1 **Title:** Effect of long-term changes in soil chemistry induced by road salt applications

2 on N-transformations in roadside soils.

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5

6 **Abstract:**

7 Of several impacts of road salting on roadside soils, the potential disruption of the

8 nitrogen cycle has been largely ignored. Therefore the fates of low-level ammonium-

9 N and nitrate-N inputs to roadside soils impacted by salting over an extended period

10 (decades) in the field have been studied. The use of road salts disrupts the

11 proportional contributions of nitrate-N and ammonium-N to the mineral inorganic

12 fraction of roadside soils. It is highly probable that that the degree of salt exposure of

13 the soil, in the longer term, controls the rates of key microbial N transformation

14 processes, primarily by increasing soil pH. Additional influxes of ammonium-N to

15 salt impacted soils are rapidly nitrified therefore and, thereafter, increased leaching of

16 nitrate-N to the local waterways occurs, which has particular relevance to the Water

17 Framework Directive. The results reported are important when assessing the fate of

18 inputs of ammonia to soils from atmospheric pollution.

19

20 **"Capsule":** Road salting effects ammonification and nitrification in roadside soils.

21

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

23

24   1. **Introduction:**

25 The application of deicing agents to roads has been widely practised in Europe and

26 North America during winter months since the 1960s to minimise the risk of accidents

27 due to ice and snow and to maintain traffic flow. Several different de-icing agents are

28 available, but most agencies in the UK use sodium chloride, which can be applied to

29 roads as a liquid or solid, depending upon the conditions (Blomqvist and Johansson,

30 1999). The salt may be relatively pure NaCl, or mixed with grits and sands, and

31 possibly an anti-caking agent such as sodium hexacyanoferrate (II) (Ohno, 1990).

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32　De-icing salts provide safer driving conditions by dissolving into precipitation, either

33　melting any ice or snow, or preventing the formation of ice on the roads. However,

34　75–90 % of the applied de-icing salt enters the roadside environment directly in runoff

35　and as splash or aerosol deposition (Astebol et al., 1996), via mechanical malfunction

36　during application or post-application ploughing, or as wash off from vegetation as

37　throughfall. Deposition occurs mainly within 10 m of the roadside (Astebol et al.,

38　1996; McBean and Al-Nassri, 1987), although elevated concentrations of Na^+ and Cl^-

39　have been observed from tens to hundreds of metres from roads (Blomqvist and

40　Johansson, 1999).

41

42　　**2.　Impacts on Soils, Plants and Freshwaters:**

43　The detrimental impacts of elevated concentrations of Na^+ and Cl^- on roadside soils,

44　vegetation, and ground- and surface-waters (as well as automobiles and road surfaces)

45　have been well documented. Effects on soils and plants include:

46

47　**Impacts on Soil:**

48　　**1.**　Possible alterations in soil structure (Bäckström et al., 2004; Norrstrom

49　　　　and Bergstedt, 2001).

50　　**2.**　An increased potential for colloid mobility and therefore associated

51　　　　heavy metal mobility (Amrhein et al., 1992; Grolimund et al., 1996;

52　　　　Norrstrom and Jacks, 1998; Shainberg and Letey, 1984).

53　　**3.**　Possible reductions in hydraulic conductivity as pores become blocked

54　　　　by the release of fine particulates and soil colloids (Norrstrom and

55　　　　Bergstedt, 2001).

56　　**4.**　Changes in the concentrations of cations on cation exchange sites and

57　　　　in soil solution leading to changes in soil and soil solution pH and ion

58　　　　concentrations, and disruption of natural and other pollutant element

59　　　　biogeochemical cycling (Bäckström et al., 2004; Bauske and Goetz,

60　　　　1993; Darban et al., 2000; Duckworth and Cresser, 1991; Löfgren,

61　　　　2001; Norrstrom and Bergstedt, 2001; Norrstrom and Jacks, 1998;

62　　　　Sarin et al., 2000; Shanley, 1994).

63　　**5.**　Changes in the soil microflora and microfaunal communities to ones

64　　　　that may be more salt tolerant.

65

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

95 high increases are sometimes associated with roadside salt piles. The precise

96 concentration increase obviously depends upon the size of unpolluted catchment

97 upstream, road length in close proximity to the stream and amounts of salt applied. In

98 the study area for the present research, for example, the Cl^- increase was six-fold

99 during the highest pollution incident studied. Potential impacts include aquatic

100 chloride toxicity (DOE & DOH, 2001; Mattson and Godfrey, 1994; Mayer et al., 1999;

101 Williams et al., 1999) and chemical stratification (Mattson and Godfrey, 1994; Smol

102 et al., 1983). There may be human health implications for those on salt-restricted

103 diets (Amrhein et al., 1992). In the UK uplands major trunk roads often run parallel

104 to rivers that supply a substantial portion of UK potable waters (Smart et al., 2001).

105 Yet it is in these areas where de-icing salts are most likely to be needed to maintain

106 the flow of traffic through the winter months on roads and have been in continuous

107 use for tens of years, and de-icing salts have been used as a winter maintenance

108 practice for as long.

109

110 **3. Potential Impacts on Soil N Cycling:**

111 Few studies have focused upon the affect on the nitrogen cycle and microbial

112 functionality, and the potential disruption that road salts may pose. It is hypothesised

113 that increasing sodium concentrations may flush ammonium ions from exchange sites

114 or prevent ammonium retention from atmospheric inputs (Duckworth and Cresser,

115 1991), and this could conceivably lead to shortages of available N for some distance

116 down slope of salted roads.

117   Spatially and temporally variable pH shifts may also modify ammonification

118 and nitrification rates, providing another mechanism for disruption. These may be

119 induced either by sodium displacing H^+ from cation exchange sites, and similar

120 effects from magnesium and calcium present as impurities in commercial road salt.

121 They may also arise from mineral insoluble residues present in the salt (7.5 % by

122 mass in the salt used in the present study, including some gypsum (Kay Monaghan,

123 Salt Union, personnel communication), or deliberately added grit. In addition, high

124 concentrations of chloride can acidify soil solution down-slope by the mobile anion

125 effect. While soil pH does not directly control N availability per se, it does affect soil

126 microbial activity. Nitrifying organisms tend to be sensitive to excessive soil acidity

127 and their activity is markedly decreased when soil pH is less than 5.0 (Pierzynski et al.,

128 2000). Naturally acidic soil conditions can limit microbial activity and slow

129 mineralization of N as well as nitrification. Thus, a shift in soil pH from acidic to

130 near neutral or above may enhance the rates or organic matter mineralization and of

131 nitrification due to release from acidity constraints, but may lead eventually to loss of

132 ammonia via volatilisation and loss of nitrate via denitrification (optimum range pH

133 6–8).

134 　　　　　There is also the possibility that the ammonification process could be

135 enhanced due to the weakened binding of organic matter to mineral structures as a

136 consequence of sodium dominance in the soil. Nitrogen transformation processes

137 could also be disturbed through the direct effect of roadside salt contamination and the

138 enhanced bioavailability of heavy metals and their chloro-complexes on the microbial

139 community itself, depending on the ecotoxicity of the chemical species. McCormick

140 and Wolf (1980) demonstrated that the application of 0.25 mg g^{-1} of NaCl

141 significantly reduced CO_2 evolution (by 16%) in soil, and increasing the NaCl

142 concentration progressively reduced rate of CO_2 evolution, with no CO_2 evolved from

143 soil receiving 100 mg NaCl g^{-1}. A decrease in O_2 consumption and CO_2 evolution

144 was also observed by Azam and Muller (2003) with increasing concentrations of

145 NaCl. At NaCl concentrations ≥ 0.25 mg NaCl g^{-1} ammonification was reduced and

146 at 0.25 mg NaCl g^{-1}, nitrification rate was significantly reduced (McCormick and

147 Wolf, 1980). This supports Laura's (1974, 1977) original findings that nitrification

148 can be severely retarded or even completely inhibited in saline conditions as a result

149 of nitrifiers being more sensitive to salinity than ammonifiers. However, such short-

150 term NaCl additions preclude possible compensatory longer-term effects of pH

151 increase of acid soils. This seriously limits the value of studies such as those

152 described above, as does their inability to take into account the highly dynamic nature

153 of soil and soil solution chemistry, and hence of the soil microbial environment,

154 during salt contamination incidents.

155 　　　　　If nitrification is inhibited, an accumulation of ammonium may occur, though

156 conversely ammonium may be leached due to cation exchange competition from

157 sodium ions (to an extent depending on relative abundance). Additionally, a potential

158 decline in N mineralisation rate may counteract any such ammonium accumulation

159 effect by limiting the amount of ammonium released into the soil; such amelioration

160 would depend on the sensitivity of the micro-organisms involved within these

161 processes to NaCl, heavy metals and chloro-complexes, as well as the chemical

162 species' concentrations. Laura (1977) and McCormick and Wolf (1980) illustrated

5

163 that ammonification was increasingly retarded with increasing concentration of NaCl;

164 beyond ≥ 25 mg NaCl g^{-1} the concentration of ammonium in the soil declined

165 (McCormick and Wolf, 1980).

166   As a result of the retardation of nitrification, any input of ammonium could lead to

167 the accumulation of ammonium in the roadside soil. Increasing ammonia deposition

168 on the roadside environment results from the use of three-way catalytic converters on

169 cars, and the incomplete reduction of NO to N_2. This leads to increased ammonia in

170 exhaust emissions, deposition declining with distance from the road (Cape et al., 2004;

171 Truscott et al., 2005). Thus, ammonium availability is enhanced in those soils that are

172 most effected by road salt. It is important to note that these previous studies

173 examined the salinity effect where a fixed concentration of salt solution is added to a

174 constant soil, with consistent chemical attributes.

175   A laboratory study was designed to study the fate of ammonium-N and nitrate-N

176 inputs to roadside soils that have been impacted by salting over an extended period

177 (decades) in the field. The objective was to quantify the extent to which microbial

178 functioning and N species transformation rates had been affected by the presence of

179 road salt contamination within the defined profiles and to identify and prioritise the

180 possible causes of effects observed. An area known to have lengthy area of very acid

181 grassland soil was explicitly chosen for the study because pH effects from salting

182 were likely to be greatest in such a soil. Moreover it could be confirmed that soil

183 above the road (upslope) was visibly uniform. This was necessary to be confident that

184 differences in soils below the road and an adjacent control plots were indeed due to

185 road runoff.

186

187   **4. Materials and methods:**

188 **Field Site:**

189 Samples of surface soil (0–10 cm) were collected from an upland site along a major

190 road, the A6, at Selside, Cumbria, UK (Fig. 1). The site of the present study is an area

191 of high relief, with altitudes up to 458 m above sea level. Soil types consist of

192 podzols and poorly developed podzols (limited evolution of E and B horizons) with

193 variable depths of organic-rich surface horizons. The bedrock in the area is primarily

194 Upper Ludlow, Ludlow series, Upper Silurian. The vegetation at the site consists

195 mainly of grasses, Juncus and some bryophytes; and the land is used for grazing cattle

196 and sheep at a low stocking density. This site was selected as it presents an unusual

197   opportunity as road drainage is piped directly onto the soil surface at regular intervals.

198   Hence this site presents three possible contamination level scenarios (a) most heavily

199   polluted, with drainage plus spray, (b) less polluted, with spray and some (minor) road

200   runoff and (c) controls on an adjacent hillside at the same attitude and aspect within

201   the catchment. A wall of a height of 1.5 m separates the road from the salt-affected

202   sampling sites. Two transects for each pollution-level scenario were sampled in

203   duplicate, sample sites being separated by at least 10 m to ensure that

204   pseudoreplication was avoided. Transects were marked out perpendicular to the road;

205   in the case of the drainage-impacted transects, they were along the line of the drainage

206   pipes (T1 & T2); spray-impacted transects (T3 & T4) were between drain-impacted

207   transects to the left; and control transects (T5 & T6) were away from, and well above,

208   the road, but with the same elevation, aspect, parent material and land use.

209

210   **Soil sampling:**

211   Soil samples from 0-10 cm were collected at 3 m from the wall, and thus 4 m from the

212   road itself on the 8th July 2006. In each case, the samples were encased in

213   polyethylene bags and placed immediately into cold storage (at 2-4ºC) in preparation

214   for the simulation experiment and chemical analysis.

215

216   **Water sampling:**

217   A water sampling survey was completed on the Crookdale Brook during the period

218   12/10/2005-08/07/2006. Conditions at the time of sampling are summarised in Table

219   1. Flow was not gauged on the Crookdale Brook directly, but discharge in the River

220   Lune, 6 km from the Crookdale, serves as a useful surrogate. Six locations were

221   sampled (S1-S5 + S7) along the course of the Brook, their locations being defined by

222   the A6 (Fig. 1). Above S1 there was negligible catchment contamination from road

223   runoff. Contamination risk increased steadily down to S5. S6 was an uncontaminated

224   tributary, which dilutes pollution impacts slightly by S7, the furthest point sampled

225   downstream on the main river channel. Each sampling point was sampled in

226   duplicate. The 140-ml polyethylene bottles were rinsed several times with the sample

227   water before a final collection was made by completely submerging the bottle and

228   capping it under water to avoid generation of headspace. Samples were placed

229   immediately into a cold box in preparation for chemical analysis on return to the

230   laboratory.

231

Soil Analysis:

233 Soil moisture content was determined by oven drying at 105°C, and LOI by ashing at

234 800°C. Soil pH was measured on moist soil at a 1:1 substrate:water ratio.

235 Ammonium-N and nitrate-N were extracted from soils with 1M KCl and ammonium-

236 N and nitrate-N determined using a standard Bran and Luebbe AutoAnalyser 3

237 procedure. Exchangeable base cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) were determined by

238 AAS using matrix-matched standards after extraction with 1M ammonium acetate.

239 CEC was determined by AutoAnalyser after washing the ammonium-saturated soils

240 with 80% aqueous ethanol, and leaching absorbed ammonium with 1 M acidified

241 NaCl. Performance of all instrumental methods was checked using synthetic

242 reference standard materials.

243

Freshwater Analysis:

245 Nitrate-N in the water samples was determined using a Bran and Luebbe

246 AutoAnalyser 3. Determinations were repeated by ion chromatography, which was

247 also used to quantify chloride concentrations (Dionex). There was no significant

248 difference between results obtained by the two methods of nitrate measurement.

249

Simulation Experiment:

251 For each soil of the three salt-impact scenarios, sixty 10-g sub-samples of freshly

252 collected, field-moist sorted and homogenised un-sieved soil were inserted into 140-

253 ml polyethylene bottles. Soils in a sub-set of 20 bottles were spiked with 50 μg of

254 ammonium-N (as ammonium chloride, added in 0.5 ml of water), soils in a second

255 sub-set of 20 bottles were spiked with 50 μg of nitrate-N (as sodium nitrate, added in

256 the same volume of water), and the remaining 20 bottles were spiked with the same

257 volume of deionised water only (as controls). Half of the bottles from each sub-set

258 were incubated at room temperature and the other half at 4°C. After defined time

259 intervals, duplicate samples for each salt-impact scenario were destructively analysed

260 for ammonium-N and nitrate-N by addition of 100 ml of 0.5 M KCl, shaking for 1 h,

261 filtration through Whatman No. 42 papers, and subsequent analysis using a Bran and

262 Luebbe AutoAnalyser 3. The time intervals used were 0 (immediately post spiking),

263 1, 2, 5 and 9 days, hereafter referred to as t_0 to t_9. A 24-hour period was allowed prior

264 to spiking for the soils incubated at room temperature to allow acclimatisation to the

265 changed temperature conditions.

266   The incubations were done at two temperatures because it was necessary to

267 assess prior salting effects on nitrogen species transformation rates under wintry

268 conditions in order to establish possible links between soil processes and river water

269 chemistry over the winter period, as well as potential links at the higher temperatures

270 over the summer period.

271

272   **5. Results:**

273 **Nitrate-N in Crookdale Brook:**

274 The freshwater survey showed that nitrate-N and chloride concentrations in the river

275 increased as the road and Crookdale Brook converged at S1, on moving downstream

276 towards S7 (Fig. 2), especially during periods when winter maintenance was

277 prominent (22/11/2005-27/01/2006). This suggests relationships between the quantity

278 of nitrate-N observed in Crookdale Brook and road salt application. Spatial trends for

279 chloride were very similar to those for nitrate, and a residual increase in chloride

280 along the river stretch was still seen in July. Nitrate concentrations are low in April

281 and July, as expected due to greater plant uptake.

282

283 **Soil Chemical Composition:**

284 Table 2 summarises the soil chemical parameters for soils from T1-T6. It

285 demonstrates clearly the differences in soil pH (significant at 1%) and base saturation,

286 expressed here as % occupation of cation exchange sites for sodium, magnesium,

287 calcium, potassium and ammonium ions. The differences in % sodium, % magnesium

288 and % calcium between pollution scenarios were significant at 5 %, 5 % and 1 %

289 respectively. There is sodium dominance for T1 and T2, with declining contribution

290 of sodium to exchangeable cations for T3 and T4 and for the controls, T5 and T6,

291 thereafter. This corresponds to a higher dominance of CEC by hydrogen ions for the

292 control transects, and progressively lower H^+ dominance for both spray contaminated

293 transects and drain-impacted transects (significant at 1%). The proportions of

294 magnesium and calcium follow the same trend as that for sodium ions. Note that

295 because of the very high salt content in T1 and T2 soils, and possibly the presence of

296 gypsum from the salt, $\sum$ cations is > CEC for T2.

9

297   Although on average the proportion of exchangeable ammonium-N is lower

298   than that of the control for both drainage- and spray-contaminated transects, because

299   of variation between replicates this is not significant. LOI increases, on average, from

300   the drainage transects to the controls.

301   The soil for drainage-influenced transects had a much higher pH (6.66 or 8.11)

302   than that from the spray-contaminated transects (4.62 or 5.11), which were in term

303   less acid than the control soils (3.79 or 3.82). This corresponds to the high sodium

304   dominance and low hydrogen content of the CEC for the salt-impacted soils.

305

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

307   Figure 3 shows how the total extractable mineral N concentration, and the

308   contributions of nitrate-N and ammonium-N to the total mineral N, changed over the

309   nine days following the addition of the 50 μg ammonium-N spikes with incubation at

310   room temperature. It is immediately obvious that in the more acidic, control soils (T5

311   & T6), ammonium remains dominant throughout the experiment. From one-way

312   ANOVA, ammonium fell significantly between t_0 and t_9 for T1, T2, T3, and T4 (1 %),

313   but not change significantly in T5 and T6. Conversely nitrate increased significantly

314   (1 %) for all transects, although differences between adjacent pairs of times were not

315   always significant. In the most salt-impacted soils (T1 & T2), however, nitrate-N is

316   the dominant mineral N form by the second day, and nitrate becomes increasingly

317   dominant over time. By the end of the experiment ammonium-N is almost

318   undetectable. The less contaminated, splash-impacted soils (T3 & T4) display

319   intermediate behaviour. The declines in nitrate-N to ammonium-N ratio over time are

320   very consistent, as can be even more clearly seen in Fig. 4. T1 to T4 contained

321   significantly (1 % level) less ammonium than T5 and T6, but not significantly

322   different amounts of nitrate.

323

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

325   Figure 5 shows how the total extractable mineral N concentration, and the

326   contributions of nitrate-N and ammonium-N to the total mineral N, changed over the

327   nine days following the addition of the 50 μg nitrate-N spikes with incubation at room

328   temperature. It is clear that in all the soils (T1 – T6), there is no evidence of nitrate

329   immobilisation by soil microbial biomass. Indeed, for T3-T6, ANOVA showed that

330   nitrate concentration actually slightly increased at t_5 and t_9 in this experiment.

331   However in the road salt-impacted soils (T1 – T4), ammonium appeared to decline by

332   nitrification over the first 1 –2 days, but this was only significant for T1. Over a

333   longer time scale there was evidence of nitrification in all six soils. Ammonium was

334   starting to accumulate by day 9, and this was especially marked and significant at 1 %

335   for the most acidic, control soils (T5 & T6), but this production of ammonium

336   resulted also in significant nitrate build up for T4 to T6. Slight accumulation might be

337   anticipated because of the elimination of any plant N-uptake in this experiment.

338

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

340   Figure 6 shows how the contributions of nitrate-N and ammonium-N to the total

341   mineral N changed over the nine days following the addition of the deionised water

342   blank spikes with incubation at room temperature. For the most heavily impacted

343   soils (T1 & T2), nitrate dominated the mineral N fraction, especially after 24 h of

344   incubation. The contribution made by ammonium-N was much greater in the

345   unpolluted, control soils (T5 & T6) throughout the experiment, and the more

346   moderately polluted soils exhibited an intermediate trend. ANOVA showed that for

347   ammonium, T6 > T1 to T4, but T5 did not differ significantly from T1 to T4. In all

348   soils though the nitrate-N to ammonium-N ratio increased significantly over time.

349

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

351   Figure 7 compares the nitrate-N and ammonium-N after ammonium spiking with the

352   nitrate-N and ammonium-N after deionised water blank spiking and with the spike

353   added flux. It shows how these values changed over 9 days with incubation at 4 °C.

354   All results are expressed on a dry weight soil basis, so although 50 µg of ammonium

355   N was always added, the spike size appears to vary because of variations in the soil

356   moisture content. The results clearly show that the spike size selected was very

357   appropriate.

358   Between t_0 and t_1, spike ammonium-N is lost in all soils to a significant extent

359   (compare bar 4 with bar 2), but interestingly not all is converted to nitrate-N (compare

360   bar 5 with bar 3). At the lower incubation temperature, nitrification initially seems

361   greater in the control soils (T5 & T6). By time t_2, ammonification is extremely

362   pronounced in all the deionised water-spiked control soils (2nd bars) and in all the

363   ammonium-N-spiked soils (4th bars). By t_5 much of the extra ammonium generated

364   appears to have been nitrified, however.

365

366   **6. Discussion:**

367   **Variation in soil properties:**

368   In the context of the present study, it is important to establish that the very substantial

369   differences in soil chemical composition for the three contamination scenarios are

370   primarily due to impacts of road drainage water and not just due to natural soil spatial

371   variations. Our preliminary field survey showed that the near-surface soils subjected

372   to the diverse pollution scenarios at the sampling distance from the road were all

373   highly organic, and when not adjacent to the road consistently very acidic (pH 3.8 to

374   4.3). There was no evidence however, compared with the soils further down-slope

375   from the road, of any foreign mineral matter from road construction. Moreover the

376   stones were similar in the control and roadside soils. However, the control soils were

377   apparently more organic rich, and was confirmed by subsequent LOI % measurement

378   (Table 2). It is therefore highly probable that differences between soils were

379   attributable not to natural variation, but to combined effects of road salt in runoff,

380   insoluble particulates from the salt, the additional water flux and associated soil

381   wetness and erosion effects, and possibly to soil particulates redistributed by vehicle

382   flow in both directions along the A6 being flushed from the road surface down drains.

383   The salt used in the area contains 7.5 % insoluble solids, which include small amounts

384   of gypsum and carbonate (Kay Monaghan, personnel communication).

385   In spite of the circum-neutral soil pH near drain outlets (Table 2), there was no

386   sign of well-developed cambisol formation, which might be expected if the variation

387   was natural. As will be seen later, and is clear in Table 2, the high sodium dominance

388   of CEC plays a major role in increasing the soil pH of these naturally highly acidic

389   soils. For one of the drain-impacted transects (T2), sodium occupied 85 % of the

390   CEC at 3 m from the road. For the same soil, calcium occupied much less of the CEC,

391   in spite of it being divalent, and the presence of significant amounts of calcium in the

392   road salt being used (ratio of 80:0.7:0.07 Na:Ca:Mg). Thus it seems that the sodium

393   in road drainage has a major impact on the soil chemistry. In addition the very high

394   concentrations of chloride in soil solutions at this site (up to 7 900 mg l^{-1} during

395   salting, Green and Cresser, 2007) add credibility to the hypothesis that road salt is the

396   major cause of observed differences between soils from the different pollution

397 scenarios, as does the observation of dramatic seasonal shifts in soil pH for salt-

398 impacted soils only (Green and Cresser, 2007). However, as % Ca > % Na on CEC

399 for T3 and T4, it is clear that particulates and/or soluble calcium in splash from the

400 road must make an important contribution to soil partial neutralization.

401

Nitrate and Chloride in Crookdale Brook:

403 The sampling sites ranged over 1.5 km of the water course from S1, where there was

404 no road salt effect, to S7, with a progressive increase in the road effect. Site S7 might

405 be expected to have the greatest potential affect as it is closest to the road, with a

406 drainage pipe entering the system up slope, just prior to the river sampling point.

407 However, the concentration of nitrate-N at S7 is diluted by the introduction of

408 additional water from the Borrowdale Brook tributary prior to the sampling point.

409 This effect is more conspicuous for Cl^- concentrations, when salting is applied after

410 22/11/2005. Above S1, the catchment area itself spans over ca. 7 km^2; hence, the

411 enhanced nitrate-N concentrations depicted in Fig. 2 are very significant, bearing in

412 mind the relative area of unaffected catchment upstream of S2. A considerable road

413 impact occurs within a few hundred metres, with enhancement being evident even in

414 mid-winter. The seasonality effect of soil microbial and plant uptake in the soil on

415 river water nitrate-N concentration at each sampling point is also apparent in Fig. 2.

416   The very wet conditions on the first two sampling dates, 12/10/2005 and

417 02/11/2005 would have contributed to the low river water nitrate concentrations by

418 dilution (Table 1). Although there was significant rainfall on 08/07/2006, much of

419 this was retained in dry soil, and probably plant N-uptake is more important over the

420 summer period.

421

Ammonium-N spiking:

423 It is clear from Figs. 3 and 4 that in the control soils (T5 & T6), if nitrification is

424 occurring at all, it is happening at a relatively slow rate compared with salt-affected

425 soils, and/or any nitrate being produced is being immobilised by soil microbial

426 biomass or lost by denitrification. The fact that ammonium-N concentration is

427 changing only slightly over time (Fig. 3) suggests that a very low nitrification rate is

428 the most likely cause. It is interesting however that when the soils were spiked only

429 with deionised water (Fig. 6), some nitrification of "native" soil ammonium-N is

430 apparent for the T5 and T6 control soils. If nitrification is being inhibited by low soil

13

431 pH in the control soils, then the additional chloride added with the ammonium spike

432 would, as a mobile anion, further lower the soil solution pH, reducing nitrification rate

433 even further upon ammonium-N spike addition. Although this explanation is

434 plausible, further experimentation, for example by NaCl spiking at corresponding

435 chloride concentrations, of the control soils would be needed to confirm a mobile

436 anion effect on pH.

437   The suggestion in the paragraph above that denitrification could be playing a

438 significant role is unlikely to be true. The nitrate concentrations over time changed

439 very little following spiking of the soils with nitrate (Fig. 5), which would not be the

440 case if denitrification rate was substantial. Moreover the soils were not particularly

441 wet even after spiking, and the amount of water added with the control deionised

442 water, ammonium-N and nitrate-N spikings was constant between treatments, so if it

443 occurred the denitrification rates would be similar for all treatments. Thus the

444 attribution of low nitrification rate to low pH is by far the most likely hypothesis.

445

446 **Nitrate-N spiking:**

447 Figure 5 showed no evidence of nitrate immobilisation by soil microbial biomass.

448 However in the road salt-impacted soils (T1 – T4), there was rapid decline in

449 ammonium-N over the first 1 –2 days. This was almost certainly by nitrification,

450 because total mineral N remained virtually constant over the first five days. This

451 suggests that the higher pH in the salt-impacted soils is again favouring nitrification.

452 Over a longer time scale nitrification was readily apparent in all six soils.   The fact

453 that ammonium was starting to accumulate by day 9, especially in the most acidic,

454 control soils (T5 & T6), supports the hypothesis that greater acidity in the control soils

455 inhibits nitrification, or rather that the increase in soil pH caused by the salting impact

456 is greatly favouring nitrification.

457

458 **Deionised water blank spiking:**

459 The data in Fig. 6 show that nitrification is particularly dominant in the salt-impacted

460 soils, as nitrate dominated the mineral N fraction for the most heavily impacted soils

461 (T1 & T2) and for the soils experiencing intermediate salt impacts (T3 & T4). As

462 mentioned in the results section, the contribution of ammonium-N was much greater

463 in the unpolluted, control soils (T5 & T6) throughout the experiment. However, as

464 the nitrate-N to ammonium-N ratio increased significantly over time in all soils,

14

465 clearly nitrification is occurring in all of the soils. In all soils mineralisation proceeds

466 at a significant rate between days 2 and 9, but the mineral N pool consistently was

467 lower when the salt impact was higher. This probably reflects the lower organic

468 matter content that has evolved in the salt impacted soils, probably from reduced plant

469 growth leading to a reduced pool of mineralisable N. However we can only speculate

470 about the extent to which this reflects enhanced leaching losses of organic C and N

471 over many years, enhanced decomposition of organic matter at the higher soil pH that

472 is a consequence of the salting impact over several decades, or reduced input of plant

473 litter as a consequence of salt impacts upon vegetation growth.

474

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

476 Although nitrification still appeared to be significant even at 4 °C and in all soils, the

477 marked long-term salt application impacts were much less pronounced at the lower

478 temperature, and indeed it appeared that nitrification was more important in the most

479 acidic, control soils (T5 & T6). Thus it could be concluded that the influence of soil

480 pH upon nitrification rate is highly temperature dependent.

481

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

483 It cannot be stated categorically that some residual salinity effect and other possible

484 effects outlined in the introduction are not occurring, but if they have adverse effects

485 upon relevant microbial activity they must be small compared to the acidity

486 neutralisation effect. This experiment points to the importance of long-term, soil pH

487 effects being very important over summer months. If over many years potentially

488 toxic heavy metals have been mobilized in the roadside soils, then in all probability

489 after decades they will have leached out of the roadside soil system. Heavy metals in

490 soil solution in these roadside soils were determined in another phase of the present

491 study, but no toxic metals were found at potentially toxic concentrations.

492 The loss-on-ignition data in Table 2 indicate much lower soil organic matter

493 content in the salt-impacted soils compared with the control soils, again suggesting

494 the importance of long-term effects. It is notable from Fig. 6 that the total mineral N

495 pools were lowest in the most salt effected soils (T1 & T2), and greatest in the control

496 soils (T5 & T6). This suggests that loss of organic matter over several decades is

497 limiting the amount of mineralisable organic N in the most polluted roadside soils.

498 This could act as a constraint to the enhanced nitrate leaching to adjacent freshwaters

499 to some extent.

500

501 **7. Conclusions:**

502 It is highly probable that that the degree of salt exposure of the soil, in the longer term,

503 controls the rates of key microbial N driven processes primarily by increasing soil pH.

504 With the increasing amounts of nitrate-N from nitrification of incoming ammonium

505 there is potential for enhanced nitrate loading of waterways in UK uplands due to

506 leaching, which has particular relevance to the Water Framework Directive.   Figure 2

507 clearly illustrates a strong influence on nitrate-N concentrations along the Crookdale

508 Brook.

509 This study differs from those that preceded it in that the soils used have

510 chemical and physical properties that have evolved over decades of varying degrees

511 of salt exposure. Theories based upon salinisation processes in arid climates or upon

512 experiments in which previously uncontaminated soils are suddenly exposed to high

513 doses of road salt are inappropriate when trying to explain current soil behaviour.

514 Some of the effects observed were almost certainly reflect influence of particulates in

515 the road runoff, as well as the effect of sodium chloride in solution.

516 The results reported here are very relevant when assessing the fate of inputs of

517 ammonium to soils from atmospheric pollution. Additional influxes of ammonium-N

518 to salt impacted soils may lead to enhanced nitrification and thereafter, increased

519 leaching of nitrate-N to the local waterways, even at 4 ^{o}C. However at winter

520 temperatures nitrification appeared to be much less sensitive to the pH effect. The use

521 of road salts thus disrupts the proportional contribution of nitrate-N and ammonium-N

522 to the mineral inorganic fraction of roadside soils, as well as being likely to lead to

523 ammonium-N leaching by cation exchange.

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668   **Table 1: Precipitation (mm) at Shap weather station (MET Office) and daily**

669   **mean flows for the River Lune, proxy for the Crookdale Brook (m^3 s^{-1})**

670   **(Environment Agency) for the freshwater sampling dates.**

671

672   **Table 2: Chemical properties of soils for T1-T6 at 3 m from the wall. All results**

673   **are means of duplicate determinations, with standard errors within the**

674   **parentheses. Soils were sampled in July, 2006.**

675

676   **Figure 1: Map showing the location of the field Site. (C) Crown Copyright**

677   **Ordnance Survey. All rights reserved.**

678

679   **Figure 2: The change in nitrate-N and chloride concentration (mg l^{-1} – means of**

680   **two replicates) with time and distance along Crookdale Brook for the period**

681   **12/10/2005 – 08/07/2006. Interval bars show 95 % confidence.**

682

683   **Figure 3: Changes over 9 days (t$_0$ - t$_9$) in the total mineral N (total bars),**

684   **ammonium-N (white bars) and nitrate-N (black bars) for sites T1 – T6 for the**

685   **ammonium-N spiking experiment with incubation at room temperature. Note**

686   **the changes in vertical scales used. All results are means of two replicates.**

687

688   **Figure 5: Changes over 9 days (t$_0$ - t$_9$) in the total mineral N (total bars),**

689   **ammonium-N (white bars) and nitrate-N (black bars) for sites T1 – T6 for the**

690   **nitrate-N spiking experiment with incubation at room temperature. Note**

691   **changes in scale for T5 and T6. All results are means of two replicates.**

692

693   **Figure 4: Change over 9 days in the percentage contributions of ammonium-N**

694   **(white bars) and nitrate-N (black bars) to total mineral-N (complete bars)**

695   **content for the ammonium-N spiking experiment at room temperature. All**

696   **results are the mean of two replicates.**

697

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.

702

Figure 7. Comparison of 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 size. The figure shows how these values changed over 9 days with incubation at 4 °C. All results are means of two replicates.

707 **Table 1: Precipitation (mm) at Shap weather station (MET Office) and daily**

708 **mean flows for the River Lune, proxy for the Crookdale Brook (m^3 s^{-1})**

709 **(Environment Agency) for the freshwater sampling dates.**

710

Sampling Date	Precipitation (mm)	Daily Mean Flow (m^3 s^{-1})	Limb Status
12/10/2005	10.2	16.2	Falling
02/11/2005	22.6	16.6	Rising
22/11/2005	0.2	1.71	Falling
09/12/2005	0.4	1.99	Falling
03/01/2006	0.6	3.95	Falling
27/01/2006	0.6	2.18	Falling
20/04/2006	0.6	2.11	Falling
08/07/2006	10.6	1.43	Peak

711

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

Transect	pH (H_2O)	Water Content (%)[*]	LOI (%)	CEC (MEQ)	NO_3^- (mg kg^{-1})	Na^+ (%)	Ca^{2+} (%)	Mg^{2+} (%)	K^+ (%)	H^+ (%)	NH_4^+ (%)
T1	6.66 (0.01)	35.7 (0.33)	16.07 (1.37)	110 (24.36)	1.47 (0.06)	30.7 (6.4)	18.9 (0.51)	1.64 (0.16)	0.44 (0.10)	48.8 (6.05)	0.79 (0.11)
T2	8.11 (0.03)	33.12 (0.05)	14.37 (1.75)	59.7 (27.02)	3.65 (0.11)	84.9 (30.3)	28.3 (8.7)	2.16 (0.18)	0.00 (0.28)	0.00 (21.35)	0.3 (0.16)
T3	4.62 0.04)	33.04 (0.67)	17.26 (0.47)	145 (1.31)	1.37 (0.03)	1.79 (0.12)	2.91 (0.25)	1.33 (0.25)	0.41 (0.20)	94.0 (0.61)	0.39 (0.09)
T4	5.11 (0.05)	40.07 (1.70)	28.97 (1.63)	91.5 (11.46)	1.92 (0.26)	5.26 (0.58)	9.55 (1.57)	1.25 (0.37)	0.53 (0.11)	84.0 (2.52)	0.64 (0.05)
T5	3.79 (0.04)	77.38 (7.39)	72.23 (1.36)	337 (116)	5.99 (0.01)	0.62 (0.26)	0.24 (0.17)	0.81 (0.17)	0.21 (0.71)	98.3 (0.59)	0.79 (0.56)
T6	3.82 (0.01)	77.51 (0.68)	54.43 (2.01)	281 (88)	5.37 (0.24)	0.96 (0.41)	0.00 (0.17)	0.8 (0.20)	0.0015 (0.038)	98.3 (0.44)	0.63 (0.44)

714 [*] **Soil water content wet weight.**

715
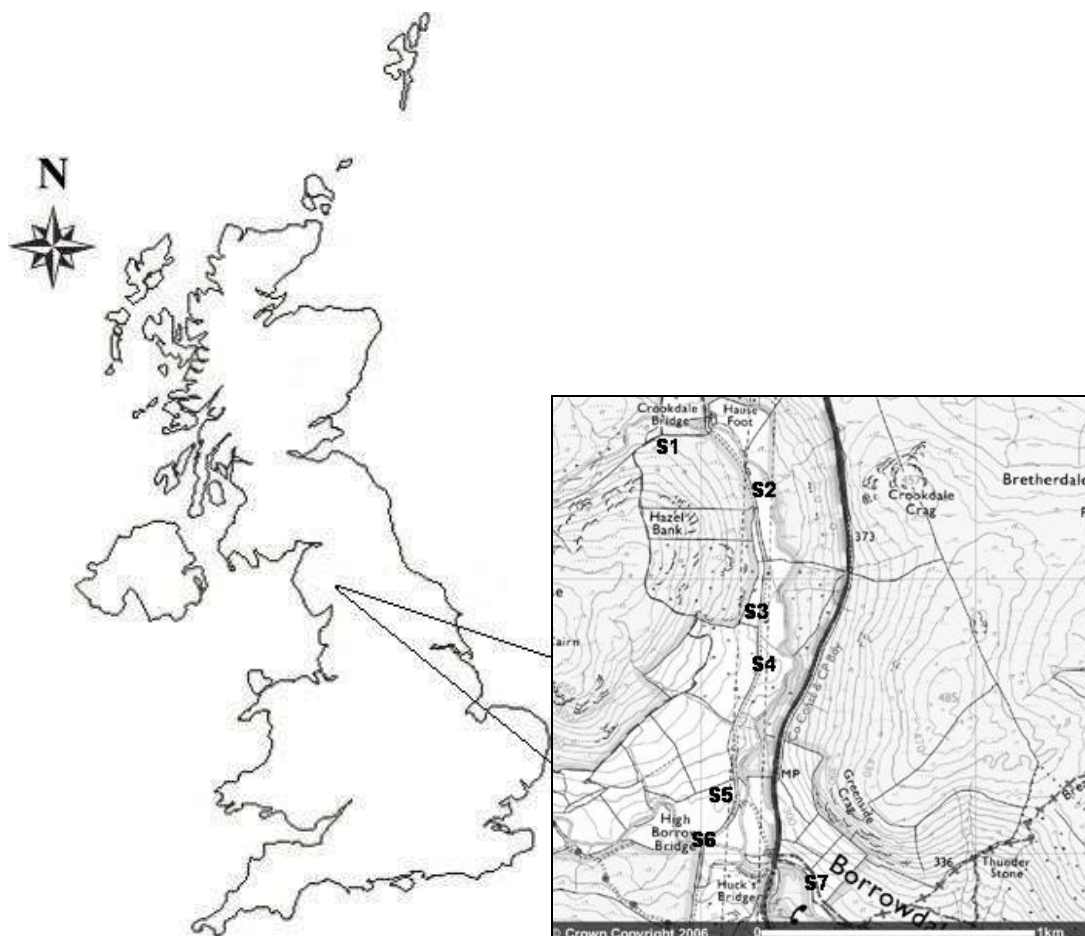
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717   **Figure 1: Map showing the location of the field Site, UK. The A6 road runs due**

718   **north across the centre of the insert map; S1 – S7 indicate the river sampling**

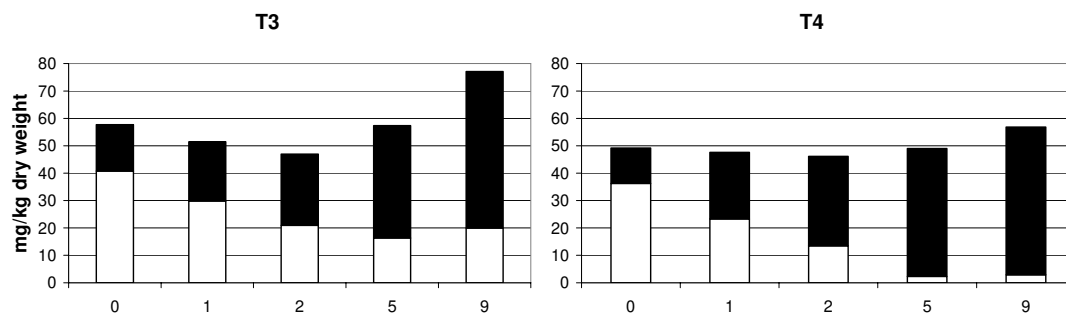719   **points. (C) Crown Copyright Ordnance Survey. All rights reserved.**
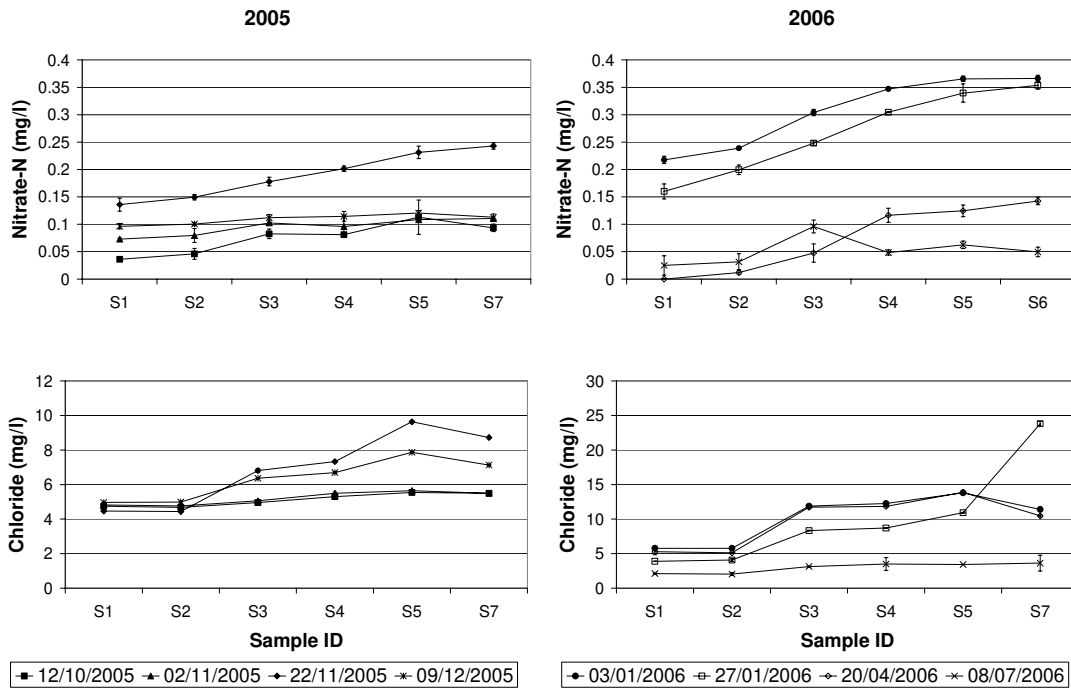
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Figure 2: The change in nitrate-N and chloride concentration (mg l^{-1} – means of two replicates) with time and distance along Crookdale Brook for the period 12/10/2005 – 08/07/2006. Interval bars show 95 % confidence.
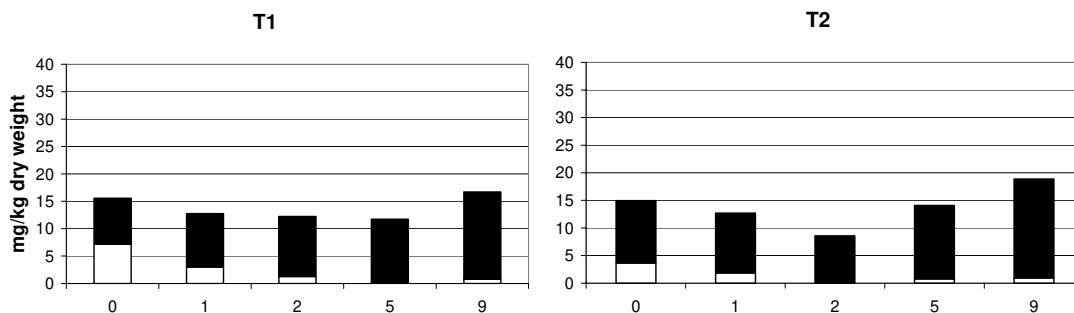
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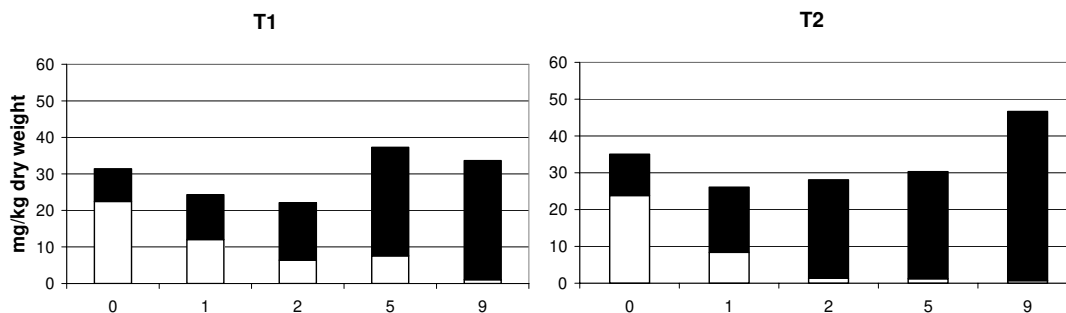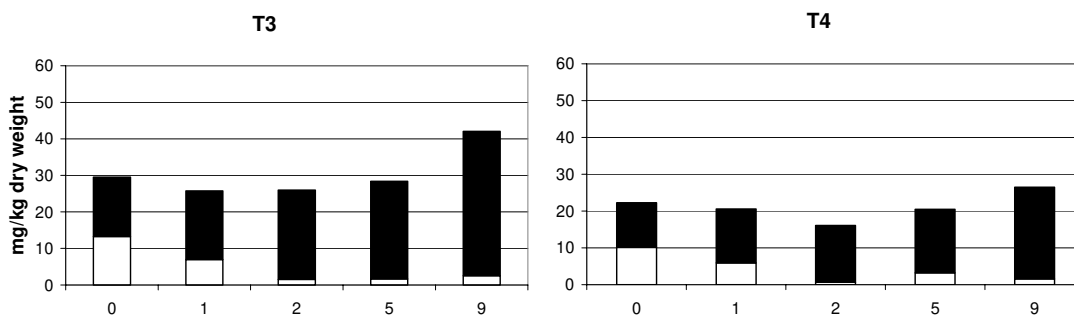
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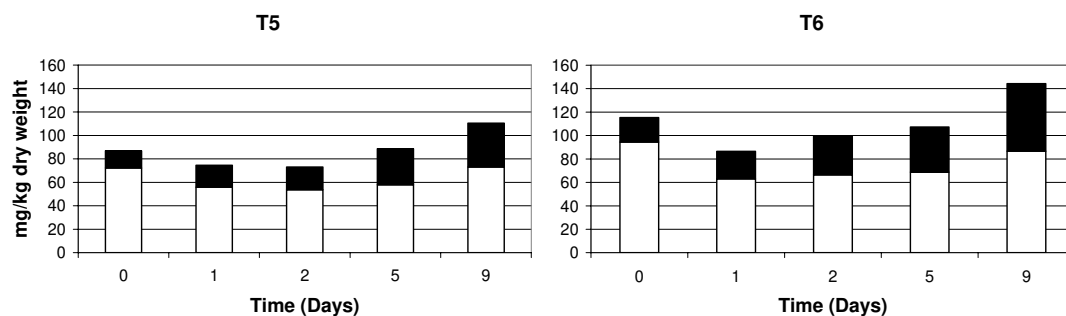
Figure 3: Changes over 9 days (t_0 - t_9) in the total mineral N (total bars), ammonium-N (white bars) and nitrate-N (black bars) for sites T1 – T6 for the ammonium-N spiking experiment with incubation at room temperature. Note the changes in vertical scales used. All results are means of two replicates.

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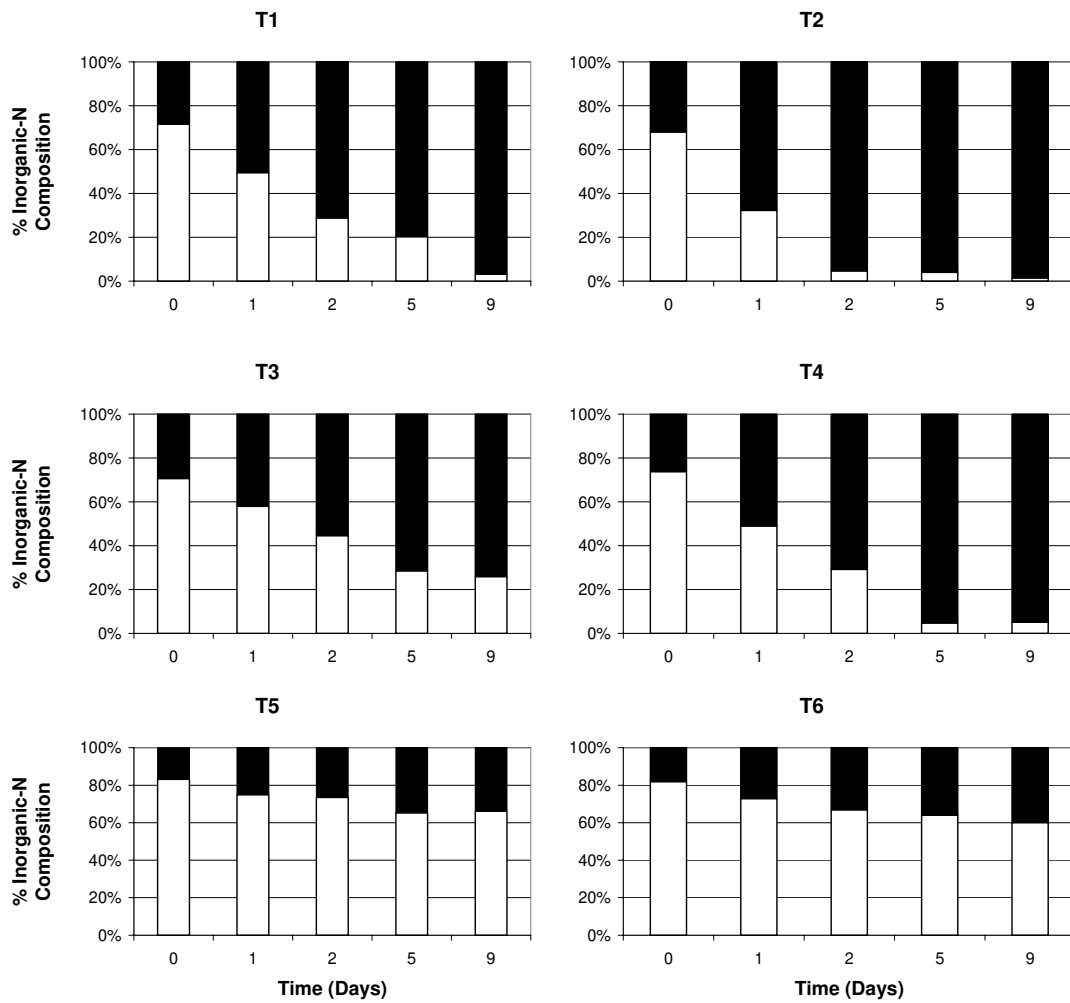
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Figure 4: Change over 9 days in the percentage contributions of ammonium-N (white bars) and nitrate-N (black bars) to total mineral-N (complete bars) content for the ammonium-N spiking experiment at room temperature. All results are the mean of two replicates.
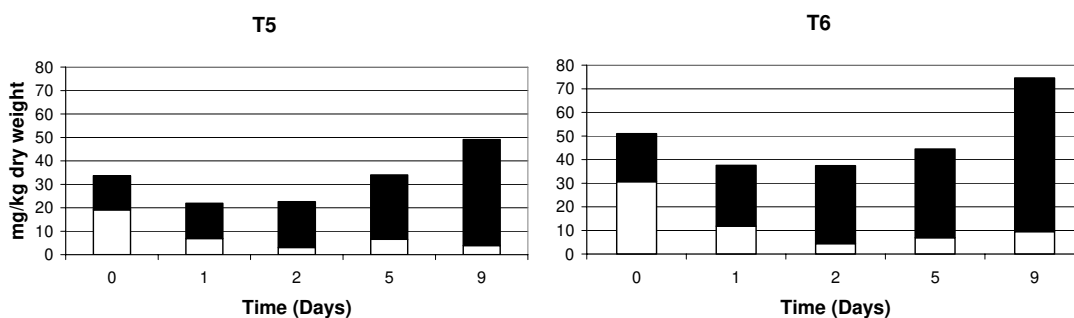
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Figure 5: Changes over 9 days (t₀ - t₉) in the total mineral N (total bars), ammonium-N (white bars) and nitrate-N (black bars) for sites T1 – T6 for the nitrate-N spiking experiment with incubation at room temperature. Note changes in scale for T5 and T6. All results are means of two replicates.
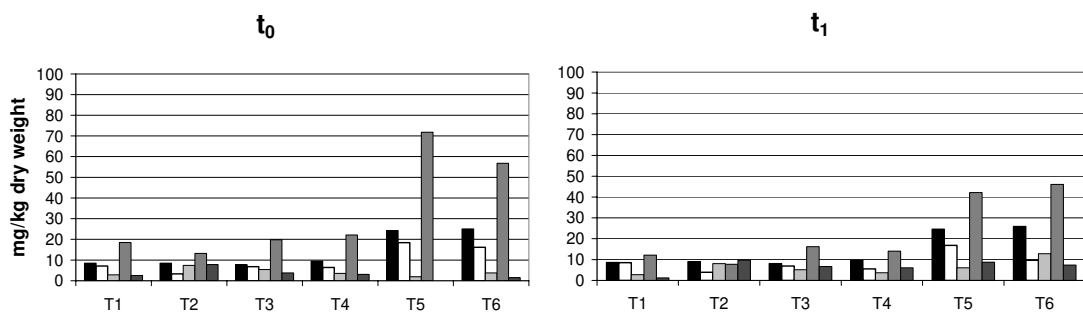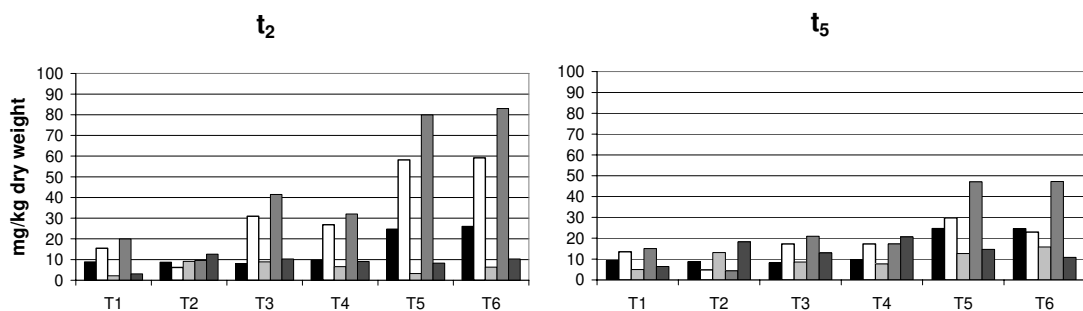
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Figure 6: Changes over 9 days (t_0 - t_9) in the total mineral N (total bars), ammonium-N (white bars) and nitrate-N (black bars) for sites T1 – T6 for the deionised water spiked controls with incubation at room temperature. Note changes in scale. All results are means of two replicates.
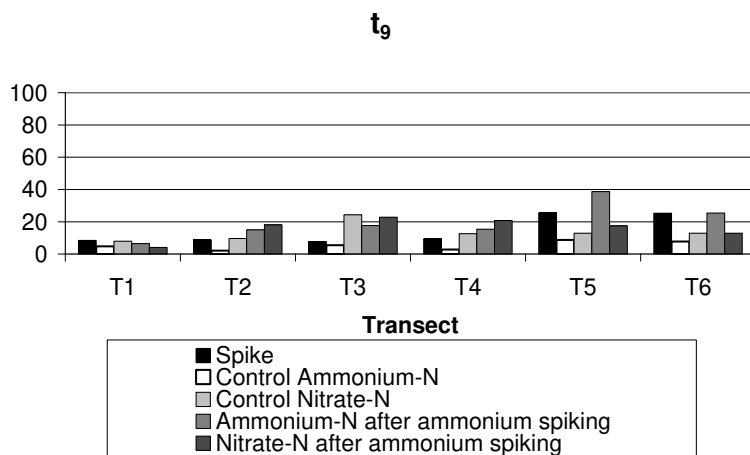
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760 **Figure 7. Comparison of the nitrate-N and ammonium-N after ammonium**

761 **spiking with the nitrate-N and ammonium-N after deionised water blank spiking**

762 **and with the spike size. The figure shows how these values changed over 9 days**

763 **with incubation at 4 °C. All results are means of two replicates.**

764