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Published paper
Title: Effect of long-term changes in soil chemistry induced by road salt applications on N-transformations in roadside soils.

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Abstract:
Of several impacts of road salting on roadside soils, the potential disruption of the nitrogen cycle has been largely ignored. Therefore 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 have been studied. The use of road salts disrupts the proportional contributions of nitrate-N and ammonium-N to the mineral inorganic fraction of roadside soils. It is highly probable that that the degree of salt exposure of the soil, in the longer term, controls the rates of key microbial N transformation processes, primarily by increasing soil pH. Additional influxes of ammonium-N to salt impacted soils are rapidly nitrified therefore and, thereafter, increased leaching of nitrate-N to the local waterways occurs, which has particular relevance to the Water Framework Directive. The results reported are important when assessing the fate of inputs of ammonia to soils from atmospheric pollution.

“Capsule”: Road salting effects ammonification and nitrification in roadside soils.

Keywords: Road salt, ammonification, nitrification, roadside soils.

1. Introduction:
The application of deicing agents to roads has been widely practised in Europe and North America during winter months since the 1960s to minimise the risk of accidents due to ice and snow and to maintain traffic flow. Several different de-icing agents are available, but most agencies in the UK use sodium chloride, which can be applied to roads as a liquid or solid, depending upon the conditions (Blomqvist and Johansson, 1999). The salt may be relatively pure NaCl, or mixed with grits and sands, and possibly an anti-caking agent such as sodium hexacyanoferrate (II) (Ohno, 1990).

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De-icing salts provide safer driving conditions by dissolving into precipitation, either melting any ice or snow, or preventing the formation of ice on the roads. However, 75–90% of the applied de-icing salt enters the roadside environment directly in runoff and as splash or aerosol deposition (Astebol et al., 1996), via mechanical malfunction during application or post-application ploughing, or as wash off from vegetation as throughfall. Deposition occurs mainly within 10 m of the roadside (Astebol et al., 1996; McBean and Al-Nassri, 1987), although elevated concentrations of Na$^+$ and Cl$^-$ have been observed from tens to hundreds of metres from roads (Blomqvist and Johansson, 1999).

2. Impacts on Soils, Plants and Freshwaters:

The detrimental impacts of elevated concentrations of Na$^+$ and Cl$^-$ on roadside soils, vegetation, and ground- and surface-waters (as well as automobiles and road surfaces) have been well documented. Effects on soils and plants include:

**Impacts on Soil:**

1. Possible alterations in soil structure (Bäckström et al., 2004; Norrstrom and Bergstedt, 2001).
2. An increased potential for colloid mobility and therefore associated heavy metal mobility (Amrhein et al., 1992; Grolimund et al., 1996; Norrstrom and Jacks, 1998; Shainberg and Letey, 1984).
3. Possible reductions in hydraulic conductivity as pores become blocked by the release of fine particulates and soil colloids (Norrstrom and Bergstedt, 2001).
4. Changes in the concentrations of cations on cation exchange sites and in soil solution leading to changes in soil and soil solution pH and ion concentrations, and disruption of natural and other pollutant element biogeochemical cycling (Bäckström et al., 2004; Bauske and Goetz, 1993; Darban et al., 2000; Duckworth and Cresser, 1991; Löfgren, 2001; Norrstrom and Bergstedt, 2001; Norrstrom and Jacks, 1998; Sarin et al., 2000; Shanley, 1994).
5. Changes in the soil microflora and microfaunal communities to ones that may be more salt tolerant.
Impacts upon Plants:

Direct impacts upon roadside plant communities include leaf and needle scorch, branch dieback, disfigurement, loss of turgidity, growth reduction and sometimes toxicity to plant life (Bryson and Barker, 2002; Bayuelo-Jiménez et al., 2003; DOE & DOH, 2001; Fostad and Pedersen, 2000; Kayama et al., 2003; Townsend, 1980; Serrano and Rodriguez-Navarro, 2001; Viskari and Kärenlampi, 2000).

Plants may be affected via several mechanisms:

1. Ions may accumulate to toxic concentrations within plant tissues (Townsend, 1980). Increasing osmotic pressure differences may cause desiccation (Bryson and Barker, 2002; Larcher, 1995; Townsend, 1980). However, damage usually results from a specific ion effect rather than from an increase in osmotic potential (Townsend, 1980).

2. Nutrient element imbalances (reduced levels of available ammonium, Ca\(^{2+}\), and K\(^+\) within the soil) may occur (Bayuelo-Jiménez et al., 2003; Serrano and Rodriguez-Navarro, 2001).

3. Plant growth may be adversely effected by alterations to soil structure.

4. Plants that are subjected to salt stress also tend to become susceptible to diseases (Bryson and Barker, 2002; Viskari and Kärenlampi, 2000).

Impacts upon Fresh Waters:

Several investigations have revealed increased sodium and chloride ion concentrations in both groundwater and surface waters in the vicinity of roads (Demers and Sage, 1990; DOE & DOH, 2001; Löfgren, 2001; Ruth, 2003; Scott, 1976 Shanley, 1994). Scott (1976) reported an increase in Na\(^+\) concentration by a factor of 50 over baseline levels in urban streams after road salt application, whilst Ruth (2003) reported a maximum 30-fold increase in urban streams in Helsinki, Southern Finland, during spring floods, and Demers and Sage (1990) reported chloride ion concentrations 31 times higher downstream from a major road as compared to upstream concentrations in four New York Adirondack Mountain streams. In the authors experience, such
high increases are sometimes associated with roadside salt piles. The precise
concentration increase obviously depends upon the size of unpolluted catchment
upstream, road length in close proximity to the stream and amounts of salt applied. In
the study area for the present research, for example, the Cl⁻ increase was six-fold
during the highest pollution incident studied. Potential impacts include aquatic
chloride toxicity (DOE & DOH, 2001; Mattson and Godfrey, 1994; Mayer et al., 1999;
Williams et al., 1999) and chemical stratification (Mattson and Godfrey, 1994; Smol
et al., 1983). There may be human health implications for those on salt-restricted
diets (Amrhein et al., 1992). In the UK uplands major trunk roads often run parallel
to rivers that supply a substantial portion of UK potable waters (Smart et al., 2001).
Yet 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 and have been in continuous
use for tens of years, and de-icing salts have been used as a winter maintenance
practice for as long.

3. Potential Impacts on Soil N Cycling:
Few studies have focused upon the affect on the nitrogen cycle and microbial
functionality, and the potential disruption that road salts may pose. It is hypothesised
that increasing sodium concentrations may flush ammonium ions from exchange sites
or prevent ammonium retention from atmospheric inputs (Duckworth and Cresser,
1991), and this could conceivably lead to shortages of available N for some distance
down slope of salted roads.

Spatially and temporally variable pH shifts may also modify ammonification
and nitrification rates, providing another mechanism for disruption. These may be
induced either by sodium displacing H⁺ from cation exchange sites, and similar
effects from magnesium and calcium present as impurities in commercial road salt.
They may also arise from mineral insoluble residues present in the salt (7.5 % by
mass in the salt used in the present study, including some gypsum (Kay Monaghan,
Salt Union, personnel communication), or deliberately added grit. In addition, high
concentrations of chloride can acidify soil solution down-slope by the mobile anion
effect. While soil pH does not directly control N availability per se, it does affect soil
microbial activity. Nitrifying organisms tend to be sensitive to excessive soil acidity
and their activity is markedly decreased when soil pH is less than 5.0 (Pierzynski et al.,
2000). Naturally acidic soil conditions can limit microbial activity and slow
mineralization of N as well as nitrification. Thus, a shift in soil pH from acidic to near neutral or above may enhance the rates or organic matter mineralization and of nitrification due to release from acidity constraints, but may lead eventually to loss of ammonia via volatilisation and loss of nitrate via denitrification (optimum range pH 6–8).

There is also the possibility that the ammonification process could be enhanced due to the weakened binding of organic matter to mineral structures as a consequence of sodium dominance in the soil. Nitrogen transformation processes could also be disturbed through the direct effect of roadside salt contamination and the enhanced bioavailability of heavy metals and their chloro-complexes on the microbial community itself, depending on the ecotoxicity of the chemical species. McCormick and Wolf (1980) demonstrated that the application of 0.25 mg g\(^{-1}\) of NaCl significantly reduced CO\(_2\) evolution (by 16%) in soil, and increasing the NaCl concentration progressively reduced rate of CO\(_2\) evolution, with no CO\(_2\) evolved from soil receiving 100 mg NaCl g\(^{-1}\). A decrease in O\(_2\) consumption and CO\(_2\) evolution was also observed by Azam and Muller (2003) with increasing concentrations of NaCl. At NaCl concentrations ≥ 0.25 mg NaCl g\(^{-1}\) ammonification was reduced and at 0.25 mg NaCl g\(^{-1}\), nitrification rate was significantly reduced (McCormick and Wolf, 1980). This supports Laura’s (1974, 1977) original findings that nitrification can be severely retarded or even completely inhibited in saline conditions as a result of nitrifiers being more sensitive to salinity than ammonifiers. However, such short-term NaCl additions preclude possible compensatory longer-term effects of pH increase of acid soils. This seriously limits the value of studies such as those described above, as does their inability to take into account the highly dynamic nature of soil and soil solution chemistry, and hence of the soil microbial environment, during salt contamination incidents.

If nitrification is inhibited, an accumulation of ammonium may occur, though conversely ammonium may be leached due to cation exchange competition from sodium ions (to an extent depending on relative abundance). Additionally, a potential decline in N mineralisation rate may counteract any such ammonium accumulation effect by limiting the amount of ammonium released into the soil; such amelioration would depend on the sensitivity of the micro-organisms involved within these processes to NaCl, heavy metals and chloro-complexes, as well as the chemical species’ concentrations. Laura (1977) and McCormick and Wolf (1980) illustrated...
that ammonification was increasingly retarded with increasing concentration of NaCl; beyond ≥ 25 mg NaCl g⁻¹ the concentration of ammonium in the soil declined (McCormick and Wolf, 1980).

As a result of the retardation of nitrification, any input of ammonium could lead to the accumulation of ammonium in the roadside soil. Increasing ammonia deposition on the roadside environment results from the use of three-way catalytic converters on cars, and the incomplete reduction of NO to N₂. This leads to increased ammonia in exhaust emissions, deposition declining with distance from the road (Cape et al., 2004; Truscott et al., 2005). Thus, ammonium availability is enhanced in those soils that are most effected by road salt. It is important to note that these previous studies examined the salinity effect where a fixed concentration of salt solution is added to a constant soil, with consistent chemical attributes.

A laboratory study was designed to study the fate of ammonium-N and nitrate-N inputs to roadside soils that have been impacted by salting over an extended period (decades) in the field. The objective was to quantify the extent to which microbial functioning and N species transformation rates had been affected by the presence of road salt contamination within the defined profiles and to identify and prioritise the possible causes of effects observed. An area known to have lengthy area of very acid grassland soil was explicitly chosen for the study because pH effects from salting were likely to be greatest in such a soil. Moreover it could be confirmed that soil above the road (upslope) was visibly uniform. This was necessary to be confident that differences in soils below the road and an adjacent control plots were indeed due to road runoff.

4. Materials and methods:

Field Site:

Samples of surface soil (0–10 cm) were collected from an upland site along a major road, the A6, at Selside, Cumbria, UK (Fig. 1). The site of the present study is an area of high relief, with altitudes up to 458 m above sea level. Soil types consist of podzols and poorly developed podzols (limited evolution of E and B horizons) with variable depths of organic-rich surface horizons. The bedrock in the area is primarily Upper Ludlow, Ludlow series, Upper Silurian. The vegetation at the site consists mainly of grasses, Juncus and some bryophytes; and the land is used for grazing cattle and sheep at a low stocking density. This site was selected as it presents an unusual
opportunity as road drainage is piped directly onto the soil surface at regular intervals. Hence this site presents three possible contamination level scenarios: (a) most heavily polluted, with drainage plus spray, (b) less polluted, with spray and some (minor) road runoff, and (c) controls on an adjacent hillside at the same attitude and aspect within the catchment. A wall of a height of 1.5 m separates the road from the salt-affected sampling sites. Two transects for each pollution-level scenario were sampled in duplicate, sample sites being separated by at least 10 m to ensure that pseudoreplication was avoided. Transects were marked out perpendicular to the road; in the case of the drainage-impacted transects, they were along the line of the drainage pipes (T1 & T2); spray-impacted transects (T3 & T4) were between drain-impacted transects to the left; and control transects (T5 & T6) were away from, and well above, the road, but with the same elevation, aspect, parent material and land use.

Soil sampling:
Soil samples from 0-10 cm were collected at 3 m from the wall, and thus 4 m from the road itself on the 8th July 2006. In each case, the samples were encased in polyethylene bags and placed immediately into cold storage (at 2-4°C) in preparation for the simulation experiment and chemical analysis.

Water sampling:
A water sampling survey was completed on the Crookdale Brook during the period 12/10/2005-08/07/2006. Conditions at the time of sampling are summarised in Table 1. Flow was not gauged on the Crookdale Brook directly, but discharge in the River Lune, 6 km from the Crookdale, serves as a useful surrogate. Six locations were sampled (S1-S5 + S7) along the course of the Brook, their locations being defined by the A6 (Fig. 1). Above S1 there was negligible catchment contamination from road runoff. Contamination risk increased steadily down to S5. S6 was an uncontaminated tributary, which dilutes pollution impacts slightly by S7, the furthest point sampled downstream on the main river channel. Each sampling point was sampled in duplicate. The 140-ml polyethylene bottles were rinsed several times with the sample water before a final collection was made by completely submerging the bottle and capping it under water to avoid generation of headspace. Samples were placed immediately into a cold box in preparation for chemical analysis on return to the laboratory.
Soil Analysis:
Soil moisture content was determined by oven drying at 105°C, and LOI by ashing at 800°C. Soil pH was measured on moist soil at a 1:1 substrate:water ratio.
Ammonium-N and nitrate-N were extracted from soils with 1M KCl and ammonium-N and nitrate-N determined using a standard Bran and Luebbe AutoAnalyser 3 procedure. Exchangeable base cations (Na⁺, K⁺, Ca²⁺ and Mg²⁺) were determined by AAS using matrix-matched standards after extraction with 1M ammonium acetate. CEC was determined by AutoAnalyser after washing the ammonium-saturated soils with 80% aqueous ethanol, and leaching absorbed ammonium with 1 M acidified NaCl. Performance of all instrumental methods was checked using synthetic reference standard materials.

Freshwater Analysis:
Nitrate-N in the water samples was determined using a Bran and Luebbe AutoAnalyser 3. Determinations were repeated by ion chromatography, which was also used to quantify chloride concentrations (Dionex). There was no significant difference between results obtained by the two methods of nitrate measurement.

Simulation Experiment:
For each soil of the three salt-impact scenarios, sixty 10-g sub-samples of freshly collected, field-moist sorted and homogenised un-sieved soil were inserted into 140-ml polyethylene bottles. Soils in a sub-set of 20 bottles were spiked with 50 μg of ammonium-N (as ammonium chloride, added in 0.5 ml of water), soils in a second sub-set of 20 bottles were spiked with 50 μg of nitrate-N (as sodium nitrate, added in the same volume of water), and the remaining 20 bottles were spiked with the same volume of deionised water only (as controls). Half of the bottles from each sub-set were incubated at room temperature and the other half at 4°C. After defined time intervals, duplicate samples for each salt-impact scenario were destructively analysed for ammonium-N and nitrate-N by addition of 100 ml of 0.5 M KCl, shaking for 1 h, filtration through Whatman No. 42 papers, and subsequent analysis using a Bran and Luebbe AutoAnalyser 3. The time intervals used were 0 (immediately post spiking), 1, 2, 5 and 9 days, hereafter referred to as t₀ to t₉. A 24-hour period was allowed prior
to spiking for the soils incubated at room temperature to allow acclimatisation to the
changed temperature conditions.

The incubations were done at two temperatures because it was necessary to
assess prior salting effects on nitrogen species transformation rates under wintry
conditions in order to establish possible links between soil processes and river water
chemistry over the winter period, as well as potential links at the higher temperatures
over the summer period.

5. Results:

Nitrate-N in Crookdale Brook:
The freshwater survey showed that nitrate-N and chloride concentrations in the river
increased as the road and Crookdale Brook converged at S1, on moving downstream
towards S7 (Fig. 2), especially during periods when winter maintenance was
prominent (22/11/2005-27/01/2006). This suggests relationships between the quantity
of nitrate-N observed in Crookdale Brook and road salt application. Spatial trends for
chloride were very similar to those for nitrate, and a residual increase in chloride
along the river stretch was still seen in July. Nitrate concentrations are low in April
and July, as expected due to greater plant uptake.

Soil Chemical Composition:
Table 2 summarises the soil chemical parameters for soils from T1-T6. It
demonstrates clearly the differences in soil pH (significant at 1%) and base saturation,
expressed here as % occupation of cation exchange sites for sodium, magnesium,
calcium, potassium and ammonium ions. The differences in % sodium, % magnesium
and % calcium between pollution scenarios were significant at 5 %, 5 % and 1 %
respectively. There is sodium dominance for T1 and T2, with declining contribution
of sodium to exchangeable cations for T3 and T4 and for the controls, T5 and T6,
thereafter. This corresponds to a higher dominance of CEC by hydrogen ions for the
control transects, and progressively lower H\(^+\) dominance for both spray contaminated
transects and drain-impacted transects (significant at 1%). The proportions of
magnesium and calcium follow the same trend as that for sodium ions. Note that
because of the very high salt content in T1 and T2 soils, and possibly the presence of
gypsum from the salt, \(\sum\) cations is > CEC for T2.
Although on average the proportion of exchangeable ammonium-N is lower than that of the control for both drainage- and spray-contaminated transects, because of variation between replicates this is not significant. LOI increases, on average, from the drainage transects to the controls.

The soil for drainage-influenced transects had a much higher pH (6.66 or 8.11) than that from the spray-contaminated transects (4.62 or 5.11), which were in term less acid than the control soils (3.79 or 3.82). This corresponds to the high sodium dominance and low hydrogen content of the CEC for the salt-impacted soils.

**Ammonium-N spiking at room temperature:**

Figure 3 shows how the total extractable mineral N concentration, and the contributions of nitrate-N and ammonium-N to the total mineral N, changed over the nine days following the addition of the 50 $\mu$g ammonium-N spikes with incubation at room temperature. It is immediately obvious that in the more acidic, control soils (T5 & T6), ammonium remains dominant throughout the experiment. From one-way ANOVA, ammonium fell significantly between $t_0$ and $t_9$ for T1, T2, T3, and T4 (1 %), but not change significantly in T5 and T6. Conversely nitrate increased significantly (1 %) for all transects, although differences between adjacent pairs of times were not always significant. In the most salt-impacted soils (T1 & T2), however, nitrate-N is the dominant mineral N form by the second day, and nitrate becomes increasingly dominant over time. By the end of the experiment ammonium-N is almost undetectable. The less contaminated, splash-impacted soils (T3 & T4) display intermediate behaviour. The declines in nitrate-N to ammonium-N ratio over time are very consistent, as can be even more clearly seen in Fig. 4. T1 to T4 contained significantly (1 % level) less ammonium than T5 and T6, but not significantly different amounts of nitrate.

**Nitrate-N spiking at room temperature:**

Figure 5 shows how the total extractable mineral N concentration, and the contributions of nitrate-N and ammonium-N to the total mineral N, changed over the nine days following the addition of the 50 $\mu$g nitrate-N spikes with incubation at room temperature. It is clear that in all the soils (T1 – T6), there is no evidence of nitrate immobilisation by soil microbial biomass. Indeed, for T3-T6, ANOVA showed that
nitrate concentration actually slightly increased at $t_5$ and $t_0$ in this experiment. However in the road salt-impacted soils (T1 – T4), ammonium appeared to decline by nitrification over the first 1 – 2 days, but this was only significant for T1. Over a longer time scale there was evidence of nitrification in all six soils. Ammonium was starting to accumulate by day 9, and this was especially marked and significant at 1% for the most acidic, control soils (T5 & T6), but this production of ammonium resulted also in significant nitrate build up for T4 to T6. Slight accumulation might be anticipated because of the elimination of any plant N-uptake in this experiment.

**Deionised water blank spiking at room temperature:**

Figure 6 shows how the contributions of nitrate-N and ammonium-N to the total mineral N changed over the nine days following the addition of the deionised water blank spikes with incubation at room temperature. For the most heavily impacted soils (T1 & T2), nitrate dominated the mineral N fraction, especially after 24 h of incubation. The contribution made by ammonium-N was much greater in the unpolluted, control soils (T5 & T6) throughout the experiment, and the more moderately polluted soils exhibited an intermediate trend. ANOVA showed that for ammonium, T6 > T1 to T4, but T5 did not differ significantly from T1 to T4. In all soils though the nitrate-N to ammonium-N ratio increased significantly over time.

**Incubations at 4 °C after ammonium-N spiking:**

Figure 7 compares the nitrate-N and ammonium-N after ammonium spiking with the nitrate-N and ammonium-N after deionised water blank spiking and with the spike added flux. It shows how these values changed over 9 days with incubation at 4 °C. All results are expressed on a dry weight soil basis, so although 50 μg of ammonium N was always added, the spike size appears to vary because of variations in the soil moisture content. The results clearly show that the spike size selected was very appropriate.

Between $t_0$ and $t_1$, spike ammonium-N is lost in all soils to a significant extent (compare bar 4 with bar 2), but interestingly not all is converted to nitrate-N (compare bar 5 with bar 3). At the lower incubation temperature, nitrification initially seems greater in the control soils (T5 & T6). By time $t_2$, ammonification is extremely pronounced in all the deionised water-spiked control soils (2nd bars) and in all the
ammonium-N-spiked soils (4th bars). By t5 much of the extra ammonium generated appears to have been nitrified, however.

6. Discussion:

Variation in soil properties:

In the context of the present study, it is important to establish that the very substantial differences in soil chemical composition for the three contamination scenarios are primarily due to impacts of road drainage water and not just due to natural soil spatial variations. Our preliminary field survey showed that the near-surface soils subjected to the diverse pollution scenarios at the sampling distance from the road were all highly organic, and when not adjacent to the road consistently very acidic (pH 3.8 to 4.3). There was no evidence however, compared with the soils further down-slope from the road, of any foreign mineral matter from road construction. Moreover the stones were similar in the control and roadside soils. However, the control soils were apparently more organic rich, and was confirmed by subsequent LOI % measurement (Table 2). It is therefore highly probable that differences between soils were attributable not to natural variation, but to combined effects of road salt in runoff, insoluble particulates from the salt, the additional water flux and associated soil wetness and erosion effects, and possibly to soil particulates redistributed by vehicle flow in both directions along the A6 being flushed from the road surface down drains. The salt used in the area contains 7.5 % insoluble solids, which include small amounts of gypsum and carbonate (Kay Monaghan, personnel communication).

In spite of the circum-neutral soil pH near drain outlets (Table 2), there was no sign of well-developed cambisol formation, which might be expected if the variation was natural. As will be seen later, and is clear in Table 2, the high sodium dominance of CEC plays a major role in increasing the soil pH of these naturally highly acidic soils. For one of the drain-impacted transects (T2), sodium occupied 85 % of the CEC at 3 m from the road. For the same soil, calcium occupied much less of the CEC, in spite of it being divalent, and the presence of significant amounts of calcium in the road salt being used (ratio of 80:0.7:0.07 Na:Ca:Mg). Thus it seems that the sodium in road drainage has a major impact on the soil chemistry. In addition the very high concentrations of chloride in soil solutions at this site (up to 7 900 mg l⁻¹ during salting, Green and Cresser, 2007) add credibility to the hypothesis that road salt is the major cause of observed differences between soils from the different pollution
scenarios, as does the observation of dramatic seasonal shifts in soil pH for salt-impacted soils only (Green and Cresser, 2007). However, as % Ca > % Na on CEC for T3 and T4, it is clear that particulates and/or soluble calcium in splash from the road must make an important contribution to soil partial neutralization.

Nitrate and Chloride in Crookdale Brook:
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. 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 nitrate-N at S7 is diluted by the introduction of additional water from the Borrowdale Brook tributary prior to the sampling point. This effect is more conspicuous for Cl\(^-\) concentrations, when salting is applied after 22/11/2005. Above S1, the catchment area itself spans over ca. 7 km\(^2\); hence, the enhanced nitrate-N concentrations depicted in Fig. 2 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, with enhancement being evident even in mid-winter. The seasonality effect of soil microbial and plant uptake in the soil on river water nitrate-N concentration at each sampling point is also apparent in Fig. 2.

The very wet conditions on the first two sampling dates, 12/10/2005 and 02/11/2005 would have contributed to the low river water nitrate concentrations by dilution (Table 1). Although there was significant rainfall on 08/07/2006, much of this was retained in dry soil, and probably plant N-uptake is more important over the summer period.

Ammonium-N spiking:
It is clear from Figs. 3 and 4 that in the control soils (T5 & T6), if nitrification is occurring at all, it is happening at a relatively slow rate compared with salt-affected soils, and/or any nitrate being produced is being immobilised by soil microbial biomass or lost by denitrification. The fact that ammonium-N concentration is changing only slightly over time (Fig. 3) suggests that a very low nitrification rate is the most likely cause. It is interesting however that when the soils were spiked only with deionised water (Fig. 6), some nitrification of “native” soil ammonium-N is apparent for the T5 and T6 control soils. If nitrification is being inhibited by low soil
pH in the control soils, then the additional chloride added with the ammonium spike
would, as a mobile anion, further lower the soil solution pH, reducing nitrification rate
even further upon ammonium-N spike addition. Although this explanation is
plausible, further experimentation, for example by NaCl spiking at corresponding
chloride concentrations, of the control soils would be needed to confirm a mobile
anion effect on pH.

The suggestion in the paragraph above that denitrification could be playing a
significant role is unlikely to be true. The nitrate concentrations over time changed
very little following spiking of the soils with nitrate (Fig. 5), which would not be the
case if denitrification rate was substantial. Moreover the soils were not particularly
wet even after spiking, and the amount of water added with the control deionised
water, ammonium-N and nitrate-N spikings was constant between treatments, so if it
occurred the denitrification rates would be similar for all treatments. Thus the
attribution of low nitrification rate to low pH is by far the most likely hypothesis.

Nitrate-N spiking:
Figure 5 showed no evidence of nitrate immobilisation by soil microbial biomass.
However in the road salt-impacted soils (T1 – T4), there was rapid decline in
ammonium-N over the first 1 – 2 days. This was almost certainly by nitrification,
because total mineral N remained virtually constant over the first five days. This
suggests that the higher pH in the salt-impacted soils is again favouring nitrification.
Over a longer time scale nitrification was readily apparent in all six soils. The fact
that ammonium was starting to accumulate by day 9, especially in the most acidic,
control soils (T5 & T6), supports the hypothesis that greater acidity in the control soils
inhibits nitrification, or rather that the increase in soil pH caused by the salting impact
is greatly favouring nitrification.

Deionised water blank spiking:
The data in Fig. 6 show that nitrification is particularly dominant in the salt-impacted
soils, as nitrate dominated the mineral N fraction for the most heavily impacted soils
(T1 & T2) and for the soils experiencing intermediate salt impacts (T3 & T4). As
mentioned in the results section, the contribution of ammonium-N was much greater
in the unpolluted, control soils (T5 & T6) throughout the experiment. However, as
the nitrate-N to ammonium-N ratio increased significantly over time in all soils,
clearly nitrification is occurring in all of the soils. In all soils mineralisation proceeds at a significant rate between days 2 and 9, but the mineral N pool consistently was lower when the salt impact was higher. This probably reflects the lower organic matter content that has evolved in the salt impacted soils, probably from reduced plant growth leading to a reduced pool of mineralisable N. However we can only speculate 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.

**Incubations at 4 °C after ammonium-N spiking:**

Although nitrification still appeared to be significant even at 4 °C and in all soils, the marked long-term salt application impacts were much less pronounced at the lower temperature, and indeed it appeared that nitrification was more important in the most acidic, control soils (T5 & T6). Thus it could be concluded that the influence of soil pH upon nitrification rate is highly temperature dependent.

**Possible salting effects on N cycling other than effects of increased soil pH:**

It cannot be stated categorically that some residual salinity effect and other possible effects outlined in the introduction are not occurring, but if they have adverse effects upon relevant microbial activity they must be small compared to the acidity neutralisation effect. This experiment points to the importance of long-term, soil pH effects being very important over summer months. If over many years potentially toxic heavy metals have been mobilized in the roadside soils, then in all probability after decades they will have leached out of the roadside soil system. Heavy metals in soil solution in these roadside soils were determined in another phase of the present study, but no toxic metals were found at potentially toxic concentrations.

The loss-on-ignition data in Table 2 indicate much lower soil organic matter content in the salt-impacted soils compared with the control soils, again suggesting the importance of long-term effects. It is notable from Fig. 6 that the total mineral N pools were lowest in the most salt effected soils (T1 & T2), and greatest in the control soils (T5 & T6). This suggests that loss of organic matter over several decades is limiting the amount of mineralisable organic N in the most polluted roadside soils.
This could act as a constraint to the enhanced nitrate leaching to adjacent freshwaters to some extent.

7. Conclusions:

It is highly probable that that the degree of salt exposure of the soil, in the longer term, controls the rates of key microbial N driven processes primarily by increasing soil pH. With the increasing amounts of nitrate-N from nitrification of incoming ammonium there is potential for enhanced nitrate loading of waterways in UK uplands due to leaching, which has particular relevance to the Water Framework Directive. Figure 2 clearly illustrates a strong influence on nitrate-N concentrations along the Crookdale Brook.

This study differs from those that preceded it in that the soils used have chemical and physical properties that have evolved over decades of varying degrees of salt exposure. Theories based upon salinisation processes in arid climates or upon experiments in which previously uncontaminated soils are suddenly exposed to high doses of road salt are inappropriate when trying to explain current soil behaviour. Some of the effects observed were almost certainly reflect influence of particulates in the road runoff, as well as the effect of sodium chloride in solution.

The results reported here are very relevant when assessing the fate of inputs of ammonium to soils from atmospheric pollution. Additional influxes of ammonium-N to salt impacted soils may lead to enhanced nitrification and thereafter, increased leaching of nitrate-N to the local waterways, even at 4 °C. However at winter temperatures nitrification appeared to be much less sensitive to the pH effect. The use of road salts thus disrupts the proportional contribution of nitrate-N and ammonium-N to the mineral inorganic fraction of roadside soils, as well as being likely to lead to ammonium-N leaching by cation exchange.

Acknowledgements:

We are grateful to NERC, DERFA and the University of York for financial support for this research, and to Kay Monaghan of Salt Union for helpful information about salt composition.
References:


Ohno, P. 1990. Levels of total cyanide and NaCl in surface waters adjacent to road salt storage facilities. Environmental Pollution, 67 (2), 123-132.


Table 1: Precipitation (mm) at Shap weather station (MET Office) and daily mean flows for the River Lune, proxy for the Crookdale Brook (m$^3$ s$^{-1}$) (Environment Agency) for the freshwater sampling dates.

Table 2: Chemical properties of soils for T1-T6 at 3 m from the wall. All results are means of duplicate determinations, with standard errors within the parentheses. Soils were sampled in July, 2006.

Figure 1: Map showing the location of the field Site. (C) Crown Copyright Ordnance Survey. All rights reserved.

Figure 2: The change in nitrate-N and chloride concentration (mg l$^{-1}$ – means of two replicates) with time and distance along Crookdale Brook for the period 12/10/2005 – 08/07/2006. Interval bars show 95 % confidence.

Figure 3: Changes over 9 days ($t_0$ - $t_9$) in the total mineral N (total bars), ammonium-N (white bars) and nitrate-N (black bars) for sites T1 – T6 for the ammonium-N spiking experiment with incubation at room temperature. Note the changes in vertical scales used. All results are means of two replicates.

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Figure 4: Change over 9 days in the percentage contributions of ammonium-N (white bars) and nitrate-N (black bars) to total mineral-N (complete bars) content for the ammonium-N spiking experiment at room temperature. All results are the mean of two replicates.
Figure 6: Changes over 9 days ($t_0 - t_9$) in the total mineral N (total bars), ammonium-N (white bars) and nitrate-N (black bars) for sites T1 – T6 for the deionised water spiked controls with incubation at room temperature. Note changes in scale. All results are means of two replicates.

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<table>
<thead>
<tr>
<th>Sampling Date</th>
<th>Precipitation (mm)</th>
<th>Daily Mean Flow (m$^3$ s$^{-1}$)</th>
<th>Limb Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>12/10/2005</td>
<td>10.2</td>
<td>16.2</td>
<td>Falling</td>
</tr>
<tr>
<td>02/11/2005</td>
<td>22.6</td>
<td>16.6</td>
<td>Rising</td>
</tr>
<tr>
<td>22/11/2005</td>
<td>0.2</td>
<td>1.71</td>
<td>Falling</td>
</tr>
<tr>
<td>09/12/2005</td>
<td>0.4</td>
<td>1.99</td>
<td>Falling</td>
</tr>
<tr>
<td>03/01/2006</td>
<td>0.6</td>
<td>3.95</td>
<td>Falling</td>
</tr>
<tr>
<td>27/01/2006</td>
<td>0.6</td>
<td>2.18</td>
<td>Falling</td>
</tr>
<tr>
<td>20/04/2006</td>
<td>0.6</td>
<td>2.11</td>
<td>Falling</td>
</tr>
<tr>
<td>08/07/2006</td>
<td>10.6</td>
<td>1.43</td>
<td>Peak</td>
</tr>
</tbody>
</table>
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<table>
<thead>
<tr>
<th>Transect</th>
<th>pH (H₂O)</th>
<th>Water Content (%)</th>
<th>LOI (%)</th>
<th>CEC (MEQ)</th>
<th>NO₃⁻ (mg kg⁻¹)</th>
<th>Na⁺ (%)</th>
<th>Ca²⁺ (%)</th>
<th>Mg²⁺ (%)</th>
<th>K⁺ (%)</th>
<th>H⁺ (%)</th>
<th>NH₄⁺ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>6.66 (0.01)</td>
<td>35.7 (0.33)</td>
<td>16.07 (1.37)</td>
<td>110 (24.36)</td>
<td>1.47 (0.06)</td>
<td>30.7 (6.4)</td>
<td>18.9 (0.51)</td>
<td>1.64 (0.16)</td>
<td>0.44 (0.10)</td>
<td>48.8 (6.05)</td>
<td>0.79 (0.11)</td>
</tr>
<tr>
<td>T2</td>
<td>8.11 (0.03)</td>
<td>33.12 (0.05)</td>
<td>14.37 (1.75)</td>
<td>59.7 (27.02)</td>
<td>3.65 (0.11)</td>
<td>84.9 (30.3)</td>
<td>28.3 (8.7)</td>
<td>2.16 (0.18)</td>
<td>0.00 (0.28)</td>
<td>0.00 (21.35)</td>
<td>0.3 (0.16)</td>
</tr>
<tr>
<td>T3</td>
<td>4.62 (0.04)</td>
<td>33.04 (0.67)</td>
<td>17.26 (0.47)</td>
<td>145 (1.31)</td>
<td>1.37 (0.03)</td>
<td>1.79 (0.12)</td>
<td>2.91 (0.25)</td>
<td>1.33 (0.25)</td>
<td>0.41 (0.20)</td>
<td>94.0 (0.61)</td>
<td>0.39 (0.09)</td>
</tr>
<tr>
<td>T4</td>
<td>5.11 (0.05)</td>
<td>40.07 (1.70)</td>
<td>28.97 (1.63)</td>
<td>91.5 (11.46)</td>
<td>1.92 (0.26)</td>
<td>5.26 (0.58)</td>
<td>9.55 (1.57)</td>
<td>1.25 (0.37)</td>
<td>0.53 (0.11)</td>
<td>84.0 (2.52)</td>
<td>0.64 (0.05)</td>
</tr>
<tr>
<td>T5</td>
<td>3.79 (0.04)</td>
<td>77.38 (7.39)</td>
<td>72.23 (1.36)</td>
<td>337 (116)</td>
<td>5.99 (0.01)</td>
<td>0.62 (0.26)</td>
<td>0.24 (0.17)</td>
<td>0.81 (0.17)</td>
<td>0.21 (0.71)</td>
<td>98.3 (0.59)</td>
<td>0.79 (0.56)</td>
</tr>
<tr>
<td>T6</td>
<td>3.82 (0.01)</td>
<td>77.51 (0.68)</td>
<td>54.43 (2.01)</td>
<td>281 (88)</td>
<td>5.37 (0.24)</td>
<td>0.96 (0.41)</td>
<td>0.00 (0.17)</td>
<td>0.8 (0.20)</td>
<td>0.0015 (0.038)</td>
<td>98.3 (0.44)</td>
<td>0.63 (0.44)</td>
</tr>
</tbody>
</table>

* Soil water content wet weight.
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.
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