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Green, S.M., Machin, R. and Cresser, M.S. (2008) Effect of long-term changes in soil chemistry induced by road salt applications on N-transformations in roadside soils. *Environmental Pollution*. pp. 20-31. ISSN 1873-6424

<https://doi.org/10.1016/j.envpol.2007.06.005>

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Published paper

Green, S.M., Machin, R. and Cresser, M.S. (2008) *Effect of long-term changes in soil chemistry induced by road salt applications on N-transformations in roadside soils*. Environmental Pollution, Volume 152, Issue 1, pp.20-31

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

66 **Impacts upon Plants:**

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

72 Plants may be affected via several mechanisms:

- 73 **1.** Ions may accumulate to toxic concentrations within plant tissues
74 (Townsend, 1980). Increasing osmotic pressure differences may cause
75 desiccation (Bryson and Barker, 2002; Larcher, 1995; Townsend,
76 1980). However, damage usually results from a specific ion effect
77 rather than from an increase in osmotic potential (Townsend, 1980).
- 78 **2.** Nutrient element imbalances (reduced levels of available ammonium,
79 Ca^{2+} , and K^{+} within the soil) may occur (Bayuelo-Jiménez et al., 2003;
80 Serrano and Rodriguez-Navarro, 2001).
- 81 **3.** Plant growth may be adversely effected by alterations to soil structure.
- 82 **4.** Plants that are subjected to salt stress also tend to become susceptible
83 to diseases (Bryson and Barker, 2002; Viskari and Kärenlampi, 2000).

85 **Impacts upon Fresh Waters:**

86 Several investigations have revealed increased sodium and chloride ion concentrations
87 in both groundwater and surface waters in the vicinity of roads (Demers and Sage,
88 1990; DOE & DOH, 2001; Löfgren, 2001; Ruth, 2003; Scott, 1976 Shanley, 1994).
89 Scott (1976) reported an increase in Na^{+} concentration by a factor of 50 over baseline
90 levels in urban streams after road salt application, whilst Ruth (2003) reported a
91 maximum 30-fold increase in urban streams in Helsinki, Southern Finland, during
92 spring floods, and Demers and Sage (1990) reported chloride ion concentrations 31
93 times higher downstream from a major road as compared to upstream concentrations
94 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 of 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 $100 \text{ mg NaCl g}^{-1}$. 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 $\geq 0.25 \text{ mg NaCl g}^{-1}$ ammonification was reduced and
146 at $0.25 \text{ mg NaCl g}^{-1}$, 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

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 N₂. 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 2-4°C) 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

232 **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

244 **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

250 **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.

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 t₅ 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

402 **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 km²; 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

422 **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

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,

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 °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.

524

525 **Acknowledgements:**

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

529

530

531

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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 ($\text{m}^3 \text{s}^{-1}$)**
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

698 **Figure 6: Changes over 9 days (t_0 - t_9) in the total mineral N (total bars),**
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700 **deionised water spiked controls with incubation at room temperature. Note**
701 **changes in scale. All results are means of two replicates.**

702

703 **Figure 7. Comparison of the nitrate-N and ammonium-N after ammonium**
704 **spiking with the nitrate-N and ammonium-N after deionised water blank spiking**
705 **and with the spike size. The figure shows how these values changed over 9 days**
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710

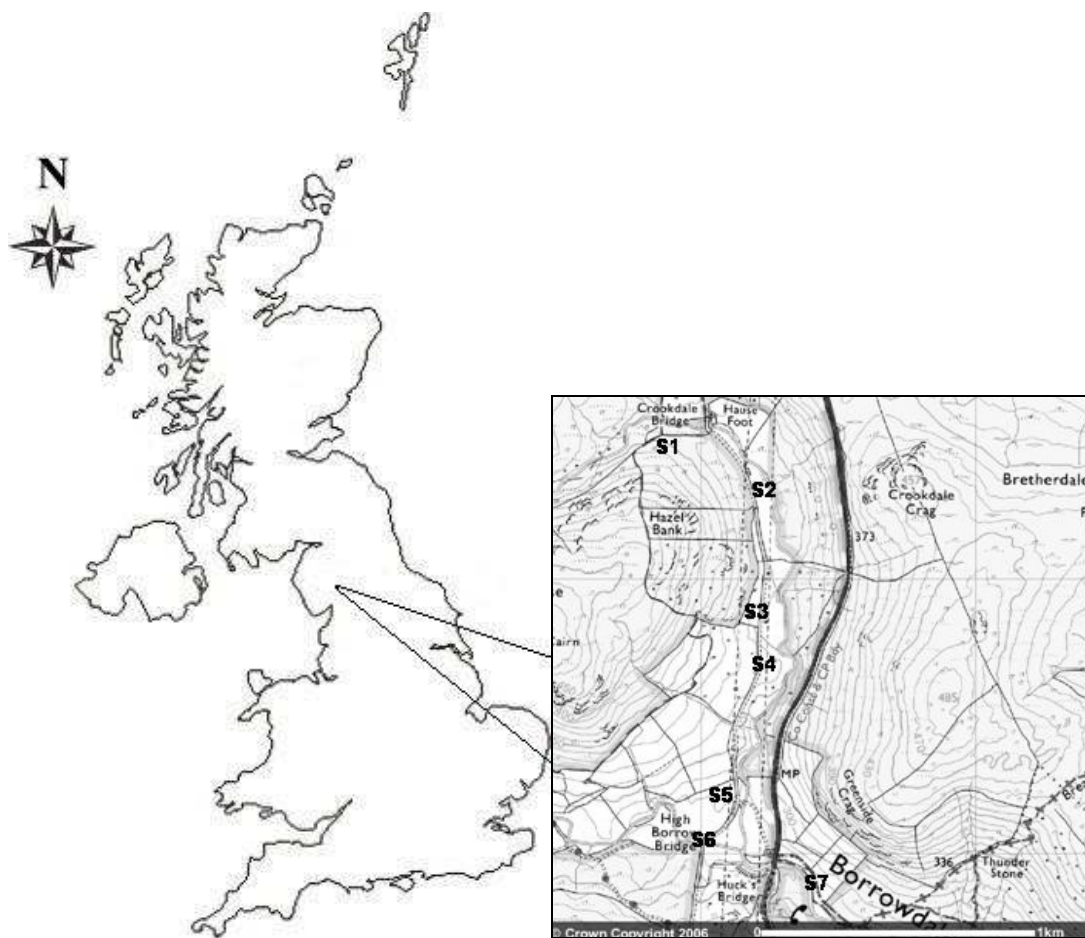
Sampling Date	Precipitation (mm)	Daily Mean Flow ($\text{m}^3 \text{s}^{-1}$)	Limb Status
12/10/2005	10.2	16.2	Falling
02/11/2005	22.6	16.6	Rising
22/11/2005	0.2	1.71	Falling
09/12/2005	0.4	1.99	Falling
03/01/2006	0.6	3.95	Falling
27/01/2006	0.6	2.18	Falling
20/04/2006	0.6	2.11	Falling
08/07/2006	10.6	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 ₂ O)	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)

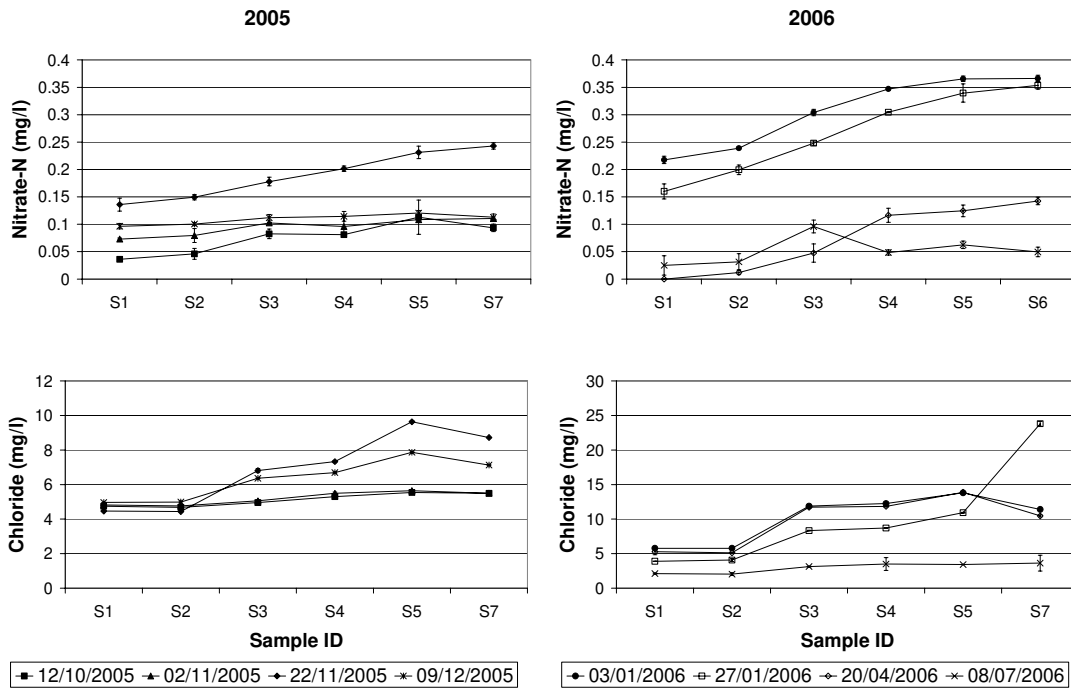
714 * Soil water content wet weight.



716

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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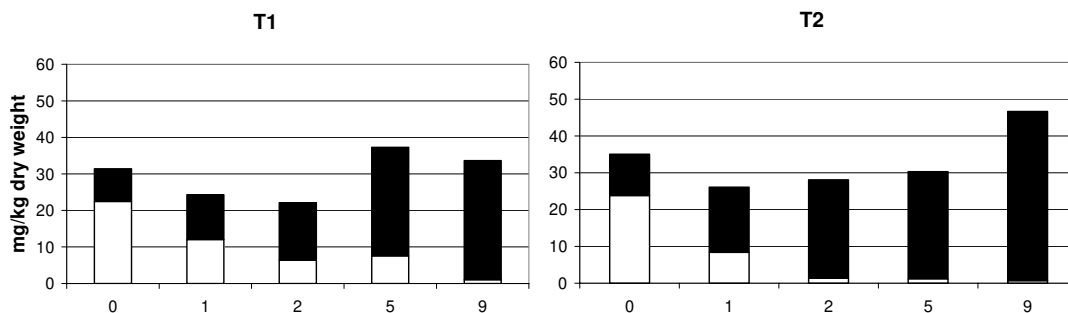


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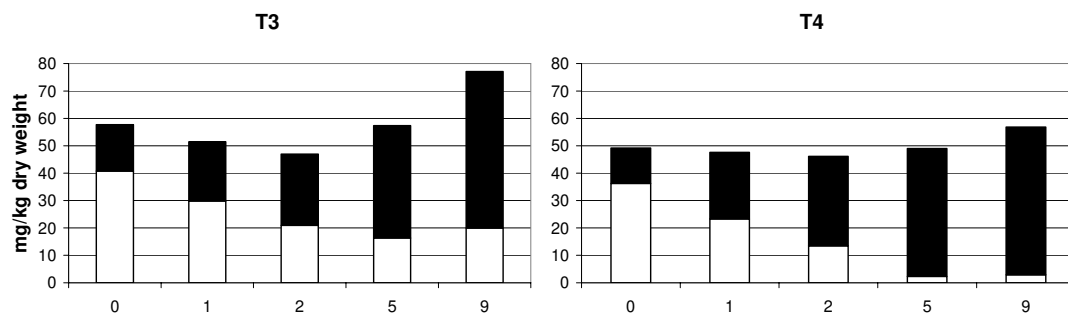
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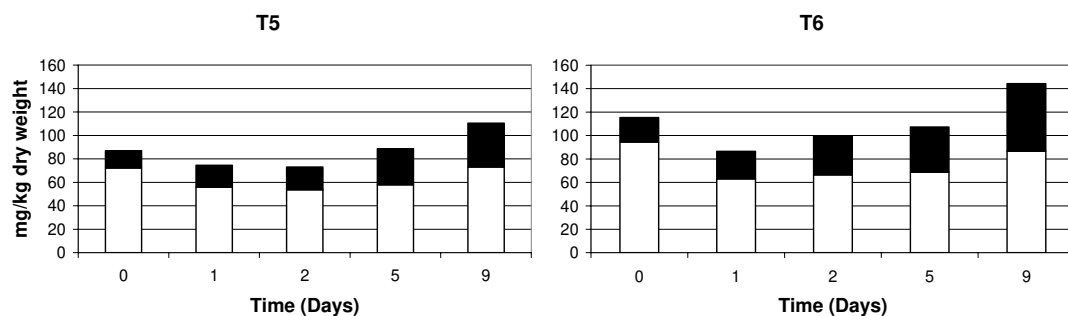
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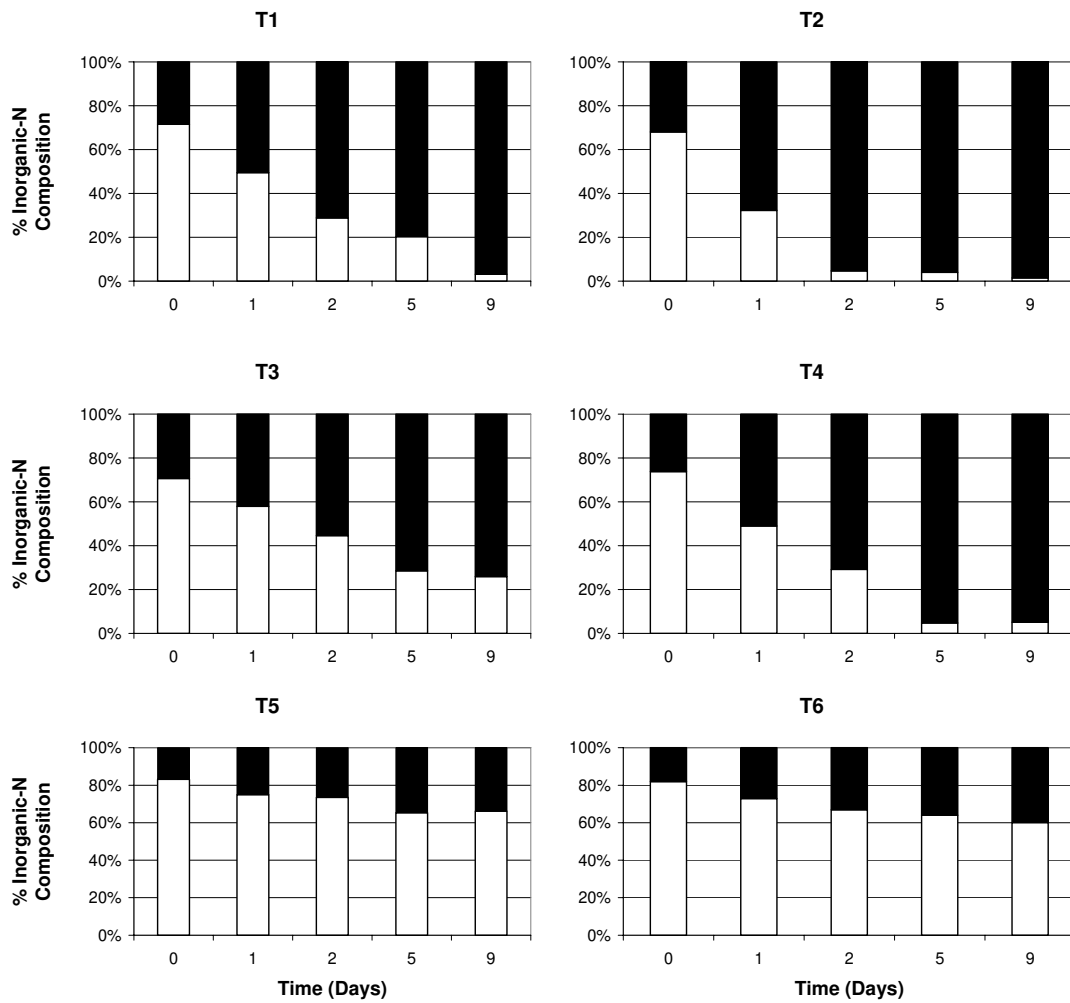


728



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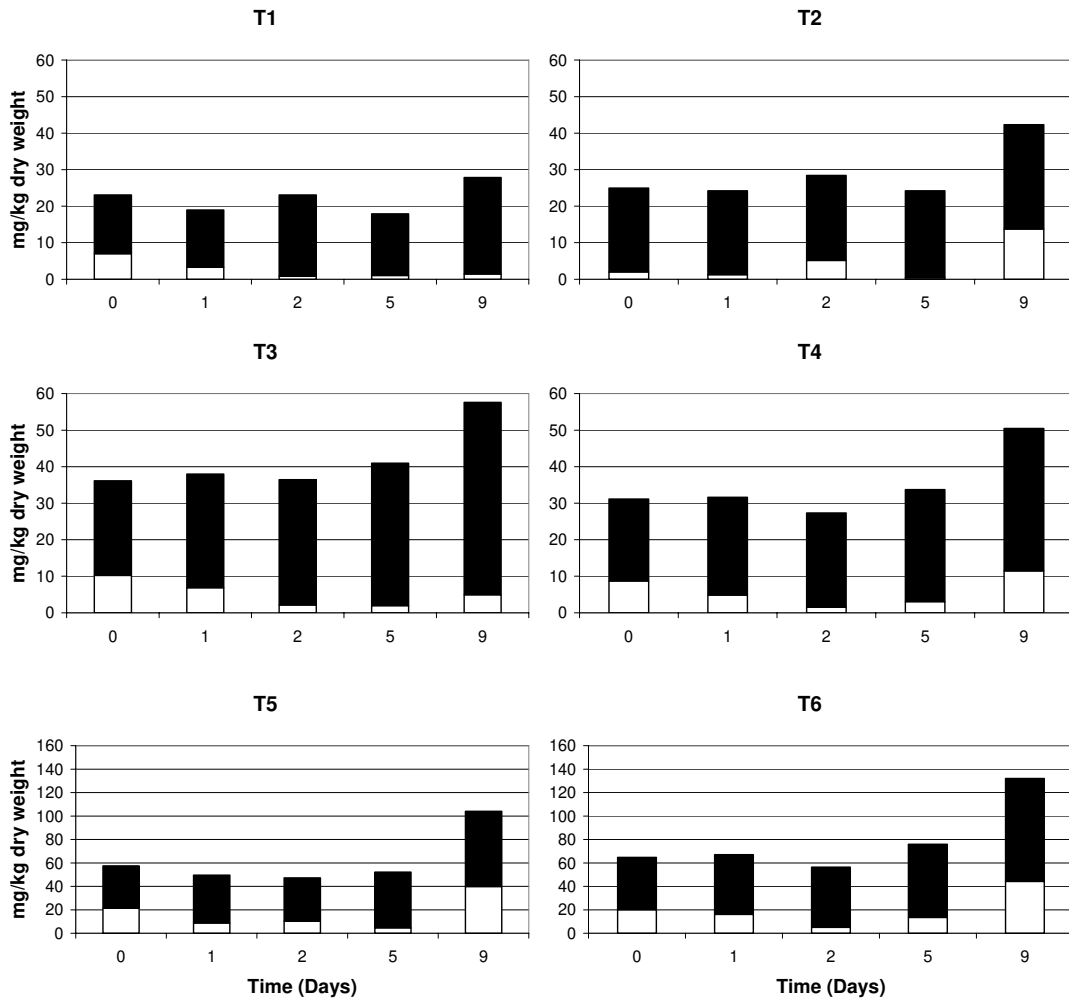


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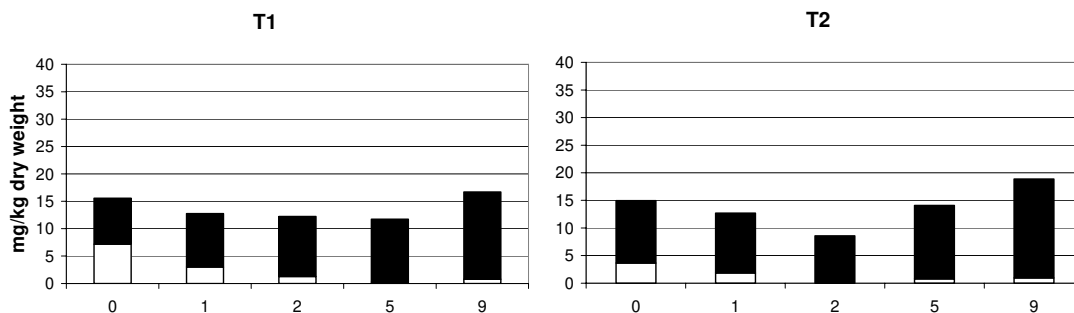


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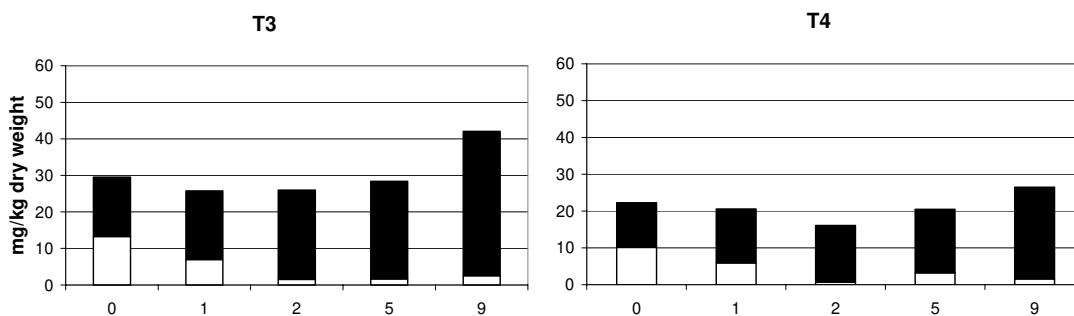
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743 **Figure 5: Changes over 9 days ($t_0 - t_9$) in the total mineral N (total bars),**
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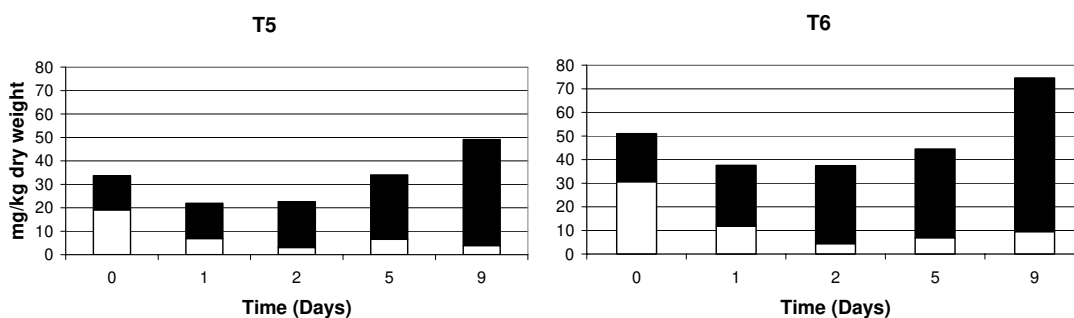
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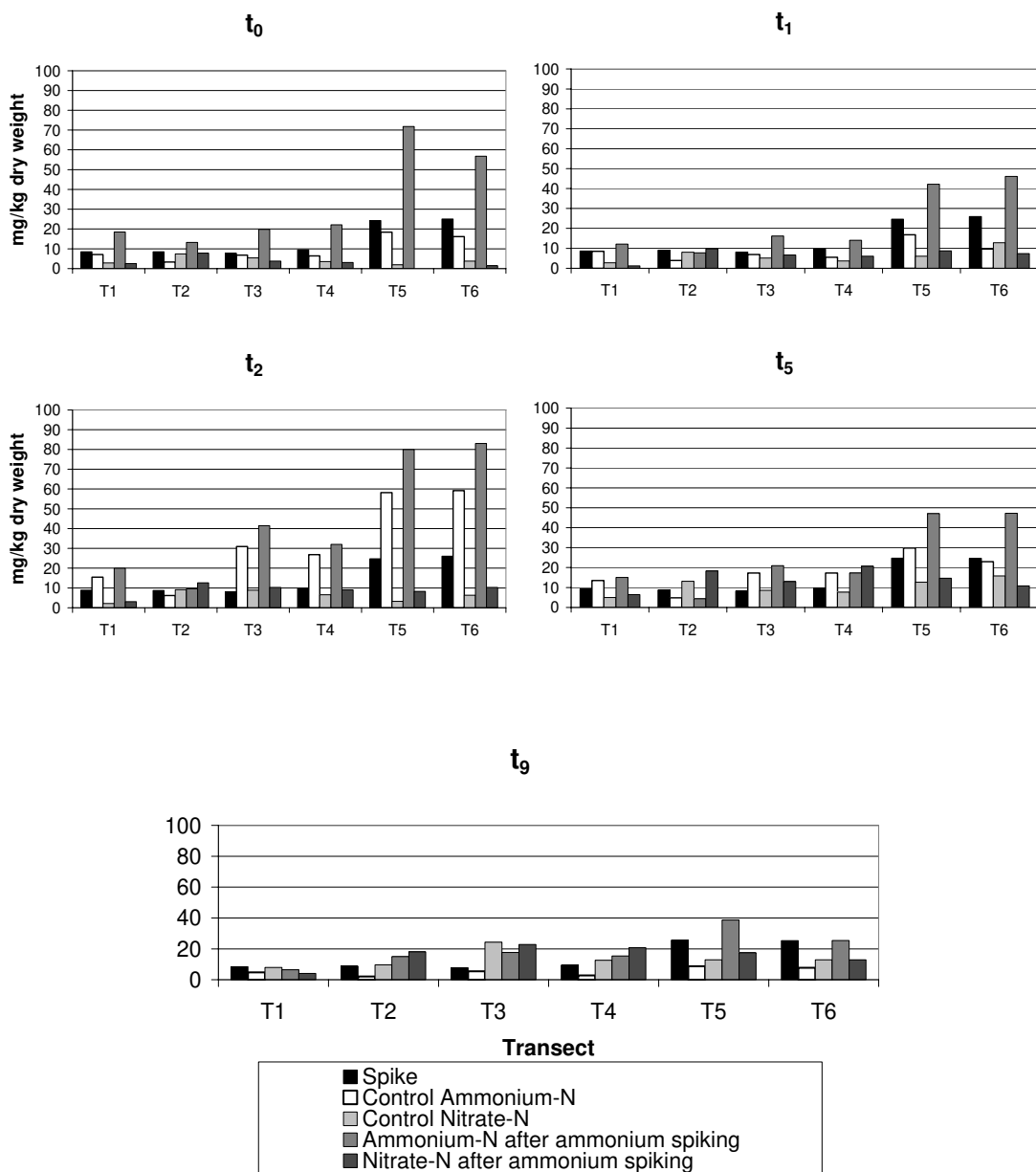


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