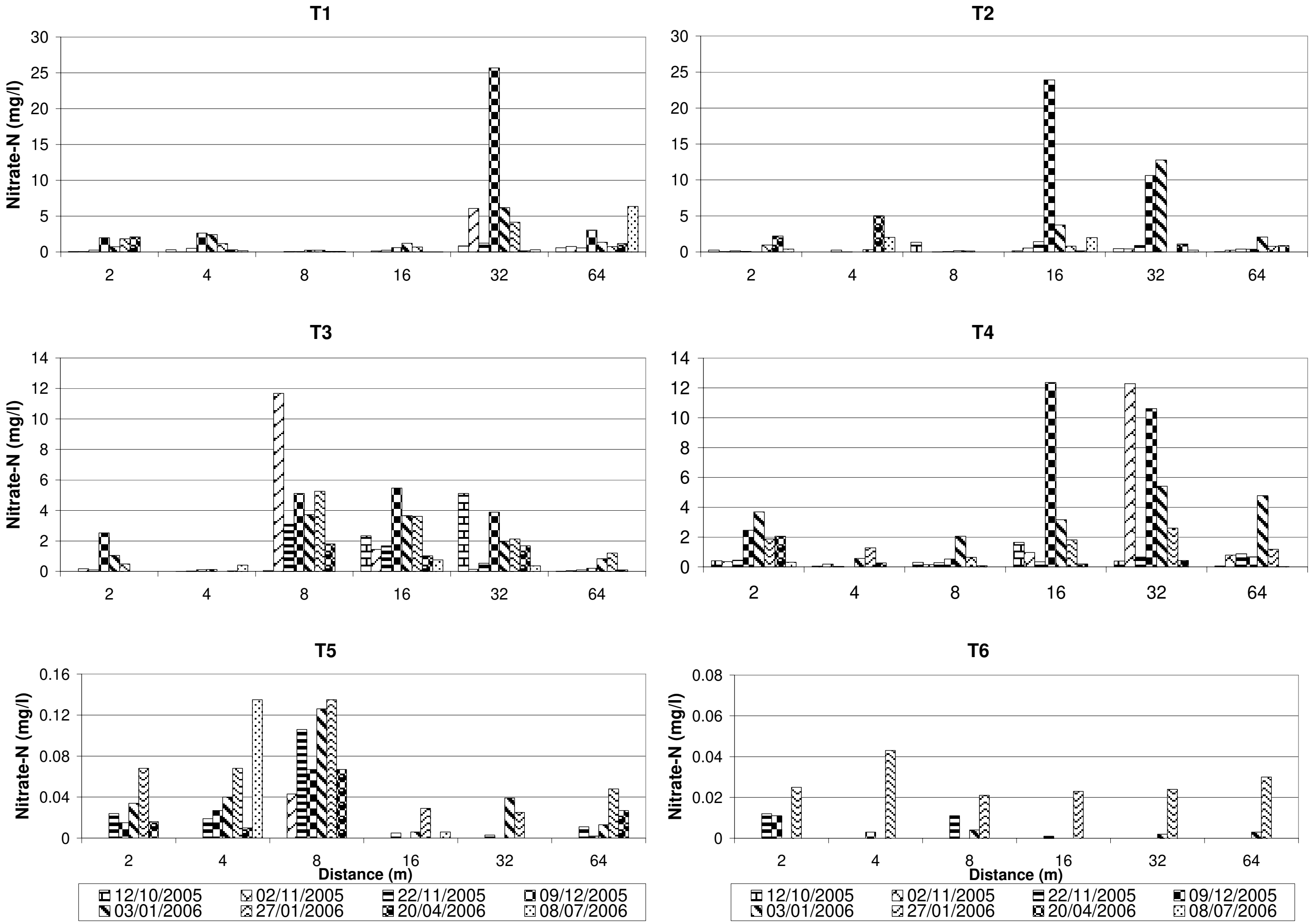

Figure 6: Nitrate-N concentration for soil solutions at 2, 4, 8, 16, 32 and 64 m for drain-affected soils (T1 &T2), spray-affected soils (T3 & T4) and control soils (T5 & T6).

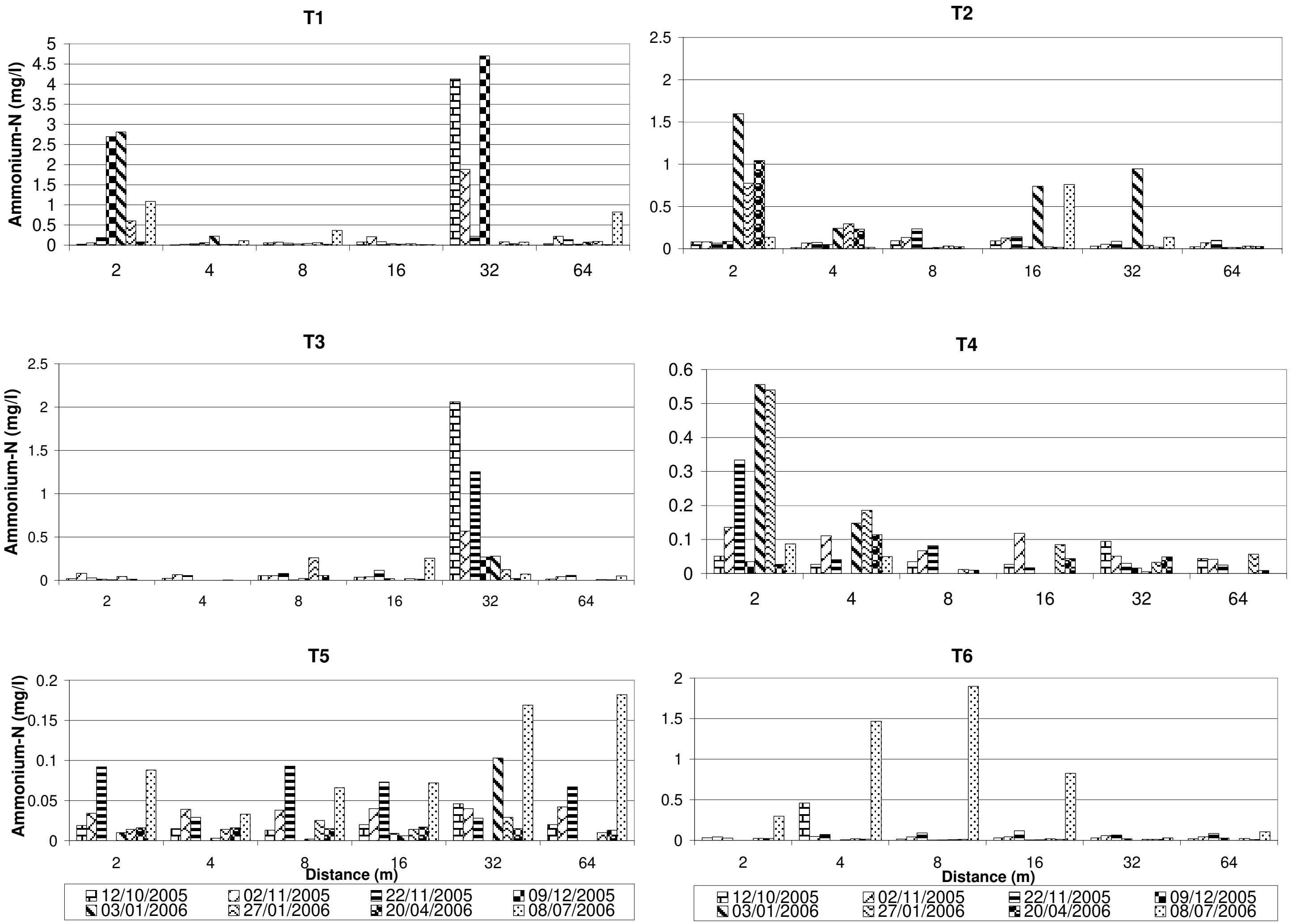

Figure 7: Ammonium-N concentration for soil solutions at 2, 4, 8, 16, 32 and 64 m for drain-affected soils (T1 &T2), spray-affected soils (T3 & T4) and control soils (T5 & T6).

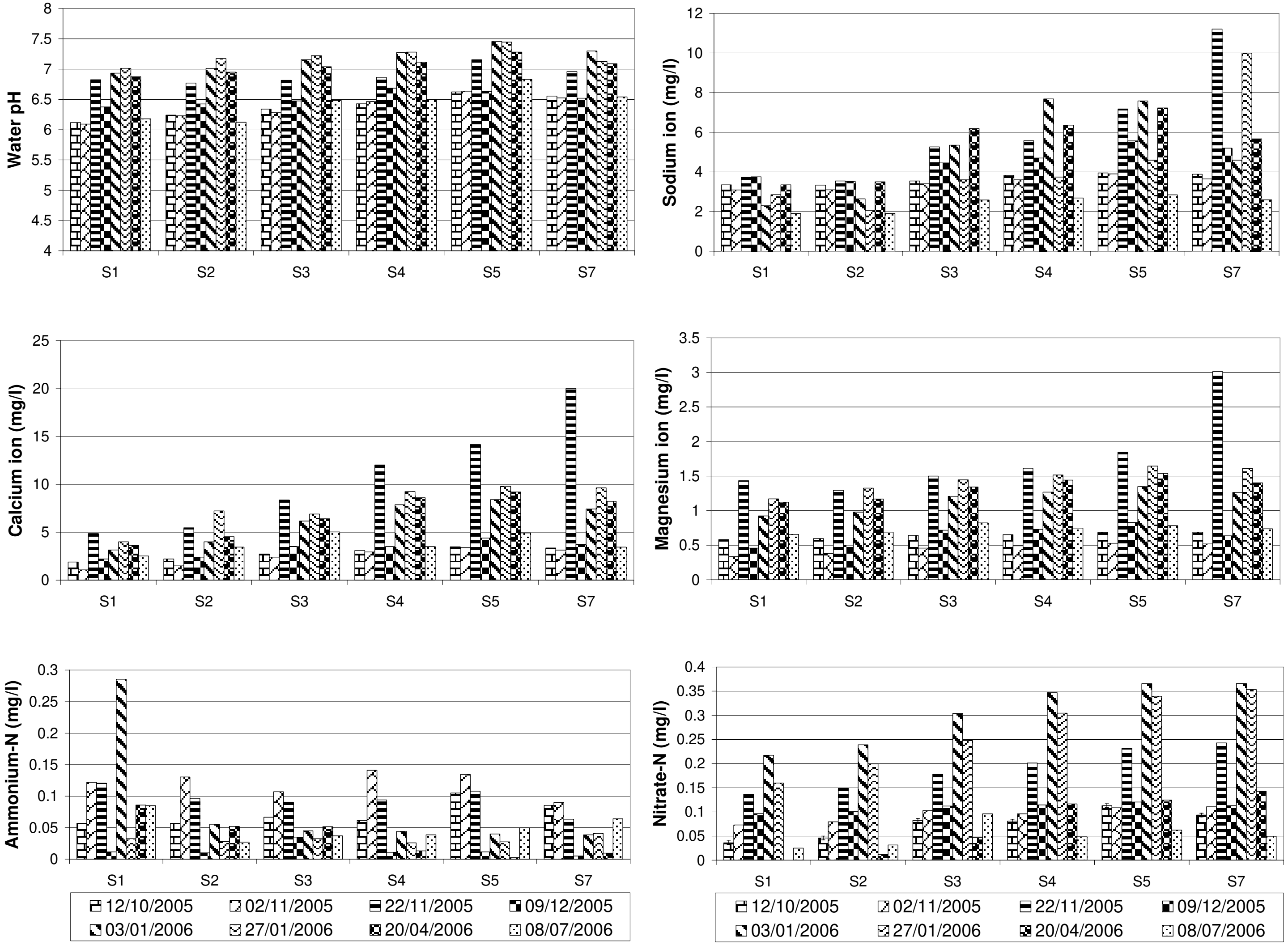

Figure 8: The change in (a) pH, (b) sodium (c) calcium (d) magnesium (e) ammonium-N and (f) nitrate-N concentration (mg l^{-1}) with time and distance along Crookdale Brook for the period 12/10/2005 – 08/07/2006.

Table 1: Soil solution and freshwater sampling dates (**Bold**) in relation to winter maintenance activities (**Y** indicates salt application) on the A6. July sampling date not shown.

OCTOBER		**NOVEMBER**		**DECEMBER**		**JANUARY**		**FEBRUARY**		**MARCH**		**APRIL**	
2005		**2005**		**2005**		**2006**		**2006**		**2006**		**2006**	
01-10-05		01-11-05		01-12-05		01-01-06	**Y**	01-02-06	**Y**	01-03-06	**Y**	01-04-06	
02-10-05		**02-11-05**		02-12-05		02-01-06	**Y**	02-02-06		02-03-06	**Y**	02-04-06	
03-10-05		03-11-05		03-12-05		**03-01-06**	**Y**	03-02-06	**Y**	03-03-06	**Y**	03-04-06	
04-10-05		04-11-05		04-12-05		04-01-06	**Y**	04-02-06		04-03-06	**Y**	04-04-06	
05-10-05		05-11-05		05-12-05	**Y**	05-01-06	**Y**	05-02-06		05-03-06	**Y**	05-04-06	
06-10-05		06-11-05		06-12-05	**Y**	06-01-06	**Y**	06-02-06		06-03-06	**Y**	06-04-06	
07-10-05		07-11-05		07-12-05	**Y**	07-01-06		07-02-06	**Y**	07-03-06	**Y**	07-04-06	
08-10-05		08-11-05		08-12-05	**Y**	08-01-06	**Y**	08-02-06	**Y**	08-03-06		08-04-06	
09-10-05		09-11-05	**Y**	**09-12-05**		09-01-06		09-02-06		09-03-06		09-04-06	
10-10-05		10-11-05	**Y**	10-12-05		10-01-06		10-02-06	**Y**	10-03-06	**Y**	10-04-06	
11-10-05		11-11-05		11-12-05	**Y**	11-01-06	**Y**	11-02-06	**Y**	11-03-06	**Y**	11-04-06	
12-10-05		12-11-05	**Y**	12-12-05	**Y**	12-01-06		12-02-06		12-03-06	**Y**	12-04-06	
13-10-05		13-11-05	**Y**	13-12-05	**Y**	13-01-06		13-02-06		13-03-06	**Y**	13-04-06	
14-10-05		14-11-05		14-12-05	**Y**	14-01-06	**Y**	14-02-06		14-03-06	**Y**	14-04-06	
15-10-05		15-11-05	**Y**	15-12-05		15-01-06	**Y**	15-02-06	**Y**	15-03-06	**Y**	15-04-06	
16-10-05		16-11-05	**Y**	16-12-05	**Y**	16-01-06	**Y**	16-02-06	**Y**	16-03-06	**Y**	16-04-06	
17-10-05		17-11-05	**Y**	17-12-05	**Y**	17-01-06	**Y**	17-02-06	**Y**	17-03-06	**Y**	17-04-06	
18-10-05		18-11-05	**Y**	18-12-05	**Y**	18-01-06		18-02-06	**Y**	18-03-06		18-04-06	
19-10-05		19-11-05	**Y**	19-12-05	**Y**	19-01-06		19-02-06	**Y**	19-03-06		19-04-06	
20-10-05		20-11-05	**Y**	20-12-05		20-01-06	**Y**	20-02-06	**Y**	20-03-06		**20-04-06**	
21-10-05		21-11-05	**Y**	21-12-05	**Y**	21-01-06	**Y**	21-02-06	**Y**	21-03-06		21-04-06	
22-10-05		**22-11-05**	**Y**	22-12-05		22-01-06	**Y**	22-02-06	**Y**	22-03-06		22-04-06	
23-10-05		23-11-05	**Y**	23-12-05	**Y**	23-01-06	**Y**	23-02-06	**Y**	23-03-06		23-04-06	
24-10-05		24-11-05	**Y**	24-12-05	**Y**	24-01-06	**Y**	24-02-06	**Y**	24-03-06		24-04-06	
25-10-05		25-11-05	**Y**	25-12-05	**Y**	25-01-06	**Y**	25-02-06	**Y**	25-03-06		25-04-06	
26-10-05		26-11-05	**Y**	26-12-05	**Y**	26-01-06	**Y**	26-02-06	**Y**	26-03-06		26-04-06	
27-10-05		27-11-05	**Y**	27-12-05	**Y**	**27-01-06**	**Y**	27-02-06	**Y**	27-03-06		27-04-06	
28-10-05		28-11-05	**Y**	28-12-05	**Y**	28-01-06	**Y**	28-02-06	**Y**	28-03-06	**Y**	28-04-06	
29-10-05		29-11-05	**Y**	29-12-05	**Y**	29-01-06	**Y**			29-03-06		29-04-06	
30-10-05		30-11-05	**Y**	30-12-05	**Y**	30-01-06	**Y**			30-03-06		30-04-05	
31-10-05				31-12-05	**Y**	31-01-06	**Y**			31-03-06			

Table 2: Mean cation exchange capacity and % Na^+, Ca^{2+}, Mg^{2+}, K^+, NH_4^+ and H^+ of CEC for April 2005, with standard errors in parentheses. ** denotes significant difference in mean for direct, spray and control transects at the 1%, * at the 5 % level. Similar superscript letters indicate no significant difference for post-hoc.

Parameter	Mean (SE)		
	Direct (T1 & T2)	Indirect (T3 & T4)	Control (T5 & T6)
CEC ($mmol_c$ kg^{-1})	306.67 (36.95)	257.45 (27.94)	396.18 (45.68)
Na^+ (%)**	9.97^a (3.23)	2.47^a (0.38)	0.51^b (0.03)
Ca^{2+} (%)**	9.32^a (1.69)	15.16^b (2.11)	3.74^c (0.62)
Mg^{2+} (%)*	2.41^a (0.30)	4.03^{ab} (0.57)	2.84^b (0.15)
H^+ (%) **	77.78^a (4.53)	77.53^a (2.91)	92.28^b (0.73)
NH_4^+ (%)**	0.25^a (0.05)	0.36^a (0.07)	0.99^b (0.10)

Table 3: Mean cation exchange capacity and % Na^+, Ca^{2+}, Mg^{2+}, NH_4^+ and H^+ of CEC for April 2005 for soils sampled at 2, 4, 8, 16, 32 ad 64 m from the wall, with standard errors in parentheses. ** denotes significant difference in mean for direct, spray and control transects at the 1%, * at the 5 % level. Similar superscript letters indicate no significant difference for post-hoc.

Dist. (m)	CEC (mmol$_c$ kg^{-1})			Na^+ (% CEC)			Ca^{2+} (% CEC)			Mg^{2+} (% CEC)			H (% CEC)		
	Direct (T1 & T2)*	Indirect (T3 & T4)	Control (T5 & T6)	Direct (T1 & T2)**	Indirect (T3 & T4)	Control (T5 & T6)	Direct (T1 & T2)	Indirect (T3 & T4)	Control (T5 & T6)	Direct (T1 & T2)	Indirect (T3 & T4)	Control (T5 & T6)	Direct (T1 & T2)*	Indirect (T3 & T4)	Control (T5 & T6)
2	170 (43.6)^a	119 (43.3)	452 (172)	34.3 (12.4)^a	3.41 (1.62)	0.62 (0.12)	14.8 (4.87)	17.7 (7.68)	6.27 (3.25)	1.21 (0.40)	5.51 (2.49)	3.17 (0.55)	49.4 (17.3)^a	71.6 (12.2)	89.4 (3.74)
4	167 (29.46)^a	305 (19.8)	524 (139)	14.3 (5.32)^a	1.40 (0.21)	0.49 (0.7)	16.8 (3.08)	12.1 (2.70)	3.39 (0.72)	1.67 (0.30)	2.36 (0.19)	2.93 (0.39)	66.8 (8.02)^a	83.3 (3.16)	92.7 (0.91)
8	203 (53.8)^a	279 (41.8)	277 (65.2)	7.31 (3.95)^{ab}	1.69 (0.76)	0.52 (0.10)	8.48 (5.67)	14.6 (6.64)	5.08 (0.91)	2.43 (0.58)	3.18 (1.06)	2.96 (0.40)	81.5 (9.43)^{ab}	80.0 (8.46)	90.8 (0.64)
16	490 (90.8)^b	367 (100)	376 (75.1)	1.38 (0.41)^{bc}	1.59 (0.64)	0.45 (0.68)	6.98 (3.55)	6.81 (3.01)	3.50 (0.96)	2.70 (0.54)	2.43 (0.29)	2.35 (0.31)	88.3 (3.73)^{ab}	88.7 (3.87)	93.4 (1.46)
32	468 (84.6)^b	287 (85.6)	326 (69.6)	1.38 (0.35)^{bc}	3.32 (0.82)	0.45 (0.48)	4.94 (1.41)	18.2 (2.40)	2.14 (0.57)	3.54 (1.37)	4.54 (0.60)	2.90 (0.20)	89.6 (3.17)^b	73.6 (3.19)	93.8 (0.61)
64	339 (72.6)^{ab}	184 (33.4)	419 (138)	1.05 (0.22)^c	3.44 (0.79)	0.54 (0.10)	3.94 (2.14)	21.6 (5.84)	2.04 (0.43)	2.92 (0.40)	6.19 (1.58)	2.71 (0.35)	91.2 (2.67)^b	67.9 (5.54)	93.7 (1.24)

Table 4: Mean loss-on-ignition (%) for April 2005 for soils sampled at 2, 4, 8, 16, 32 ad 64 m from the wall, with standard errors in parentheses. * denotes significant difference in mean LOI (%) for direct, spray and control transects at the 5 % level for the defined distance. Similar superscript letters indicate no significant difference for post-hoc.

	Mean LOI (%)		
Distance (m)	Direct (T1& T2)	Spray (T3 & T4)	Control (T5 & T6)
2*	14.7 (1.0)^{a}	11.4 (0.8)^{a}	37.7 (11.0)^{b}
4*	12.1 (1.7)^{a}	24.2 (0.7)^{ab}	38.1 (9.5)^{b}
8*	12.6 (2.0)^{a}	21.9 (0.6)^{b}	21.4 (2.8)^{b}
16	29.4 (4.4)	26.9 (5.5)	20.5 (3.6)