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1   Running head: Road salting disrupts N cycle.

2   Article type: Full Research Paper

3   **Nitrogen cycle disruption through the application of de-icing salts on upland**

4   **highways.**

5

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8

9   **Abstract**

10   It is hypothesized that episodic introductions of road salt severely disrupt the soil

11   nitrogen cycle at a range of spatial and temporal scales. A field-scale study has

12   confirmed impacts on the nitrogen cycle in soil, soil solution and river samples.

13   There is evidence that ammonium-N retention on cation exchange sites has been

14   reduced by the presence of sodium ions, and that ammonium-N has been flushed from

15   the exchange sites. Increases in soil pH have been caused in naturally acidic uplands.

16   These have enhanced mineralization of organic-N, especially nitrification, leading to a

17   reduction in the mineralizable-N pool of roadside soils. There is evidence to support

18   the hypothesis that organic matter content has been lowered over decades either

19   through desorption or dispersal processes. Multiple drivers are identified that

20   contribute to the disruption of nitrogen cycling processes, but their relative

21   importance is difficult to quantify unequivocally. The influence of road salt on soil

22   and soil solution declines with distance from the highway, but impacts on water

23   chemistry in a local stream are still strongly evident at some distance from the road.

24

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

26

27   **1   Introduction**

28   Episodic introductions of road salt have the potential to severely disrupt the soil

29   nitrogen cycle. Road salting is utilized to minimize the risk of accidents under icy

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30 and snowy conditions. In the UK the preferred de-icing agent is sodium chloride

31 (pure or mixed with grits and sands, often with an anti-caking agent), applied in solid

32 or liquid form at a rate of 10-40 g m^{-2}, depending on conditions. Although high

33 impacts of Na$^+$ and Cl$^-$ on N cycling may be envisaged, there have been few studies to

34 date that focus on such impacts (Green *et al.*, 2007).

35 It may be hypothesized that high sodium inputs will flush ammonium ions from

36 exchange sites and also reduce the extent of ammonium retention from atmospheric

37 inputs, as reported for sea-salt deposition (Duckworth & Cresser, 1991), and this

38 could conceivably lead to shortages of available N for some distance down slope of

39 salted roads, and ammonium enhancement further down slope.

40 Road salts also may increase organic colloid mobility (Amrhein *et al.*, 1992;

41 Grolimund *et al.*, 1996; Norrström & Bergstedt, 2001; Shainberg & Letey, 1984) and

42 alter the structure of the soil (Bäckström *et al.*, 2004; Norrström & Bergstedt, 2001).

43 High exchangeable sodium percentage and low salt solution concentration lead to

44 enhanced dispersal of soil colloids (Shainberg & Letey, 1984). Thus it may be further

45 hypothesized that salting will lead to a reduction in the organic matter content of soil

46 adjacent to roads, and thus to a decline in the pool of mineralizable soil N. Such an

47 effect may be modified by salting effects on the mineralization of soil organic matter,

48 however. Soil aggregate stability deteriorates through the accelerated leaching of

49 calcium and magnesium ions from the soil exchange sites as a result of enhanced

50 competition with sodium ions (Bäckström *et al.*, 2004; Norrström & Bergstedt, 2001),

51 reducing the bonding with the organic matter that aids flocculation and soil structural

52 stability.

53 It is plausible that ammonification may increase as a result of the weakened

54 tendency for organic matter and mineral structures to bind, as desorption reduces the

55 physico-chemical protection of the organic matter. Moreover, increases in soil pH

56 induced by cationic exchange with sodium may facilitate mineralization of organic N,

57 and especially nitrification (Green *et al.*, 2007). Green *et al.* (2007) assessed the fates

58 of low-level ammonium-N and nitrate-N inputs to roadside soils impacted by salting

59 over an extended period (decades) in the field using spiking equilibration

60 experiments. They discovered that the use of road salts disrupted the proportional

61 contributions of nitrate-N and ammonium-N to the mineral inorganic fraction of

62 roadside soils; they suggested that is was highly probable that that the degree of salt

63   exposure of the soil, in the longer term, controlled the rate of key microbial N

64   transformation processes, primarily by increasing soil pH.

65   In addition, increases in sodium dominance of the CEC potentially increase

66   dispersal of organic colloids when soils are first exposed to high salinity. Such an

67   increase is unlikely to be evident in roadside soils exposed for decades to road salt, as

68   once the organic matter has dispersed and leached from the soil it's gone from the

69   system forever (Green *et al.*, under revision). Green *et al.* (under revision) applied

70   salt at concentrations recorded in soil solution in the field (0, 10, 1000, 10 000 mg l^{-1}),

71   simulating a road salting flush, to quantify the extent that dissolved organic carbon

72   (DOC) and dissolved organic nitrogen (DON) are still being mobilized from soils that

73   have experienced varying degrees of road salt exposure in the field. A balance occurs

74   between the effects on organic matter of long-term soil pH increase (which enhances

75   organic matter solubility and mineralization), short-term pH suppression via a mobile

76   anion effect (which reduces organic matter solubility), and short- and long-term

77   sodium-induced dispersion, which now determines the influence of road salt on

78   organic matter leaching from roadside soils and into associated drainage waters.

79   Spatial and temporal pH shifts will also influence microbial activity and

80   thereafter transformation rates of inorganic N species. Green *et al.* (2007) concluded

81   from their series of laboratory equilibration experiments that road salt-induced pH

82   shifts may lead to enhanced nitrification of influxes of ammonium-N to salt impacted

83   soils, thereby increasing leaching of nitrate-N to the local waterways, even at 4 ^{o}C. If

84   nitrification is enhanced, leaching of nitrate-N into soil solution and freshwater bodies

85   is likely (Green *et al.*, 2007). Hence, it is hypothesized that freshwaters below

86   roadside soils should show evidence of disruption of N cycling. In summary we

87   predict:

88   • High sodium inputs flushing ammonium from soils and a reduction in the

89   extent of ammonium retention on exchange sites close to a highway;

90   • Ammonium retention increasing with down slope distance from a highway;

91   • Lowered organic matter content in soils close to roads and possible

92   accumulation in soil down slope, and hence a decline in the pool of

93   mineralizable-N;

94   • Increased mineralisation of organic-N;

95 • Increased nitrate concentrations in soil solution, rivers, and streams adjacent to
96   the highway.

97 Therefore, this paper examines and assesses spatial and temporal variations in soil,

98 soil solution and freshwater down slope of a highway in upland Cumbria, UK, to

99 determine the affects road salt has on N-processes and test the above hypothesis.

100

101 **2   Materials and methods**

102 2.1   Field site

103 The study site was an upland area adjacent to the A6 at Selside, Cumbria, UK (NY

104 554 046 GB Grid), with altitudes up to 458 m above sea level (Fig. 1). Soil types

105 consist of podzols with variable degrees of development and depths of organic-rich

106 surface horizons (organic-rich leached horizon, iron-rich mottled gley B horizon (in

107 places with signs of gley development), gravel layer C horizon with shale/slate),

108 derived from Upper Ludlow, Ludlow series, Upper Silurian bedrock. The vegetation

109 consists mainly of grasses, Juncus and bryophytes and the land is used for grazing

110 cattle and sheep. This site presents an unusual opportunity as the road drainage is

111 piped directly onto the soil surface at regular intervals. Hence the site presents three

112 possible transect scenarios (a) impacted by direct (channelled from a pipe) drainage

113 and by spray, (b) impacted by indirect drainage and spray and (c) an un-impacted

114 control within the catchment on an adjacent hillside with the same altitude, aspect and

115 land use. A dry stone wall ca. 1.5 m high down slope separates the road from the salt-

116 affected sampling sites. For further details refer to Green *et al*. (2007).

117

118 2.2   Sample collection

119 2.2.1   Soil sampling

120 Transects for each transect-type scenario were marked out in duplicate, at a spacing of

121 at least 10 m to ensure that pseudoreplication was avoided, perpendicular to the road;

122 direct (drain-affected) transects (T1/T2) were immediately down slope of drainage

123 pipe outlets; indirect transects (T3/ T4) were to the north of T1 and T2, respectively.

124 The un-impacted control transects are referred to as T5 and T6. Soil samples from 0-

125 10 cm were collected with a stainless steel trowel at 2, 4, 8, 16, 32 and 64 m from the

126   wall, and thus 4 to 68 m from the road itself, for transects T1 to T4, and from

127   corresponding distances on control transects T5 and T6, on the 7th April 2005.

128   Further soil sampling was completed at 2, 8 and 32 m from the wall on the 12th

129   October 2005, when residual salting impacts should be minimal, to provide an inter-

130   seasonal comparison.

131   The samples were stored field moist in polyethylene bags at 2-4 ^{o}C in

132   preparation for chemical analysis. Stones and residual identifiable vegetation

133   fragments and roots were removed by rapid careful hand sorting immediately prior to

134   use.

135

136   2.2.2   Soil solution sampling

137   Soil solutions at 2, 4, 8, 16, 32 and 64 m from the wall for each transect scenario were

138   sampled using sets of three *in situ* MOM 0.1 μm pore Eijkelkamp MOM rhizon soil

139   solution samplers (Rhizon SSS; Eijkelkamp Agrisearch Equipment, Giesbeek, The

140   Netherlands). MOM rhizon samplers 10 cm long and 2.5 mm in external diameter

141   were inserted at a depth of 5-10 cm, and evacuated with 60 ml syringes. Soil solution

142   sampling was completed on 8 occasions between 12/10/2005 and 08/07/2006 (Table

143   1). Thus sampling was conducted prior to, during and after road salt application

144   (Table 1). Sampling was more frequent over the salt application period. The air was

145   purged from the sample syringes, which were then stored at 2-4 ^{o}C prior to chemical

146   analysis. These samples were not filtered, as the rhizon sampler acts as a membrane

147   filter.

148

149   2.2.3   Freshwater sampling

150   Runoff from the investigated 1500-m section of the A6 road drains eventually into

151   Crookdale Brook (Fig. 1). A water sampling survey was completed on the Crookdale

152   Brook during the period from 12/10/2005 to 08/07/2006. Six locations were sampled

153   (S1 – S5 and S7) along the course of the Brook parallel to the A6, at intervals of

154   approximately 200 m (Fig. 1). S6 was a tributary between S5 and S7. The water at

155   each point was sampled in duplicate to confirm reproducibility of analytical

156   procedures; 125-ml polyethylene bottles were rinsed several times with the sample

157   water before a final collection was made. Samples were stored at 2-4 ^{o}C prior to

158   chemical analysis.

159   Chemical analyses for soil, soil solution and freshwater samples were conducted

160   as soon as possible after returning to the laboratory, with appropriate prioritization.

161

162   2.2.4   Bulk precipitation and drainage chemistry

163   Bulk precipitation samplers were used to assess spray inputs to the soil. Four

164   samplers were installed at the study site (4, 8, 16 and 32 m from the wall), and one at

165   the control site. Duplicate precipation samples were collected on the sampling dates

166   outlined in Table 1.

167   Drainage water samples were obtained when flow was occuring from T1 and

168   T2 (12/10//2005 and 08/07/2006). The samples were stored at 2-4 ^{o}C, prior to

169   analysis these samples were filtered through Whatman no. 42 filter papers.

170   2.3   Soil analysis

171   Soils were analysed for pH (H$_2$O), loss-on-ignition (ashing at 800 ^{o}C), potassium

172   chloride-extractable ammonium and nitrate, exchangeable base cations (1 M

173   ammonium-acetate) and cation exchange capacity (CEC – 1 M acidified NaCl after

174   ammonium saturation and 80 % ethanol washing) as previously described by Green *et*

175   *al*. (2007).   All extractions were completed on field moist, un-sieved semi-structured

176   soil. Performance of all instrumental methods was checked using synthetic reference

177   standard materials.

178

179   2.4   Freshwater, precipitation, road drainage and soil solution analysis

180   Water samples were analyzed for base cations, ammonium-N, nitrate-N, chloride, and

181   sulphate using ICP-OES (base cations), ion chromatography (Dionex, anions) and a

182   Bran and Luebbe AutoAnalyser 3 (N-species). Prior to analysis freshwater samples

183   were filtered using Whatman no. 42 filter papers, whilst soil solutions were filtered by

184   the 0.1 μm Rhizon membrane. Performance of all instrumental methods was checked

185   using synthetic standard reference materials. Nitrate concentrations obtained by ion

186   chromatography and automated colorimetry did not differ significantly.

187

188   2.5   Statistical analysis

189   For soil data, an one-way ANOVA non-parametric alternative test was utilised, the

190   Kruskal-Wallis test, as there is debate and scepticism about whether two-way

191   ANOVA extension of the identically named test is valid (Dytham, 2003 p.145). The

192   non-parametric test will not indicate whether there is an interaction between site and

193   distance, as this portion is not computed. For all statistical tests, significance was

194   accepted at $\alpha \leq 0.05$. Statistical analyses were performed using SPPS version 11.0.1

195   (2001).

196

197   **3   Results**

198   3.1   Road drainage and bulk precipitation chemistry

199   Sodium ion concentration in the control site bulk precipitation ranged between 1.21

200   and 4.37 mg l^{-1}, in comparison to bulk precipitation at 4 m from the wall where

201   concentrations ranged from 0.03 and 40.51 mg l^{-1}. The lowest sodium and chloride

202   concentrations being detected before the winter maintenance season had commenced

203   (02/11/2005). Sodium and chloride concentrations were significantly higher (at the

204   1% level) at 4 m than those of the controls after the salting-runs had been initiated.

205   Spray data from the bulk precipitators is incomplete as a proportion of the samples

206   were lost (i.e. bags dislodged, ripped or removed by on-site sheep/cattle), especially

207   for the 27/01/2006. 9/12/2005 and 03/01/2006 are the only dates for which a

208   complete set of data for the five bulk precipitators is available, both indicate a

209   reduction in sodium and chloride concentration as the distance from the road is

210   increased. There was no significant difference between water from the control and

211   that from the salt-affected bulk precipitation collections for ammonium-N and nitrate-

212   N, and no apparent distance affect for these N species.

213   All heavy metals (Ba, Cd, Cu, Mn, Pb, Zn) concentrations were below the

214   detection limits of ICP-OES (< 0.02 mg l^{-1}) for both bulk precipitation and drainage

215   water (T1 & T2) samples.

216   Road drain water samples contained higher concentrations of sodium and

217   chloride in July (31.2 and 45.8 mg l^{-1}, respectively) as compared to October (1.5 and

218   0.93 mg l^{-1}, respectively). The ammonium and nitrate concentrations observed in the

219 drainage water were 0.76 and 0.44 mg l^{-1}, respectively. The samples are not from the

220 salt application period.

221

222 3.2   Base cation and hydrogen ion occupation of the CEC

223 Table 2 shows mean values of ammonium acetate-extractable base cations and KCl-

224 extractable ammonium as a percentage occupation of CEC for T1/T2, T3/T4 and

225 T5/T6 transects. These means are across all 6 distances. Table 3 shows the data

226 disaggregated by distance (2, 4, 8, 16, 32 and 64 m) and transect type. The mean Na

227 % occupancy of CEC (across all distances: Table 2) for T1/T2, T3/T4 and T5/T6

228 transects differ significantly at the 1% level (direct > indirect > control). Percentage

229 occupation by sodium on the CEC never exceeds 0.65 % for T5/ T6, compared to

230 maximum values of 3.5 and 34 % for T3/T4 and T1/T2, respectively. The percentage

231 contribution for T1/T2 of sodium to the CEC declines to 16 m, and converges towards

232 the control values thereafter. The spray-affected transects (T3/T4) do not follow a

233 significant spatial pattern (Table 3) but always exceed the control soil values.

234   In October (data not shown) there was a reduction in Na % of CEC close to

235 the road on the salt-affected transects, especially for the T1/T2 (34 to 5% at 2 m).

236 Below 32 m there was no significant difference between the two sampling dates.

237   Ca % occupation of CEC for both sets of salt-affected transects is significantly

238 above that for the control (1% level, Table 2). The Ca % of CEC for all salt-affected

239 transects declines consistently with distance from the highway (Table 3), but results

240 for T3/T4 again show a irregular spatial trend.

241   The Mg % of CEC at 2 m follows the order T3/T4 > T5/T6 > T1/T2 (Table 3).

242 Differences between transect types are much smaller at 4 m, and Mg % of CEC

243 generally increases further down slope for T1/T2 and T3/T4. Spatial variation is

244 much less for T5/T6 than for salt-impacted transects, as would be expected where

245 there is no salt impact.

246   For Ca and Mg % of CEC (data not shown) there was a general decline

247 between April and October for all three transect scenarios at 2 and 8 m. However, Ca

248 % of CEC for T1/T2 increases from less than 5% in April to more than 10% in

249 October.

250   The H$^+$ % of CEC values, calculated by subtracting Σ base cations from CEC

251 for the three scenarios show significant differences, with T5/T6 > T3/T4 = T1/T2 (1%

252 level). At 2 m the H^+ % of CEC for T1/T2 falls to 49%, compared to 72 and 89% for

253 T3/T4 and T5/T6, respectively. Acidity increases down the salt-affected transects

254 from 2 to 16 m, to ~ 88%. T5/T6 maintain a constant acidity at ~ 92% (Table 3).

255 Below 16 m T1/T2 give values approaching control levels (64 m = 91%), while H^+ %

256 of CEC for T3/T4 declines to 67% at 64 m reflecting the higher Ca % and Mg %

257 values. H^+ % of CEC generally showed an increase for all transects in October (data

258 not shown), indicating partial reversibility of the neutralizing effect of high sodium

259 inputs over winter.

260   The CEC % occupation by base cations and hydrogen ions are also reflected in

261 the soil pH (H_2O).

262

263 3.3   Soil pH

264 Soil pH (H_2O) at 2-4 m during April 2005 for the T1/T2 transects was higher by more

265 than two units than that for the T3/T4 transects, and two and a half to three units

266 higher than that for the T5/T6 transects (Fig. 2, 1% level). This corresponds to the

267 high sodium dominance and low hydrogen occupancy of the CEC in the soils of the

268 T1/T2 transect (Tables 2 & 3).

269   The T1/T2 soils at 2 m maintain a pH above 7 in October (Fig. 2), whilst for

270 the T3/T4 soils pH has increased by over half a unit compared with the April value,

271 almost certainly due to a lower mobile anion (Cl^-) effect in October. At 8 m all the

272 soils still have a pH after summer at ~ 4.5 units, but the T5/T6 soils are still most

273 acidic in October. Over time, the T5/T6 soil pH remains constant at ~ 4. All three

274 scenarios are statistically significantly different from each other, in both April and

275 October at the 1% level with T1/T2 > T3/T4 > T5/T6.

276

277 3.4   Soil extractable ammonium-N

278 Figure 3 shows KCl-extractable ammonium in April, at the end of the salting period,

279 as a percentage occupation of CEC at 2, 4, 8, 16, 32 and 64 m for each transect type.

280 It is immediately obvious that the T5/T6 transects contain significantly more

281 extractable ammonium (on average 0.99%, Table 2) than either of the transects for

282 other pollution scenarios (0.25 and 0.36% on average for T1/T2 and T3/T4,

283 respectively) (1% level). In the most salt-impacted soils (T1/T2) the proportion of

9

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

291   The percentage occupancy of the CEC by ammonium for all pollution
292 scenarios was significantly lower in October (0.23, 0.24 and 0.14 % for T1/T2, T3/T4
293 and T5/T6, respectively) than in April (0.25, 0.36 and 0.99% for T1/T2, T3/T4 and
294 T5/T6, respectively), and the % ammonium on the CEC for the three scenarios
295 converged to similar values. Plant uptake would be lower in April than in October,
296 and more nitrification would occur over the summer prior to October, hence, reducing
297 the ammonium concentration.
298

299 3.5   Soil extractable nitrate-N
300 Figure 4 shows the concentrations of KCl-extractable nitrate-N for T1/T2, T3/T4, and
301 T5/T6 soils at 2, 4, 8, 16, 32 and 64 m in April 2005. The nitrate-N concentrations for
302 T5/T6 (mean of 0.58 mg kg^{-1}) are significantly lower than those of either type of salt-
303 affected transect (means of 2.34 and 3.34 mg kg^{-1} for T1/T2 and T3/T4, respectively).
304 The T3/T4 soils contained the highest concentrations (1% level) but nitrate
305 concentration did not differ significantly between the two salt impact scenarios (Fig.
306 4). Nitrate-N peaks on the salt-affected soils between 8 and16 m, which coincides
307 with the decline in soil pH (Fig. 2) for T1/T2. Nitrate-N concentration on the T1/T2
308 transects is significantly higher at 16 m than at all other distances. However neither
309 the T3/T4 nor the T5/T6 transects show a significant difference in mean nitrate-N
310 concentration with distance from the wall. By October 2005 nitrate-N concentration
311 was higher (results not shown) for salt impacted transects (7.27 and 5.19 mg kg^{-1} for
312 T1/T2 and T3/T4, respectively) than for T5/T6 (3.35 mg kg^{-1}), but there was no
313 significant difference between the three scenarios.
314   Seasonally, soil nitrate-N concentration for T5/T6 was overall statistically
315 significantly higher in October (3.35 mg kg^{-1}) than in April (0.01 mg kg^{-1}) (1% level).

316　However, there was no significant difference between October and April for either of

317　the salt-affected transects.

318

319　3.6　Soil loss-on-ignition and C:N

320　Table 4 shows soil loss of ignition for T1/T2, T3/T4, and T5/T6 from 2-16 m from the

321　wall. It clearly shows a significant difference between T1/T2, T3/T4 and T5/T6 at 2,

322　4 and 8 m (5% level). At 2 m, LOI (%) is significantly lower for the T1/T2 and T3/T4

323　than for T5/T6. Further from the road LOI% in T3/T4 soils converges to the T5/T6

324　soil LOI (%) content, with the T3/T4 soils differing significantly from the T1/T2 soils

325　up to 8 m. By 16 m the difference is not significant.

326　　　　Figure 5 shows the C:N disaggregated by pollution exposure scenario and

327　distance from the wall for April 2005. It is immediately obvious that the C:N is

328　consistently and significantly lower across all distances for the control transects (T5/

329　T6) than either salt-impacted scenarios (1% level). Ratios for T1/T2 significantly

330　change with distance (1% level). As the distance from the highway increases the C:N

331　declines from 24.3 at 2 m to 14.4 at 64 m. Neither T3/ T4 nor T5/ T6 show

332　significant changes in soil C:N ratio down slope from the road.

333

334　3.7　Soil solution sodium

335　Soil solutions from impacted soils from 12th October 2005 to the 8th July 2006

336　highlighted high concentrations of sodium ions, declining with distance from the road.

337　Concentrations as high as 5800 mg Na l^{-1} were observed 2 m from the road for T1/T2.

338　In comparison, soil solutions for T3/T4 contained < 200 mg Na l^{-1} at 2 m, declining to

339　21-48 mg Na l^{-1} at 64 m; the controls had background concentrations of 2-2.5 mg Na

340　l^{-1} across all distances on the 03/01/2006. The trends in sodium ion concentration in

341　the soil solution were reflected in chloride data, although chloride concentrations were

342　higher due to the nature of the two elements, with some sodium tending to be retained

343　within the soil due to its cationic properties. The large episodic increases in both

344　sodium and chloride concentrations were closely associated with road salt application

345　dates throughout the winter period, while data from 12/10/2005 and 03/11/2006

346　provide background soil solution concentrations prior to initiation of salt application

347　for winter maintenance.

11

348

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.

361

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).

377

378   3.10   Crookdale Brook

379   Water pH and concentrations of the base cations Ca, Mg and Na in the river increased

380   as the road (Fig. 8) and Crookdale Brook converged (Fig. 1). However base cation

381   concentrations varied over time too, and were especially high during periods when

382   winter maintenance was prominent (22/11/2005- 27/01/2006). This suggests

383   relationships between the quantities of base cations observed in Crookdale Brook and

384   road salt application.

385   The sampling sites ranged over 1.5 km of the water course from S1, where

386   there was no road salt effect, to S7, with a progressive increase in the road effect (Fig.

387   1). Site S7 might be expected to have the greatest potential affect as it is closest to the

388   road, with a drainage pipe entering the system up slope, just prior to the river

389   sampling point. However, the concentration of sodium ions at S7 is diluted by the

390   introduction of additional unpolluted water (S6) from the Borrowdale Brook tributary

391   prior to the sampling point. Up stream of S1, the catchment area spans over ca. 7

392   km^2; hence, the enhancements in base cation concentrations depicted in Fig. 8 are

393   very significant, bearing in mind the relative area of unaffected catchment upstream of

394   S2. A considerable road impact occurs within a few hundred metres. This trend is

395   also apparent in chloride concentration, and there were positive significant

396   relationships between the concentrations of base cations (Na, Mg and Ca) and

397   chloride (all at the 1% level). S7 data was excluded in drawing up the correlation

398   matrix for reasons discussed earlier.

399   Figure 8 shows that nitrate-N in the river increased as the road and Crookdale

400   Brook converged, especially during periods when winter maintenance was prominent

401   (22/11/2005- 27/01/2006). There is a relationship between the concentrations of

402   nitrate and sodium observed (5% level). There does not appear to be a spatial trend

403   with respect to the river ammonium concentrations (Fig. 8), although the high

404   ammonium concentrations in autumn reflect temporal trends also observed in

405   October/November in upland streams in Scotland (Clark *et al.*, 2004).

406

407   **4   Discussion**

408   Organic matter is mobilized as a result of a high pH desorption process as well as via

409   a loss of soil aggregate stability following displacement of calcium and magnesium

410   ions from soil organic matter cation exchange sites by sodium ions. From Table 4 it is

411 clear that organic matter loss from salt-impacted soils has occurred between 2 and 8

412 m, which correspond to dominance of the base cations by sodium (Tables 2 & 3), but

413 also higher pH (Fig. 2). Organic matter within 2-8 m has probably shifted down slope

414 due to the sodium dispersal effects on organic matter. This mobilization would be

415 facilitated by the higher soil pH in the salt-effected soils (Fig. 2), especially at 2-4 m,

416 which would also favour loss of organic matter by mineralization. There would be

417 less organic matter input near drain-affected areas too which, coupled to past heavy

418 leaching losses, could lead to the apparent accumulation down slope. Lower organic

419 matter input is a likely result of lower root density and/or faunal activity (Peinemann

420 *et al.*, 2005). Visual examination of the soil profiles clearly showed reduced organic

421 horizon depths at salt-affected sites at 2-8 m, which is indicative of a degenerative

422 long-term process. This would make less organic N available for mineralization. The

423 reduced organic matter depth is unlikely to be a result of pedological processes as the

424 trend depicted between the salt-exposure scenarios close to the road has been

425 consistently replicated in several studies completed by the authors at 4 m from the

426 wall (Green *et al.*, 2007, under revision). In addition the C:N ratio for the control

427 transect (2-32 m) is significantly and consistently lower than ratios for either of the

428 salt-impacted transects (Fig. 5). The C:N ratio provides some evidence towards a

429 greater mineralization as a result of a higher pH at salt-impacted transects (Fig. 2),

430 although this is not unequivocally proven here.

431   A high negative charge is essential in the bonding of soil organic matter to the

432 layered clay minerals by cation bridges (calcium and magnesium ions) and to iron and

433 aluminium oxides. Steric changes of the organic matter associated with this bonding

434 and the formation of the cross linkages between polymers by polyvalent cations

435 stabilize the organic molecules against both chemical and biological attack

436 (Peinemann *et al.*, 2005). If the calcium and magnesium ions are displaced from the

437 organic matter cation exchange sites, the organic fraction becomes vulnerable to

438 mobilization. However, it is clear from Tables 3 & 4 that there are elevated calcium

439 contents in salt-affected transects close to the highway over and above the control

440 values. This is a product of the road salt itself containing a portion of calcium ions, as

441 well as sparing soluble residues (i.e.7.5% by mass, which includes gypsum) (Kay

442 Monoghan, Salt Union, Pers. Comm). Hence, the organic matter loss at this site is

443 more likely to be controlled by pH.

444   It must be noted that most of the organic matter that was potentially mobile

445   has already been dispersed close to the road (Green *et al*., under revision), so evidence

446   of such facilitated movement of organic matter in soil solution now is unlikely as road

447   salting has been conducted in this region for several decades. The freshwater data

448   (Fig. 8) illustrate a sudden increase in both calcium and magnesium concentrations for

449   the first salting event sampled (22/11/2006). However, this was not reflected in the

450   soil solution data for the soils upslope where no sudden increase in concentration of

451   either cation was detected (results not shown). The effect is due to the higher chloride

452   input acting as a mobile anion on soils further down slope, with calcium and

453   magnesium being displaced from soils in the riparian zone.

454   Ammonium will be competitively displaced through cationic exchange

455   processes. Duckworth & Cresser (1991) noted that environments receiving salt inputs

456   from marine sources (although episodic in nature) may experience greater mobility of

457   NH_4^+ in the soil system, due to competitive ion-exchange effects from the weak

458   neutral soluble salts. The proportion of ammonium on the CEC is also markedly

459   lower than that of the control for both T1/T2 and T3/T4 (Fig. 3); this is as

460   hypothesised. Such displacement may lead to ammonium limitation, which may also

461   generate plant stress and growth suppression. It could be made worse by faster

462   nitrification (Fig. 4) at the higher pH in salt-effected soils, coupled to nitrate leaching.

463   The interpretation of the possible influence of road salting on the nitrogen

464   cycle is complex due to the number of possible drivers involved which may be

465   affected by salting. Soil pH (Fig. 2), salinity and the displacement of organic matter

466   (including organic-N) and cation exchange effects all influence key processes in the

467   nitrogen cycle such as ammonification and nitrification. It is very clear though that

468   ammonium % occupancy of the soil CEC has been reduced over time in the salt-

469   affected transects, by displacement and/or enhanced nitrification at higher soil pH.

470   Therefore no major displacement flush would necessarily be expected in the soil

471   solution data in this study. However, there is an initial increase in ammonium-N in

472   soil solution at 2 m after December; thus some displacement may be occurring at very

473   high mobile anion concentrations or a direct road runoff influence is present (Fig. 7,

474   T1/T2). The ammonium and nitrate concentrations observed in the drainage water

475   (0.76 and 0.44 mg l^{-1}, respectively) and road salt analysis (0.02 and 0.05 mg l^{-1} per

476   200 mg NaCl l^{-1}, respectively) could explain a portion of this observation, but is a

477 small contribution compared to concentrations in soil solution detected at 2 m from

478 the highway for T1/T2.

479   The sodium and chloride concentrations observed at the A6 are likely to be

480 typical of A roads in the UK. The heavier traffic loads tend to be on trunk routes and

481 motorways, which will tend to have a greater number of applications within the winter

482 maintenance period.

483   The reduction in CEC (Table 2) has a knock-on effect on bioavailability of

484 ammonium for further microbial transformation processes or direct plant uptake.

485 What also needs to be considered is the role of salinity and pH shifts on the microbial

486 population as well as effects upon soil structure stability and the enhanced organic

487 matter mobility; these together ultimately affect microbial functioning. Heavy metal

488 contamination from spray or road drainage, and hence interfering with microbial

489 processes in the soil are unlikely due to the concentrations of manganese, copper,

490 lead, cadmium, zinc and barium all being below < 0.02 mg l^{-1}.

491   There are clear spatial variations between and within transects with respect to

492 pH (Fig. 2) which will enhance or suppress nitrification within the study area.

493 Elevated nitrate-N concentrations above control levels are evident in both drainage-

494 and spray-affected soils, suggesting that nitrification has been enhanced by the

495 elevated pH. The decline in KCl-extractable nitrate-N below 32 m (Fig. 4)

496 corresponds with the start of ammonium-N build up in soil solution (Fig. 7) in salt-

497 affected soils, probably as a result of less nitrification due to more acidic conditions at

498 16-32 m and beyond, and increasingly organic soils as the distance from the highway

499 increases. The elevated nitrate-N concentrations in soil solution along polluted

500 transects also indicate an enhanced potential for leaching to surface waters (Fig. 7).

501   Green *et al*. (2007) showed that the concentration of ammonium-N was much

502 greater in unpolluted control soils. As well as the ammonium leaching from salt-

503 impacted soils, this probably reflects the lower organic matter content, and hence

504 lower CEC (Tables 2 & 3), that has evolved in impacted soils, leading to a reduced

505 pool of mineralizable N and lower content of stored ammonium. However, it can

506 only be speculated about the extent to which this reflects enhanced leaching losses of

507 organic C and N over many years, enhanced decomposition of organic matter at the

508 higher soil pH that is a consequence of the salting impact over several decades, or

509 reduced input of plant litter as a consequence of salt impacts upon vegetation growth.

510   There is clearly potential for enhanced nitrate loading of waterways due to
511   leaching, which has particular relevance to the Water Framework Directive. This is
512   especially true in the UK uplands where major trunk roads often run parallel to rivers
513   that supply a substantial portion of UK potable waters (Smart *et al*., 2001). However,
514   it is in these areas where de-icing salts are most likely to be needed to maintain the
515   flow of traffic through the winter months on roads.
516

517   **5   Conclusion**
518   There is clear evidence that a number of effects on the nitrogen cycle are induced by
519   highway winter maintenance activities. There is evidence indicative of high sodium
520   inputs flushing ammonium from soils and a reduction in the extent of ammonium
521   retention on exchange sites close to the highway (Fig. 3 and Table 2), while with
522   increasing distance from the highway down slope ammonium retention increases (Fig.
523   3). In addition there is evidence to support the hypothesis that organic matter content,
524   and hence the pool of mineralizable-N, of roadside soils is lowered, with a possible
525   increase down slope. Evidence to support the theory that enhanced mineralization of
526   organic-N, especially nitrification, is promoted by the increase in soil pH on soil
527   processes is provided in this paper, along with evidence of increased soil solution
528   nitrate-N in rivers and soil solutions.
529   Multiple drivers are involved in the processes, but their relative importance is
530   difficult to establish unequivocally. The experiments performed by Green *et al*.
531   (2007; under revision) complement the field study discussed above. The influence of
532   road salt declines as the distance from the highway increases; however, the impacts on
533   the Crookdale Brook, many tens of metres from the road, are still prominent.
534

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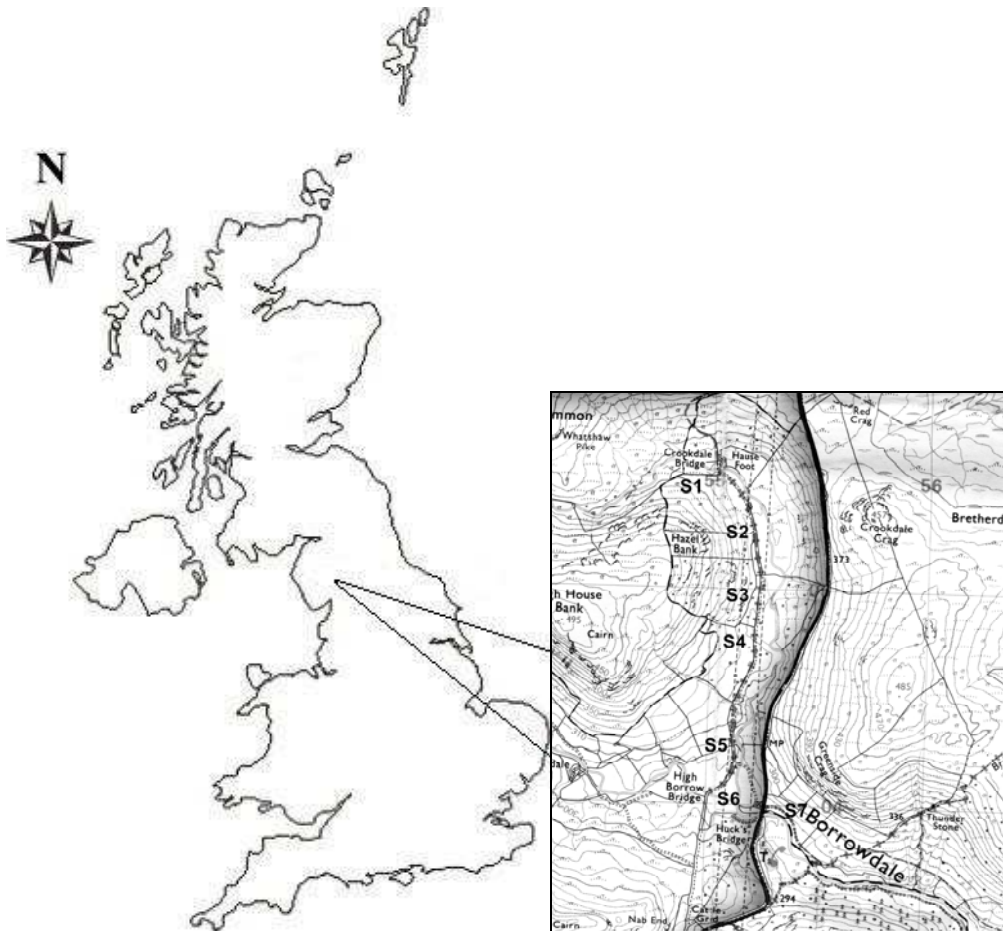
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Figure 1: Map showing the location of the field Site, UK. The A6 road runs due north
across the centre of the insert map; S1 – S7 indicate the river sampling points. (C)
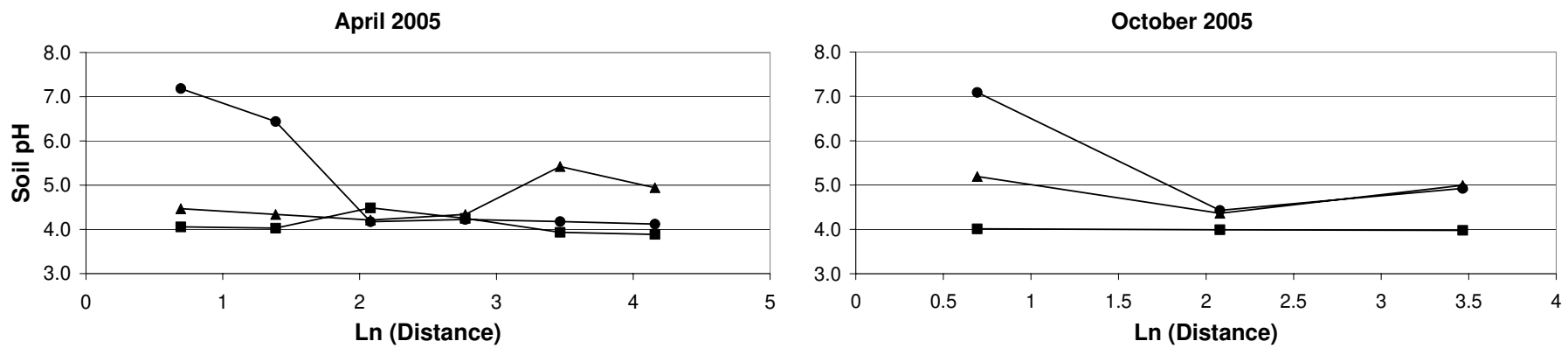Crown Copyright Ordnance Survey. All rights reserved.
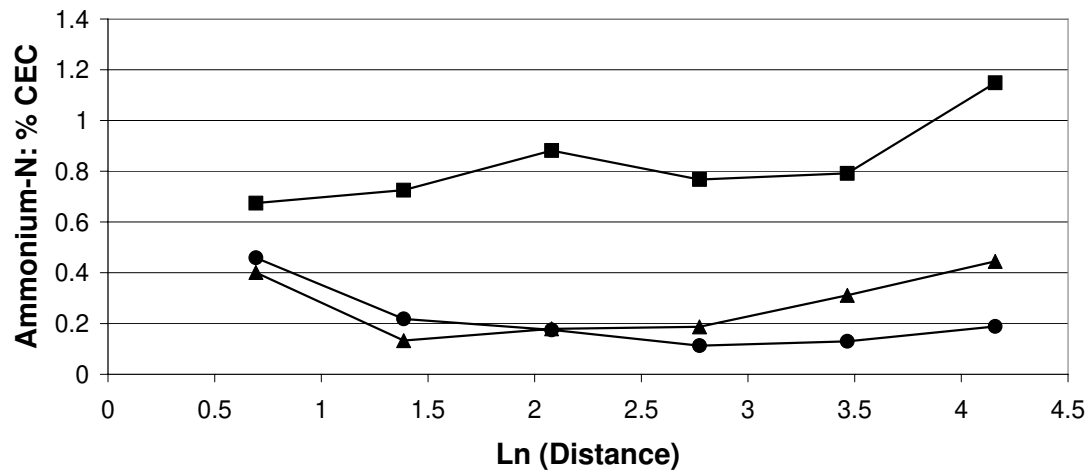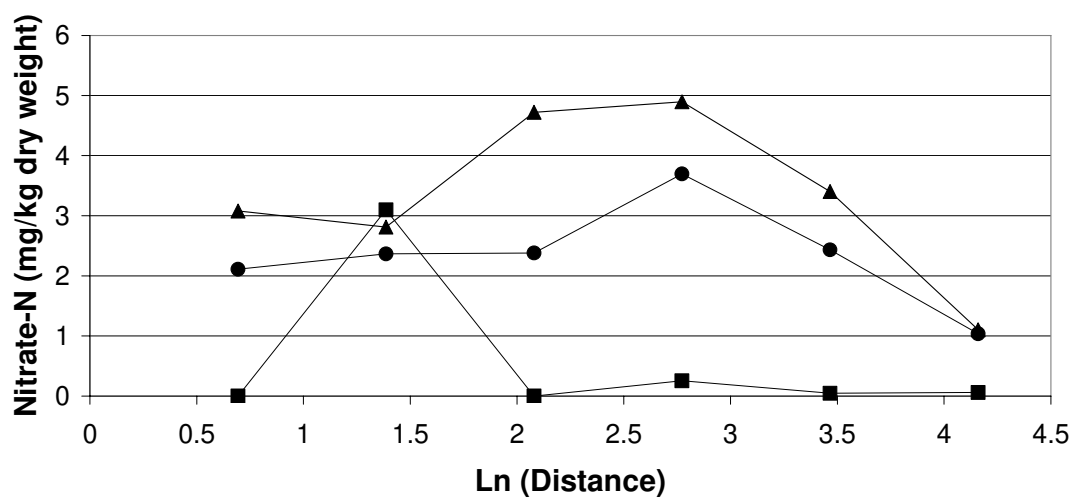
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588   Figure 2: Soil pH (H_2O) for April and October 2005 for soil samples at 2, 4, 8, 16, 32 and 64 m from the wall for the controls (T5 &

589   T6: squares), drain-impacted soils (T1 & T2: circles) and indirectly affected soils (T3 & T4: triangles).

21

590

591   Figure 3: Mean percentage ammonium-N occupation of the CEC for April 2005 for 2,

592   4, 8, 16, 32 and 64 m from the wall for the controls (T5 & T6: squares), drain-

593   impacted soils (T1 & T2: circles) and indirectly affected soils (T3 & T4: triangles).

594

595

596   Figure 4: KCl-extractable nitrate-N concentration (mg/kg) for April 2005 for soils

597   sampled at 2, 4, 8, 16, 32 and 64 m from the wall for the controls (T5 & T6: squares),

598   drain-impacted soils (T1 & T2: circles) and indirectly affected soils (T3 & T4:

599   triangles).

600

601

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
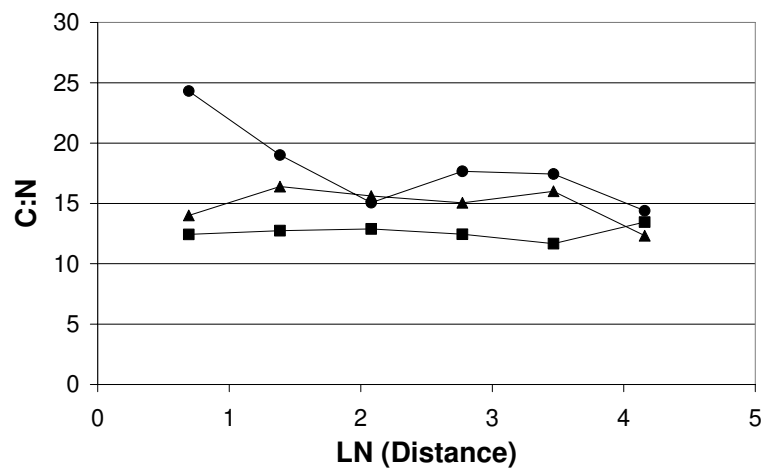indirectly affected soils (T3 & T4: triangles).

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

609 affected soils (T3 & T4) and control soils (T5 & T6).

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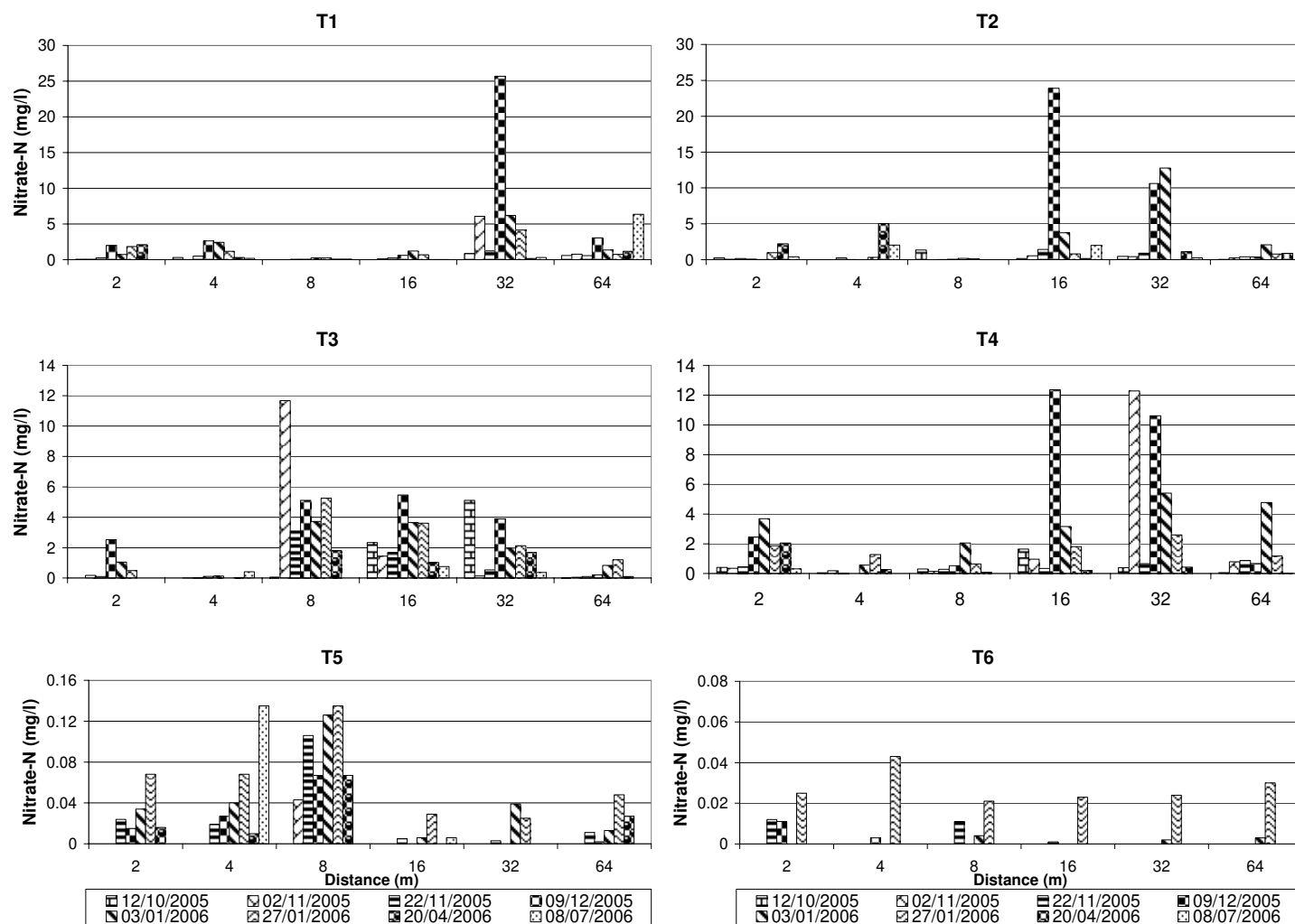613   Figure 7: Ammonium-N concentration for soil solutions at 2, 4, 8, 16, 32 and 64 m for drain-affected soils (T1

614   &T2), spray-affected soils (T3 & T4) and control soils (T5 & T6).
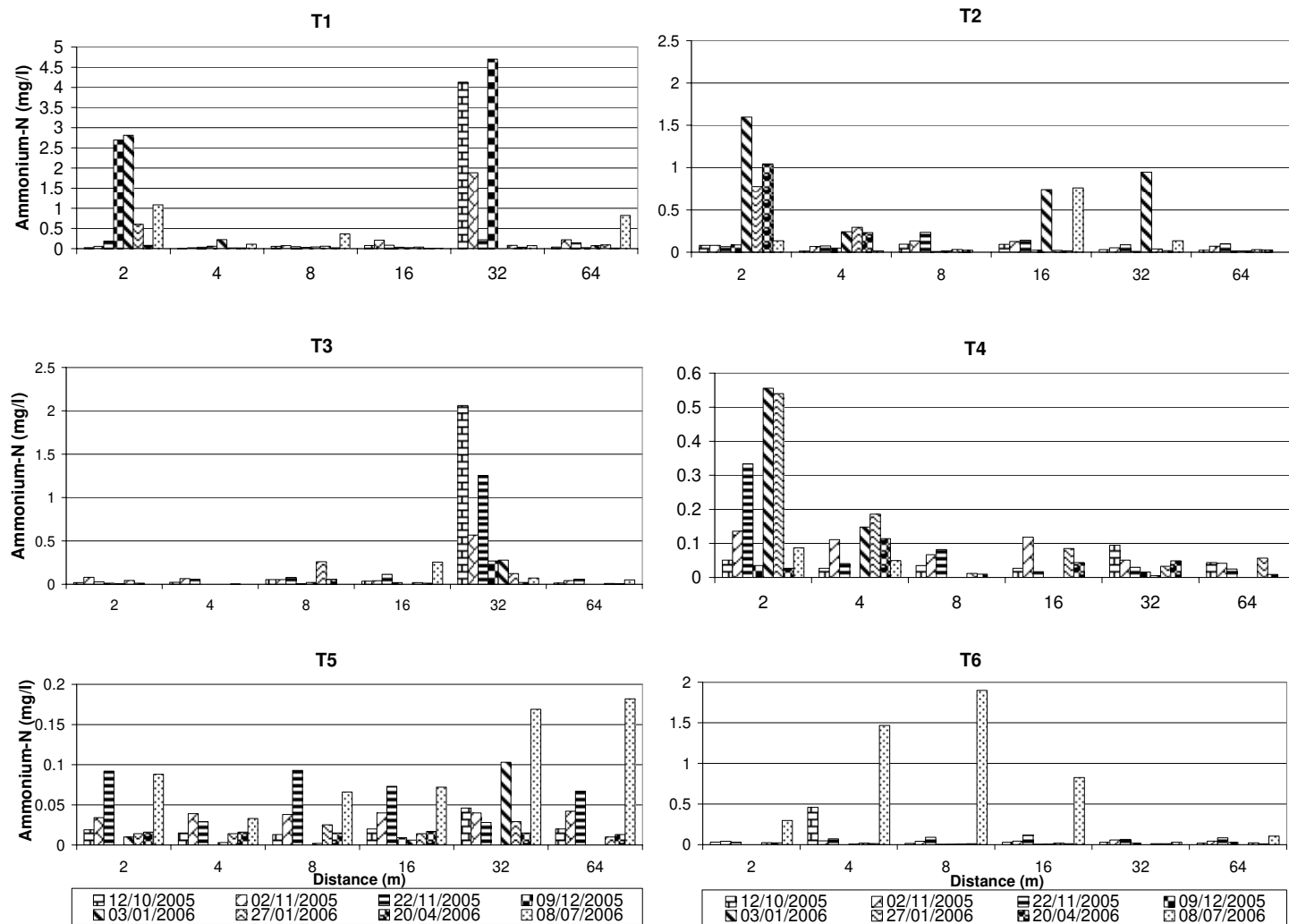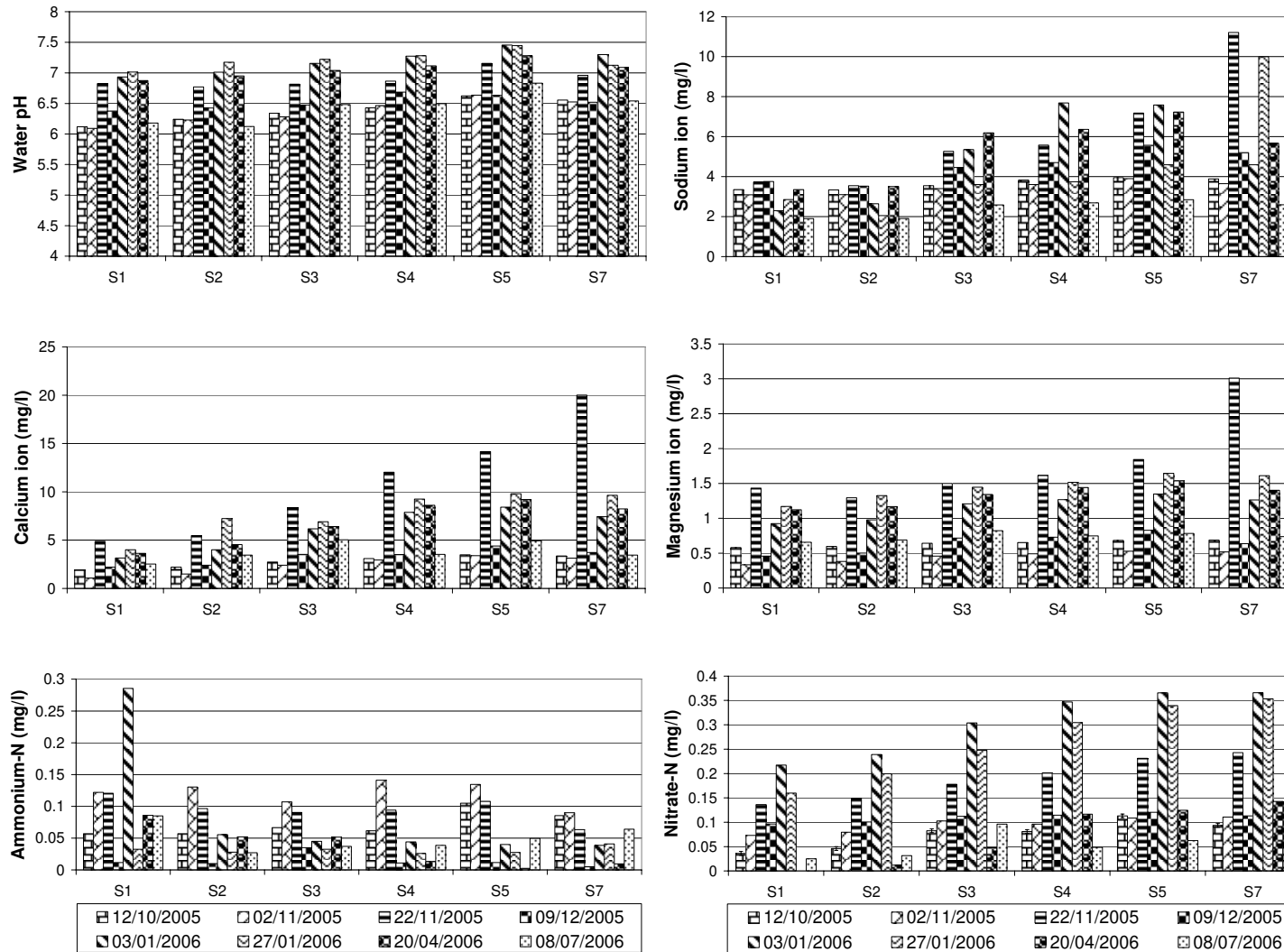
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Figure 8: The change in (a) pH, (b) sodium (c) calcium (d) magnesium (e) ammonium-N and (f) nitrate-N concentration

619

620 (mg l^{-1}) with time and distance along Crookdale Brook for the period 12/10/2005 – 08/07/2006.

621

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

OCTOBER 2005		NOVEMBER 2005		DECEMBER 2005		JANUARY 2006		FEBRUARY 2006		MARCH 2006		APRIL 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			

624 Table 2: Mean cation exchange capacity and % Na^+, Ca^{2+}, Mg^{2+}, K^+, NH_4^+ and H^+ of

625 CEC for April 2005, with standard errors in parentheses. ** denotes significant

626 difference in mean for direct, spray and control transects at the 1%, * at the 5 % level.

627 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)

628 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

629 the wall, with standard errors in parentheses. ** denotes significant difference in mean for direct, spray and control transects at the 1%, * at the 5 %

630 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)

631

632 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. *

633 denotes significant difference in mean LOI (%) for direct, spray and control transects at the 5 % level for the defined distance. Similar superscript letters

634 indicate no significant difference for post-hoc.

Distance (m)	Mean LOI (%)		
	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)

635