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## **Published paper**

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## Are calcareous soils in uplands less prone to damage from road salting than acidic soils?

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Previous studies of upland roadside soils in Cumbria, that would normally be naturally acidic, have highlighted that (a) runoff from roads subjected to long-term road salting can dramatically raise soil pH down slope in upland areas; (b) the soil pH increase dramatically changes N cycling in soils down slope, increasing mineralization of organic matter, ammonification, ammonium leaching down slope and nitrification and nitrate leaching; (c) the increase in nitrification substantially increases nitrate leaching to down-slope rivers, and this is readily detectable in field studies; and (d) loss of soil organic matter over decades of salting is so great that organic matter is no longer substantially solubilized by high salt concentrations found in soil solution below road drains. This paper tests and supports the hypothesis that such effects are minimal for more calcareous soil ecosystems. It examines the soil and soil solution chemistry on another Cumbrian upland highway, the A686 near Leadgate, Alston. Sodium % of soil CEC values for soil transects affected by spray containing road salt are similar at both the A6 and A686 sites. However, spatial trends in calcium, magnesium, ammonium, and nitrate concentrations as well as pH differ, as a direct result of the higher weathering rate of parent material and possibly also the presence of limestone walls above both spray-affected and control transects at the A686 site.

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Keywords: Road salt; sodium; chloride; base cations; weathering rate; N cycling

## 1. Introduction

- De-icing agents are widely applied to roads around the world under sub-zero temperature or
- 27 snowy conditions to prevent the formation (or reformation) of ice and thus maintain safe
- 28 driving conditions. Materials used include rock salt (sodium chloride), calcium chloride,

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calcium magnesium acetate (CMA), magnesium chloride, potassium chloride, sodium formate and urea [1-4]. Sodium chloride tends to be the preferred agent in the UK, applied in solution or as a solid, depending upon the conditions. It may be mixed with grit, and sometimes contains an anti-caking agent [5,6]. Much of the applied material ends up being transferred to roadside soils, especially down-slope of the highway.

Road salt is used on 64.5% of roads in the County of Cumbria in North West England. Thus for 2262 km of road in the county, episodically the roadside soils are exposed to incoming road salt (i.e. impure NaCl) via spray, runoff and drainage. Green and Cresser [7,8] and Green *et al.* [9-11] assessed the impacts of road salt on a soil that would naturally be very acidic adjacent to a highway, on its soil solution, and on water in an adjacent, down-slope river. The study site at the A6, Selside, Cumbria experiences directly piped runoff onto the soil surface and/or spray. They reported the following main findings:

- **1.** Runoff from an upland road subjected to long-term road salting dramatically raised soil pH down slope [7].
- 2. The pH increase markedly changed N cycling in soils down slope, increasing mineralization of organic matter, ammonification and nitrification and nitrate leaching [8, 10]. Further modification was caused by displacement of ammonium by sodium ions and mobile anion effects on soil H and cation mobility's.
- **3.** The increase in nitrification substantially increased nitrate leaching to a down-slope river, and this was readily detectable in field studies [10].
- **4.** Loss of soil organic matter over decades of salting was so great that immediately beside the road organic matter was no longer substantially solubilized by the high salt concentrations found in soil solution below road drains [9, 11].

It might be expected, however, that such impacts would be much less in roadside soils with higher biogeochemical mineral weathering rates (thus a naturally higher pH). The relative contribution of calcium to the total cation pool would naturally be much higher, making the impact of seasonal high sodium inputs less dominant. Incoming sodium ions are energetically unfavorable to displace divalent calcium ions compared to those of hydrogen on the CEC.

Therefore, the effects observed on acidic upland soils are likely to be dampened on calcareous soils. This hypothesis has been tested for spray–affected roadside soils at a second sampling site, using a similar protocol and methodology.

#### 2. Materials and methods

#### 2.1 Field site

- The study site was an upland area along the A686 at Leadgate, Alston, Cumbria, UK (NY 688 430 GB Grid; Lat: 54.780929N Long: 2.486611W), with altitudes up to 609 m above sea level (Fig. 1). The road section used runs parallel to the Black Burn; however, the river could not be sampled at this site due to health and safety implications (especially in winter). The A686 is a priority two route and has a speed limit of 60 mph. In terms of traffic density, the A686 has 927 vehicles eastbound and 996 westbound per day (John Robinson, Cumbria County Council, pers. comm.). During the sampling period (October 2005-July 2006), 114 salting outings were completed at a rate of 10-40 g m<sup>-2</sup>, depending on the predicted conditions and previous salting regime applied (John Robinson, pers. comm.).
  - The soils are brown earths (Cambisols), with a minimal litter layer but varying degrees of gleying in places. The bedrock is primarily limestone and sandstone. The vegetation is predominately grasses, Juncus and bryophytes and the land is grazed by sheep. Two possible transect scenarios were studied; (a) spray-affected soils (A1 and A2 south of the A686 between the milestone and Blackburn Bank) and (b) control soils (A3 and A4) directly above the road; the two scenarios differ in altitude by only 15 m. Both contaminated and control sampling areas are minimally managed, and have evolved from the same parent material. A wall ca. 1 m high separates the road from the salt-affected sampling sites and an identical wall is above the control transects.

## 2.2 Soil sample collection

Soils for the two salting impact scenarios were sampled in duplicate, with a horizontal spacing of at least 10 m. Transects were laid perpendicular to the road; two were immediately down slope of the highway (A1 & A2). The control (un-impacted) transects, referred to as A3 & A4, were above the road, at ~ 100 m from the highway. Soil samples were collected to 10 cm

depth with a stainless steel trowel at 2, 4, 8, 16, 32 and 64 m from the wall (1 m away from the road) on the 20<sup>th</sup> April 2006, soon after a full period of winter salting. Initial soil sampling was completed on the 5<sup>th</sup> October 2005 for an inter-seasonal comparison of samples prior to the winter maintenance period commencing. This was done to quantify probable maximum and minimum effects throughout a single salting year.

The samples, in polyethylene bags, were stored at 2-4 °C prior to chemical analysis. Stones, identifiable vegetation fragments and roots were removed as quickly as possible by careful hand sorting immediately prior to use.

## 2.3 Soil solution sampling

- To ensure sufficient sample was obtained for analyses, soil solutions for each transect were sampled using sets of three MOM Eijkelkamp rhizon soil solution samplers, 10 cm long and 2.5 mm in diameter, evacuated with 60-ml syringes. Soil solutions were sampled at 2, 4, 8, 16, 32 and 64 m from the walls, over a depth interval of 5-10 cm.
- Soil solutions were sampled most intensively throughout the winter period. Sampling was conducted from 12/10/2005-08/07/2006. The air was purged from the syringes, and thereafter, they were stored at 2-4 °C prior to chemical analysis of the samples.

#### 2.4 Soil and soil solution analyses

Soil samples were chemically analyzed for exchangeable base cations, pH, KCl-extractable ammonium-N and nitrate-N, loss on ignition (LOI) and cation exchange capacity (CEC). Soil solution was analyzed for major base cations (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>), ammonium-N, nitrate-N, chloride, sulphate, DOC and pH. Identical techniques to those outlined in Green *et al.* [10] were used. Performance of all instrumental methods was checked using synthetic reference standards.

## 2.5 Statistical analysis

Data from paired soil transects were combined to enhance the representation of each transect scenario (a) indirect and (b) control by increasing the sample size, and non-parametric tests applied. The Kruskal-Wallis test was used to determine whether means were significantly different between control and spray-affected transects, and with distance for each scenario.

Significance of correlations was tested using Spearman's rank. For all statistical tests, significance was accepted at  $\alpha \le 0.05$ . Analyses were performed using SPSS version 11.0.1

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## 3. Results

- 3.1 Soil data
- Figure 2 shows ammonium acetate-extractable base cations, exchange acidity and KCl-
- extractable ammonium as a percentage occupation of CEC at 2, 4, 8, 16, 32 and 64 m, plotted
- on a log scale, disaggregated by transect type (i.e. spray vs. control). The Na % occupancy of
- 129 CEC for spray-affected and control transects differs significantly at the 1% level (indirect >
- 130 control). Percentage occupation of the CEC by sodium does not exceed 0.32% for control
- soils, compared to maximum value of 1.68% for spray-affected transects at 4 m. The
- percentage contribution for the impacted transects of sodium to the CEC steadily declines from
- 4 to 64 m, but remained well above the levels observed for the control transects.
- 134 Calcium % occupation of CEC for salt-affected transects is not significantly below that
- for the control (Fig. 2). The Ca % of CEC for control transects declines slightly with distance
- along the control transect from 4 to 64 m. In both control and spray-affected soils Ca %
- occupation remains relatively high, as hypothesized for the more calcareous soil, and is never
- at values that would cause concern.
- At 2 to 4 m the Mg % occupation of CEC for the spray-affected soils exceeds that of
- the controls. Values for transect types tend to converge at 8 m.
- The K % of CEC for the salt-impacted soils exceeds that in the control soils at all
- distances from the highway (1 % level). The control generally appears to fluctuate between
- 143 0.04 0.2%, with no significant difference observed with distance. For the spray-affected
- transects K % declines from 3% at 4 m to 0.44% at 32 m (5 % level).
- For H<sup>+</sup> % of CEC the two scenarios show no significant difference. At 2 m the H<sup>+</sup> % of
- 146 CEC for the both impacted and control soils was 65% (Fig. 2). Soil pH for the control soils
- showed a significant increase in acidity with distance (at the 5% level).
- 148 It is immediately obvious (Fig. 2) that CEC for the salt-impacted transects contains
- 149 consistently (and significantly) higher ammonium % than the control transects (1% level);
- neither scenario shows a significant change in ammonium % of CEC with distance.

Figure 3 shows the percentage occupation of CEC by base cations, hydrogen and ammonium at 2, 8 and 32 m on the  $15^{th}$  October 2005; it may be used to assess seasonal differences from the data from April in Fig. 2. There is a slight reduction in Na % of CEC close to the road,  $\sim 0.2\%$ , on the salt-affected transects compared with the April data, whilst the control maintains a steady and consistent Na % occupation of the CEC.

Between 2 and 32 m, Mg % occupation of CEC increases from 2 or 3.7% to just over 5 % for control and spray-affected scenarios respectively in October (Fig. 3). Over the same distance Ca % of CEC on the salt-impacted transects increases from 25.2% to 40.5%, whilst Ca % occupation of the control declines from 40 to 27.1%, similar to the decline seen for the control transects in April.

The K % of CEC increased in October for the control transect from the April value of < 0.5% to 1.5 - 2%. For the salt-impacted transect, K % of CEC showed a lower degree of variability, and was almost consistent at 2 and 8 m between the two time periods. At 32 m the % occupation of K increased from 0.44 to 2.66% however for spray-affected soils.

The H<sup>+</sup>% of CEC generally shows relatively very little overall change in the degree of acidity between April and October (Fig. 3). For the salt-impacted soils there appears to be a decline in acidity with distance from 2 - 32 m (68-52% of CEC); in contrast the H<sup>+</sup>% for the control appears to increase from 2 - 32 m (56 to 66% of CEC); however, neither trend is significant at the 5% level.

Ammonium as a % of CEC was similar in April and October for the control soils over the spatial range studied, but was apparently higher for the salt-affected soils from 2-8 m in April. Though consistent, the effect was not however significant. In these soils, similar spatial trends are apparent for both time periods, with sharp increases in % occupation of CEC by ammonium between 32-64 m.

The spray-affected transects have, on average, a pH at 2 m approximately 0.5 units lower in April 2005 than the control transects (Fig. 4a; 1% level). This corresponds to the higher calcium dominance of the CEC for the control (Fig. 2). Soil pH of the control transects apparently declines from 5.84 to 5.35 over 64 m, whilst the spray-affected soil pH apparently increases from 5.32 to 5.64, but neither trend is significant. In October (Fig. 4b) the spray-affected soils are still the most acidic, with the difference between the scenarios now being significant at the 1% level.

Figure 5 shows the concentrations of KCl-extractable nitrate-N for spray-affected and control transect soils in April 2006 and October 2005. There is no significant difference between the spray-affected and control soils with regard to nitrate-N content for either time period. The spatial variation generally exceeded variation between transects.

Figure 6 shows the spatial variation in soil LOI (%) for April 2006 and October 2005 for the two transect scenarios. Organic matter loss apparently has occurred from salt-impacted soils compared with control soils. Control soils have a significantly higher LOI (1% level) in both April and October, at a generally consistent level. Salt-impacted soils at 64 m possess a significantly higher LOI (1% level) than those at every other distance; LOI% is highly correlated to the soil water content (70.2%) in April 2006, reflecting greater water retention in more organic soils.

#### 3.2 Soil solution data

Sodium concentrations as high as 156 mg  $\Gamma^1$  were observed 2 m from the road at spray-affected transects beside the A686, but values varied with the prevailing weather conditions. The sodium concentrations for the spray-impacted transects declined to 5-15 mg  $\Gamma^1$  at 64 m down slope; the controls gave a background level of 4.4 mg  $\Gamma^1$  across all distances. The observed trends in sodium ion concentrations were also apparent in chloride data (significantly correlated to Na<sup>+</sup> at the 1% level). However, whereas at the A6 site Na<sup>+</sup> was largely displacing H<sup>+</sup>, so soil pH increased substantially, at the A686 site there is also strong competition from Ca<sup>2+</sup> from biogeochemical weathering. Therefore the more strongly retained divalent Ca<sup>2+</sup> ions have a bigger effect on the composition of the cations occupying the CEC, and the Ca<sup>2+</sup>:Na<sup>+</sup> ratio in soil solution is much higher for spray-affected soils at the A686 than it was at the same time of year (April) at the A6 site. This can be very clearly seen in Fig. 7 (note the change in scales between sites).

Calcium concentrations as high as 86 mg  $l^{-1}$  were observed in soil solutions at (data not shown) 4 m from the spray-affected transects. They ranged between 5-12 mg  $l^{-1}$  for spray-affected transects between 8-16 m. The controls on average had an elevated concentration at 2 - 4 m ( from 13 - 25 mg  $l^{-1}$ ), thereafter declining and stabilizing from 8-64 m at 10-12 mg  $l^{-1}$ , suggesting a significant  $Ca^{2+}$  input from the walls by weathering.

Magnesium concentrations were less than 2.5 mg l<sup>-1</sup> for control transects. Spray-

affected transects had the highest  $Mg^{2+}$  concentration at 4 m, ~35 mg  $l^{-1}$ , and thereafter  $Mg^{2+}$  concentration generally declined.

Soil solution pH ranged from 6 - 7.5 for spray-affected and 6 - 6.6 for the control transects. As the distance from the highway increased the pH for A1 and A2 tended to decline, whilst A3 and A4 also showed a tendency towards pH decline as distance from the wall increased (Fig. 8). However these trends were nothing like as marked as those seen at the A6 site, where the increase in pH attributable to salting was much more consistently around 1 to 1.5 pH units. These trends at the A686 site probably reflect the impact of the limestone walls.

In the earlier study at the A6 site, the soil solutions from the spray-affected transects consistently contained much higher (more than an order of magnitude) nitrate concentrations than the control soil solutions. This resulted in substantially increases in the nitrate concentration in a local, adjacent river [8]. The control soil solutions in the A686 study also contained minimal amounts of nitrate-N (generally < 1 mg l<sup>-1</sup>), whilst the salt-affected transects had spatially and temporally variable concentrations (Fig. 9; note change in scale). Nitrate-N concentrations on spray-affected transects showed no consistent trend attributable to a road salting effect, although 9 out of 96 samples contained a concentration > 5 mg nitrate-N l<sup>-1</sup>.

At 2 - 4 m, and (more consistently) at 64 m, ammonium-N concentrations apparently tended to be higher for the salt-affected transect soil solutions (Fig. 10). This might have been anticipated from the apparent increase in ammonium % of CEC for the salt-affected transects, but that effect was not significant, as discussed earlier. Ammonium-N concentrations in control soil solutions were very low, mostly below 0.2 mg  $\Gamma^1$ . For salt-affected transect A1 (but not for transect A2), ammonium-N concentration was consistently high from 2 to 16 m on 08/07/2006, but for no obvious reason.

#### 4. Discussion

Some sodium ion effects are clear from the differences between the spray-affected and control transects. Figure 2 demonstrates the percentage occupation of cation exchange sites for sodium, magnesium, calcium, potassium, ammonium-N and hydrogen ions in April 2005. There is clear sodium elevation for the spray-affected transects as compared to the control over 2 - 64 m. However the contribution of Na<sup>+</sup> to exchangeable base cations is lower than at the A6 site [7]. The higher Na % occupation of CEC does not directly correspond to a lower H<sup>+</sup> %

of CEC for the control transects, and thus a lower  $H^+$  % of CEC for spray-contaminated transects at the A686 site, in marked contrast to observations for the A6 site [7]. The  $H^+$  % of CEC is inversely correlated with the % Ca and Mg of CEC (1% level) at the A686 site. Thus, it is more likely that the exchangeable hydrogen ions are competitively displaced by incoming calcium and magnesium ions than by sodium. Evidence presented earlier suggests this is partly from the limestone walls above all transects at the site.

Green and Cresser [7] hypothesized that close to the highway a reduction would be observed in the calcium and magnesium % occupation of the CEC in the acid soils of the A6 site, but the opposite was observed in practice. It was thought that the higher levels of calcium were a result of the calcium content in the rock salt [7, 10]. Hence, it would not be surprising to observe the same trend at the A686 as a result of the same road salt product being used. However, Ca and Mg % of CEC values are elevated above those observed at the A6 for the spray-affected and control sites, suggesting additional source(s) of calcium and magnesium. This is also reflected in the raised calcium concentrations in soil solutions for the controls.

It is clear that the calcium input via limestone dissolution (parent material or wall components) is having an affect on pH and Ca % on the CEC. The Ca % of CEC is greater for the A686 at 2 m (26.6%) than for the A6 (17.7%) in April. This is also apparent in October for the spray-affected transects. It is thought that the additional calcium from the limestone wall constructed above both the control and spray-affected transects is very significant because pH declines with distance for the control transect. Mobile anion effects contribute to the lower soil solution pH for the spray-affected transects. The sodium input effects on pH are effectively negligible at the A686 sites.

Initially there appeared to be some evidence to suggest that the N-cycle is being disrupted by the use of road salts at the A686 site. However, spatial and temporal shifts in pH will not be modifying mineralization and nitrification rates significantly, so none of the apparent effects on the N cycle were significant statistically. Green and Cresser [7, 8] showed, in contrast, that displacement of ammonium ions from the exchange sites occurred in reaction to increased sodium concentrations during salting of the A6. It is interesting to note that the percentage CEC occupation by ammonium observed at the A686 is consistent with that of the spray-affected soils at the A6.

Spray from road salting had a very strong and significant effect on soil solution nitrate

concentration in the naturally acidic soils alongside the A6 [8]. Figure 9 showed that no such strongly consistent significant effect occurred at the A686 site. This is almost certainly because of the lack of consistent significant pH change at the A686 site.

LOI is, as for the A6 soils [8], greater for the control soils than for the spray-affected soils (Fig. 6 - 1% level). In comparison to the A6, however, there does not appear to be a build up of organic matter down slope from organic matter dispersal by high Na<sup>+</sup> concentrations. This may be is a product of topography (lesser degree of slope angle for the A686). It seems most likely that at the A686 site the dominant cause is roadside pollution of diverse types lowering the annual input of organic litter to the roadside soils.

The A686 shows signs of reversibility of salt effects there after road salt application had ceased for the season, *via* reduction in sodium ion % of CEC between April and October.

The acidic upland site of the A6 possesses a host of ecological implications through the introduction of elevated concentrations of road salt (cation exchange reactions) and the significant temporal/spatial pH shift. Changes in pH lead to changes in microbial activity which is highlighted by the enhanced nitrification observed at the A6, which have a reverberation on the N cycle. Displacement of ammonium ions from the CEC may lead to N deficiencies in roadside soils. In addition toxicity effects of high salinity on microbes may be masked by the signal observed. Vegetation may be affected by road salt in several ways: by accumulating Na<sup>+</sup> in toxic concentration within plant tissues (Townsend, 1980); by increasing osmotic pressure differences causing desiccation (drying) (Bryson & Barker, 2002; Larcher, 1995; Townsend, 1980); by altering mineral nutrition balances (reduced levels of available ammonium, and K<sup>+</sup> within the soil) (Bayuelo-Jiménez et al., 2003; Serrano & Rodriquez-Navarro, 2001); and by altering soil structure. However, damage usually results from a specific ion effect rather than from an increase in osmotic potential (Townsend, 1980). The specific ion effect involves movement of the ions such as sodium and chloride into plant cells, where they adversely affect cell membrane stability, metabolism and growth, and at high concentrations is toxic, possibly leading to fatality (Larcher, 1995; Townsend, 1980). In addition ammonium and nitrate leaching may also suppress vegetal growth.

Furthermore, elevated chloride concentrations are known to interfere with photosynthesis in algae in surface waters (Williams *et al.*, 1999), with shifts in population occurring with 12–235 mg l<sup>-1</sup> due to the varying degree of sensitivity between algae species

(DOE & DOH, 2001). In higher organisms they can result in potentially fatal metabolic acidosis and osmotic stress, as well as behavioural changes (Williams *et al.*, 1999). It is possible that changes in population, community structure and/or biodiversity may occur due to acute and chronic toxicity of road salts, in combination with other physical and chemical impacts generated directly or indirectly from the application of road salt.

Raised levels of sodium ions in water can cause high blood pressure and hypertension, so individuals whom already suffer from this condition and on salt-restricted diets should not ingest greater than 20 mg l<sup>-1</sup>. Several states in the northeast US and Canada have measured sodium from road salt in well waters at concentrations that are 2-140 times the recommended limit for individuals on salt-restricted diets (Amrhein *et al.*, 1992). Hence, increases in sodium and chloride ions can also cause problems with water balance in the human body. This is a particular concern when considering upland soils and associated freshwater bodies as these tend to be used as potable sources in the UK (Smart *et al.*, 2001).

In addition enhanced loadings of nitrate and ammonium may occur as product of cation displacement and enhanced nitrification as a result of the effect of pH on the soil microbe community, both of which have an eutrophication risk.

In the case of the A686 such implications are unlikely to be realized due to the presence of the higher rate of weathering of parent material. The occupation of the CEC with Ca<sup>2+</sup> and Mg<sup>2+</sup> in the first instance protects the soil ecosystem for a shift in pH due to the displacement of H<sup>+</sup> ions. This effectively protects the roadside environment to the long-term episodic influxes of road salt. Furthermore, such ecological implications outlined above may only occur in extreme cases.

#### 5. Conclusion

The data from the A6 and A686 spray-affected transects, compared with the relevant control transects, conform well only in terms of Na<sup>+</sup> % occupation of the CEC. The high weathering rate of the calcareous parent material within the wall and in the soil itself, rather than high salt input, regulates the soil pH down-slope at the A686 site. As a consequence at the A686 site the disruption of the N cycle is negligible compared with that reported earlier for the A6 sites. It may be concluded that major N cycle disruption that occurs as a consequence of road salting when roads run through naturally very acidic soil ecosystems is much less of an issue when the

- roadside soil ecosystems are calcareous. That said, the lower organic matter content in salt
- 338 impacted soils of both types (indicated by significantly lower LOI values) warrants further
- investigation.

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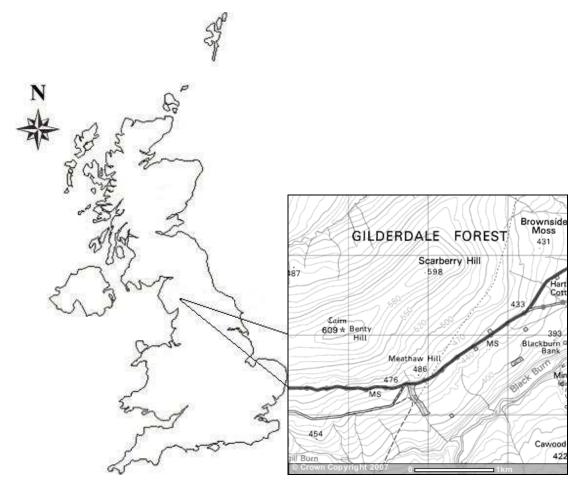


Figure 1. Map showing the location of the A686 field site, Leadgate, Alston, UK. (C) Crown Copyright Ordnance Survey. All rights reserved.

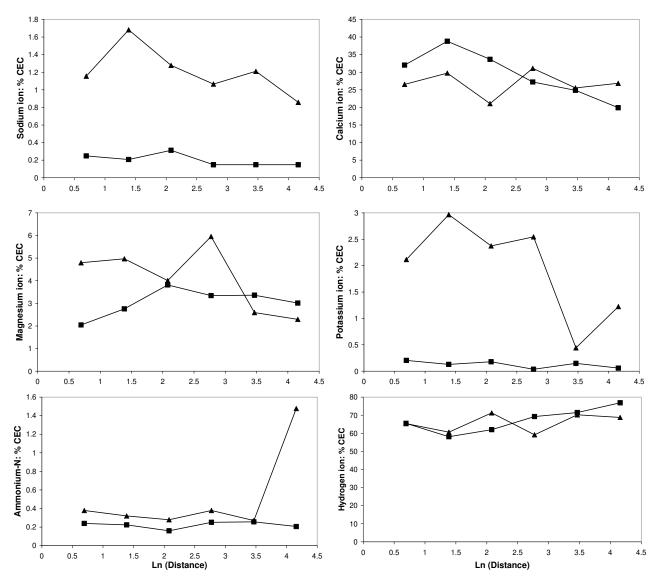


Figure 2. Proportion of base cations, ammonium-N and hydrogen of CEC (%), April 2006 at 2, 4, 8, 16, 32 and 64 m away from the wall for spray-affected (triangles) and control transects (squares).

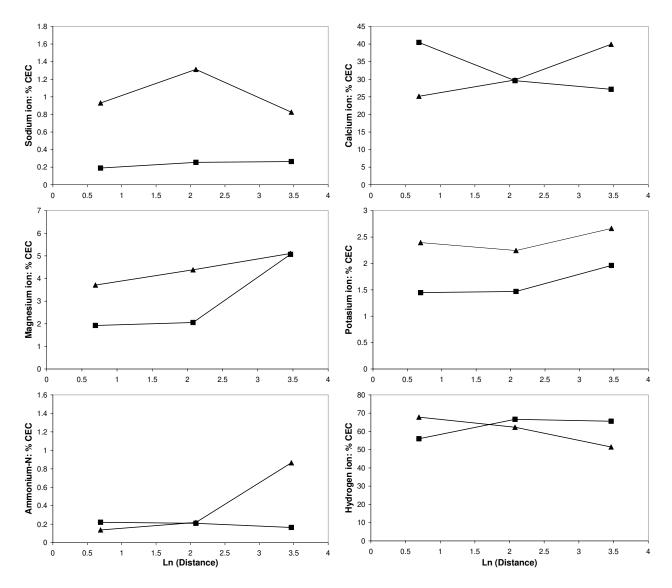


Figure 3. Proportion of base cations, ammonium-N and hydrogen on the CEC, October 2005 (%) at 2, 8 and 32 m from the wall, for spray-affected (triangles) and control transects (squares).

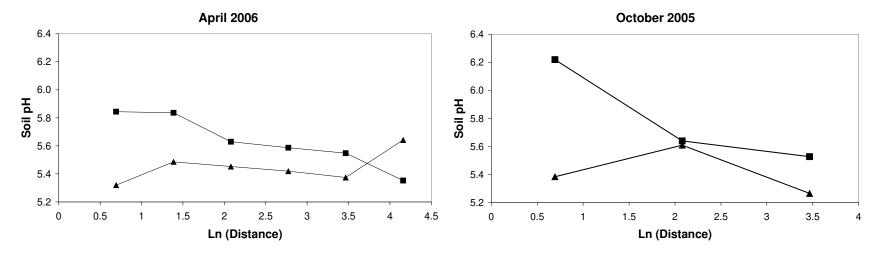


Figure 4. Soil pH (H<sub>2</sub>O) for April 2006 and October 2005 for soil samples at 2, 4, 8, 16, 32 and 64 m from the wall in April and 2, 8 and 32 m in October, for spray-affected (triangles), and control (squares) soils.

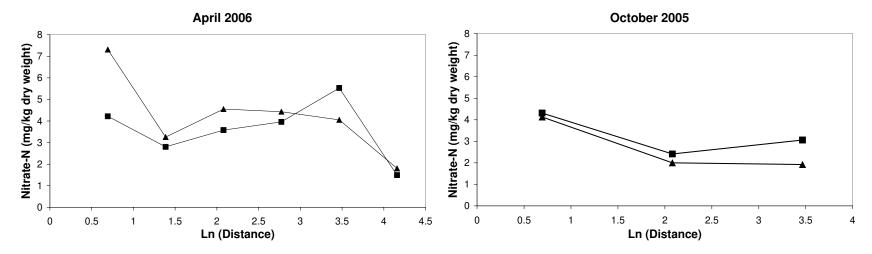


Figure 5. KCl-extractable nitrate-N concentration (mg/kg) for April 2006 and October 2005 for soils sampled at 2, 4, 8, 16, 32 and 64 m from the wall in April and 2, 8 and 32 m in October, for spray-affected (triangles) and control (squares) soils.

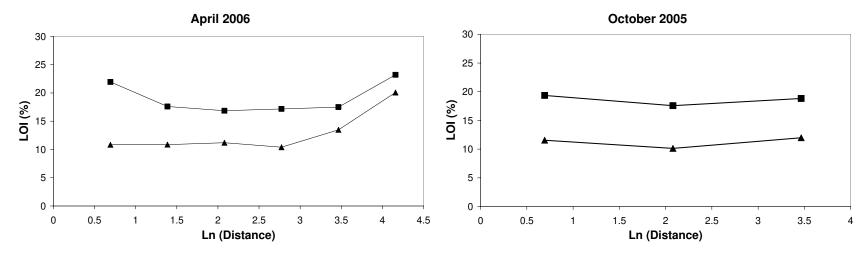


Figure 6. Loss-on-ignition (%) for April 2006 for soils sampled at 2, 4, 8, 16, 32 and 64 m from the wall (April) or 2, 8 and 32 m (October) for salt-affected (triangles) or control (squares) soils.

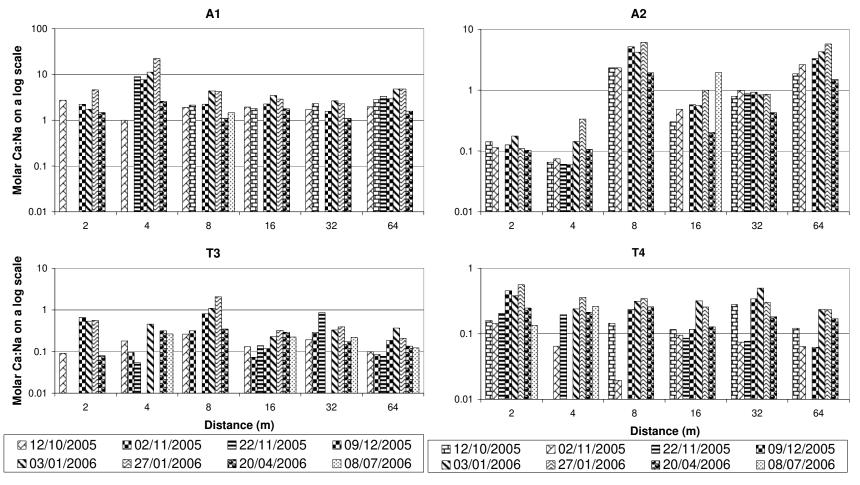


Figure 7. Comparison of the ratio of calcium to sodium concentrations, expressed on a mol<sub>c</sub> basis on a log scale, in soil solutions along the lengths of the spray effect transects in this study (A1 and A2, top) and in the earlier A6 study (T3 and T4, bottom). Note changes in scale.

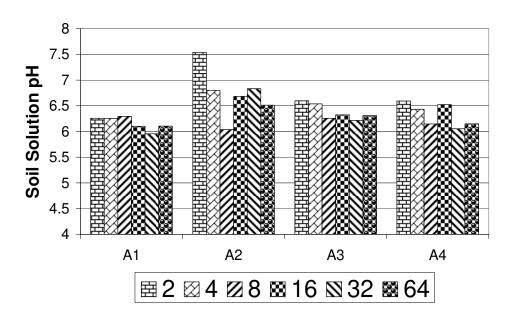


Figure 8. Soil solution pH at 2, 4, 8, 16, 32 and 64 m for spray-affected soils (A1 & A2), and control soils (A3 & A4).

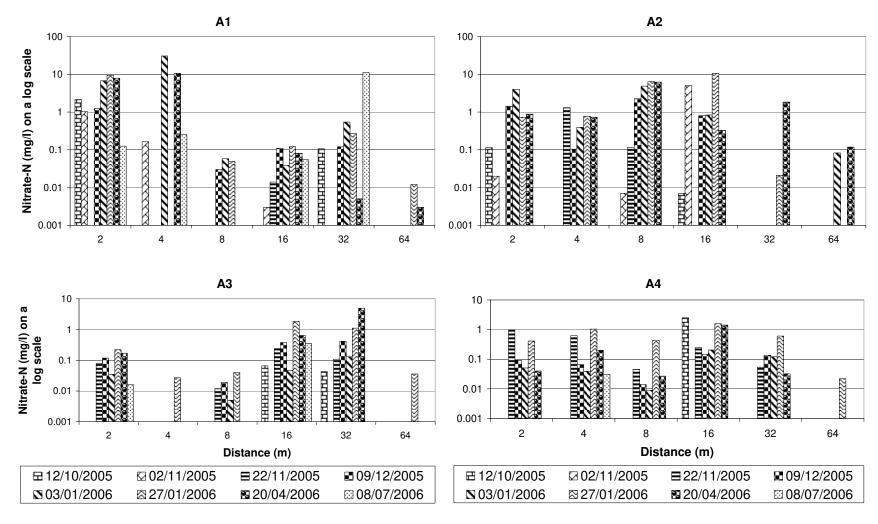


Figure 9. Nitrate-N concentration on a log scale for soil solutions at 2, 4, 8, 16, 32 and 64 m for spray-affected soils (A1 & A2) and control soils (A3 & A4). Note changes in scale.

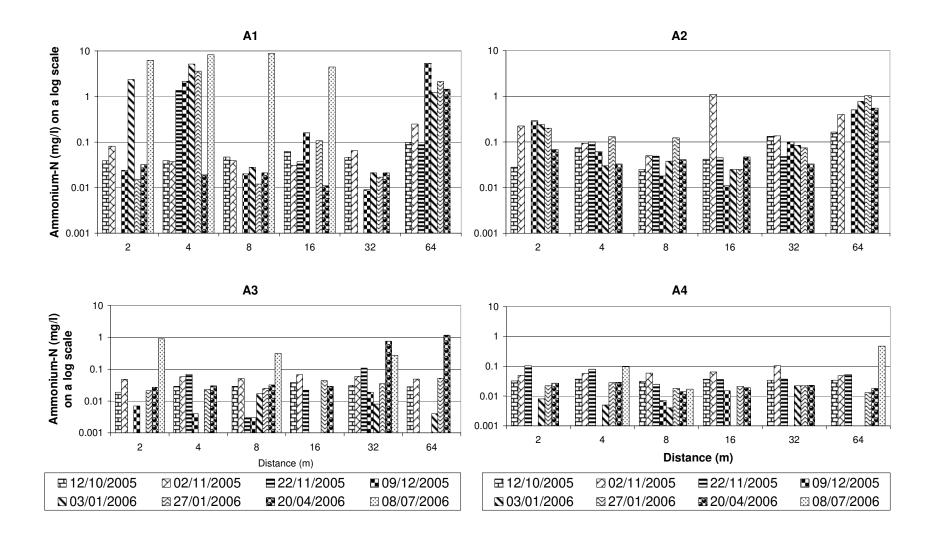


Figure 10. Ammonium-N concentration on a log scale for soil solutions at 2, 4, 8, 16, 32 and 64 m for spray-affected soils (A1 &A2), and control soils (A3 & A4).