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1 Running head: Road salting disrupts N cycle.

2 Article type: Full Research Paper

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

5

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8

9 **Abstract**

10 It is hypothesized that episodic introductions of road salt severely disrupt the soil
11 nitrogen cycle at a range of spatial and temporal scales. A field-scale study has
12 confirmed impacts on the nitrogen cycle in soil, soil solution and river samples.
13 There is evidence that ammonium-N retention on cation exchange sites has been
14 reduced by the presence of sodium ions, and that ammonium-N has been flushed from
15 the exchange sites. Increases in soil pH have been caused in naturally acidic uplands.
16 These have enhanced mineralization of organic-N, especially nitrification, leading to a
17 reduction in the mineralizable-N pool of roadside soils. There is evidence to support
18 the hypothesis that organic matter content has been lowered over decades either
19 through desorption or dispersal processes. Multiple drivers are identified that
20 contribute to the disruption of nitrogen cycling processes, but their relative
21 importance is difficult to quantify unequivocally. The influence of road salt on soil
22 and soil solution declines with distance from the highway, but impacts on water
23 chemistry in a local stream are still strongly evident at some distance from the road.

24

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

26

27 **1 Introduction**

28 Episodic introductions of road salt have the potential to severely disrupt the soil
29 nitrogen cycle. Road salting is utilized to minimize the risk of accidents under icy

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30 and snowy conditions. In the UK the preferred de-icing agent is sodium chloride
31 (pure or mixed with grits and sands, often with an anti-caking agent), applied in solid
32 or liquid form at a rate of 10-40 g m⁻², depending on conditions. Although high
33 impacts of Na⁺ and Cl⁻ on N cycling may be envisaged, there have been few studies to
34 date that focus on such impacts (Green *et al.*, 2007).

35 It may be hypothesized that high sodium inputs will flush ammonium ions from
36 exchange sites and also reduce the extent of ammonium retention from atmospheric
37 inputs, as reported for sea-salt deposition (Duckworth & Cresser, 1991), and this
38 could conceivably lead to shortages of available N for some distance down slope of
39 salted roads, and ammonium enhancement further down slope.

40 Road salts also may increase organic colloid mobility (Amrhein *et al.*, 1992;
41 Grolimund *et al.*, 1996; Norrström & Bergstedt, 2001; Shainberg & Letey, 1984) and
42 alter the structure of the soil (Bäckström *et al.*, 2004; Norrström & Bergstedt, 2001).
43 High exchangeable sodium percentage and low salt solution concentration lead to
44 enhanced dispersal of soil colloids (Shainberg & Letey, 1984). Thus it may be further
45 hypothesized that salting will lead to a reduction in the organic matter content of soil
46 adjacent to roads, and thus to a decline in the pool of mineralizable soil N. Such an
47 effect may be modified by salting effects on the mineralization of soil organic matter,
48 however. Soil aggregate stability deteriorates through the accelerated leaching of
49 calcium and magnesium ions from the soil exchange sites as a result of enhanced
50 competition with sodium ions (Bäckström *et al.*, 2004; Norrström & Bergstedt, 2001),
51 reducing the bonding with the organic matter that aids flocculation and soil structural
52 stability.

53 It is plausible that ammonification may increase as a result of the weakened
54 tendency for organic matter and mineral structures to bind, as desorption reduces the
55 physico-chemical protection of the organic matter. Moreover, increases in soil pH
56 induced by cationic exchange with sodium may facilitate mineralization of organic N,
57 and especially nitrification (Green *et al.*, 2007). Green *et al.* (2007) assessed the fates
58 of low-level ammonium-N and nitrate-N inputs to roadside soils impacted by salting
59 over an extended period (decades) in the field using spiking equilibration
60 experiments. They discovered that the use of road salts disrupted the proportional
61 contributions of nitrate-N and ammonium-N to the mineral inorganic fraction of
62 roadside soils; they suggested that it was highly probable that the degree of salt

63 exposure of the soil, in the longer term, controlled the rate of key microbial N
64 transformation processes, primarily by increasing soil pH.

65 In addition, increases in sodium dominance of the CEC potentially increase
66 dispersal of organic colloids when soils are first exposed to high salinity. Such an
67 increase is unlikely to be evident in roadside soils exposed for decades to road salt, as
68 once the organic matter has dispersed and leached from the soil it's gone from the
69 system forever (Green *et al.*, under revision). Green *et al.* (under revision) applied
70 salt at concentrations recorded in soil solution in the field (0, 10, 1000, 10 000 mg l⁻¹),
71 simulating a road salting flush, to quantify the extent that dissolved organic carbon
72 (DOC) and dissolved organic nitrogen (DON) are still being mobilized from soils that
73 have experienced varying degrees of road salt exposure in the field. A balance occurs
74 between the effects on organic matter of long-term soil pH increase (which enhances
75 organic matter solubility and mineralization), short-term pH suppression via a mobile
76 anion effect (which reduces organic matter solubility), and short- and long-term
77 sodium-induced dispersion, which now determines the influence of road salt on
78 organic matter leaching from roadside soils and into associated drainage waters.

79 Spatial and temporal pH shifts will also influence microbial activity and
80 thereafter transformation rates of inorganic N species. Green *et al.* (2007) concluded
81 from their series of laboratory equilibration experiments that road salt-induced pH
82 shifts may lead to enhanced nitrification of influxes of ammonium-N to salt impacted
83 soils, thereby increasing leaching of nitrate-N to the local waterways, even at 4 °C. If
84 nitrification is enhanced, leaching of nitrate-N into soil solution and freshwater bodies
85 is likely (Green *et al.*, 2007). Hence, it is hypothesized that freshwaters below
86 roadside soils should show evidence of disruption of N cycling. In summary we
87 predict:

- 88 • High sodium inputs flushing ammonium from soils and a reduction in the
89 extent of ammonium retention on exchange sites close to a highway;
- 90 • Ammonium retention increasing with down slope distance from a highway;
- 91 • Lowered organic matter content in soils close to roads and possible
92 accumulation in soil down slope, and hence a decline in the pool of
93 mineralizable-N;
- 94 • Increased mineralisation of organic-N;

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

97 Therefore, this paper examines and assesses spatial and temporal variations in soil,
98 soil solution and freshwater down slope of a highway in upland Cumbria, UK, to
99 determine the affects road salt has on N-processes and test the above hypothesis.
100

101 **2 Materials and methods**

102 2.1 Field site

103 The study site was an upland area adjacent to the A6 at Selside, Cumbria, UK (NY
104 554 046 GB Grid), with altitudes up to 458 m above sea level (Fig. 1). Soil types
105 consist of podzols with variable degrees of development and depths of organic-rich
106 surface horizons (organic-rich leached horizon, iron-rich mottled gley B horizon (in
107 places with signs of gley development), gravel layer C horizon with shale/slate),
108 derived from Upper Ludlow, Ludlow series, Upper Silurian bedrock. The vegetation
109 consists mainly of grasses, *Juncus* and bryophytes and the land is used for grazing
110 cattle and sheep. This site presents an unusual opportunity as the road drainage is
111 piped directly onto the soil surface at regular intervals. Hence the site presents three
112 possible transect scenarios (a) impacted by direct (channelled from a pipe) drainage
113 and by spray, (b) impacted by indirect drainage and spray and (c) an un-impacted
114 control within the catchment on an adjacent hillside with the same altitude, aspect and
115 land use. A dry stone wall ca. 1.5 m high down slope separates the road from the salt-
116 affected sampling sites. For further details refer to Green *et al.* (2007).

117

118 2.2 Sample collection

119 2.2.1 Soil sampling

120 Transects for each transect-type scenario were marked out in duplicate, at a spacing of
121 at least 10 m to ensure that pseudoreplication was avoided, perpendicular to the road;
122 direct (drain-affected) transects (T1/T2) were immediately down slope of drainage
123 pipe outlets; indirect transects (T3/ T4) were to the north of T1 and T2, respectively.
124 The un-impacted control transects are referred to as T5 and T6. Soil samples from 0-
125 10 cm were collected with a stainless steel trowel at 2, 4, 8, 16, 32 and 64 m from the

126 wall, and thus 4 to 68 m from the road itself, for transects T1 to T4, and from
127 corresponding distances on control transects T5 and T6, on the 7th April 2005.
128 Further soil sampling was completed at 2, 8 and 32 m from the wall on the 12th
129 October 2005, when residual salting impacts should be minimal, to provide an inter-
130 seasonal comparison.

131 The samples were stored field moist in polyethylene bags at 2-4 °C in
132 preparation for chemical analysis. Stones and residual identifiable vegetation
133 fragments and roots were removed by rapid careful hand sorting immediately prior to
134 use.

135

136 2.2.2 Soil solution sampling

137 Soil solutions at 2, 4, 8, 16, 32 and 64 m from the wall for each transect scenario were
138 sampled using sets of three *in situ* MOM 0.1 µm pore Eijkelkamp MOM rhizon soil
139 solution samplers (Rhizon SSS; Eijkelkamp Agrisearch Equipment, Giesbeek, The
140 Netherlands). MOM rhizon samplers 10 cm long and 2.5 mm in external diameter
141 were inserted at a depth of 5-10 cm, and evacuated with 60 ml syringes. Soil solution
142 sampling was completed on 8 occasions between 12/10/2005 and 08/07/2006 (Table
143 1). Thus sampling was conducted prior to, during and after road salt application
144 (Table 1). Sampling was more frequent over the salt application period. The air was
145 purged from the sample syringes, which were then stored at 2-4 °C prior to chemical
146 analysis. These samples were not filtered, as the rhizon sampler acts as a membrane
147 filter.

148

149 2.2.3 Freshwater sampling

150 Runoff from the investigated 1500-m section of the A6 road drains eventually into
151 Crookdale Brook (Fig. 1). A water sampling survey was completed on the Crookdale
152 Brook during the period from 12/10/2005 to 08/07/2006. Six locations were sampled
153 (S1 – S5 and S7) along the course of the Brook parallel to the A6, at intervals of
154 approximately 200 m (Fig. 1). S6 was a tributary between S5 and S7. The water at
155 each point was sampled in duplicate to confirm reproducibility of analytical
156 procedures; 125-ml polyethylene bottles were rinsed several times with the sample

157 water before a final collection was made. Samples were stored at 2-4 °C prior to
158 chemical analysis.

159 Chemical analyses for soil, soil solution and freshwater samples were conducted
160 as soon as possible after returning to the laboratory, with appropriate prioritization.
161

162 2.2.4 Bulk precipitation and drainage chemistry

163 Bulk precipitation samplers were used to assess spray inputs to the soil. Four
164 samplers were installed at the study site (4, 8, 16 and 32 m from the wall), and one at
165 the control site. Duplicate precipitation samples were collected on the sampling dates
166 outlined in Table 1.

167 Drainage water samples were obtained when flow was occurring from T1 and
168 T2 (12/10//2005 and 08/07/2006). The samples were stored at 2-4 °C, prior to
169 analysis these samples were filtered through Whatman no. 42 filter papers.

170 2.3 Soil analysis

171 Soils were analysed for pH (H₂O), loss-on-ignition (ashing at 800 °C), potassium
172 chloride-extractable ammonium and nitrate, exchangeable base cations (1 M
173 ammonium-acetate) and cation exchange capacity (CEC – 1 M acidified NaCl after
174 ammonium saturation and 80 % ethanol washing) as previously described by Green *et*
175 *al.* (2007). All extractions were completed on field moist, un-sieved semi-structured
176 soil. Performance of all instrumental methods was checked using synthetic reference
177 standard materials.

178

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

180 Water samples were analyzed for base cations, ammonium-N, nitrate-N, chloride, and
181 sulphate using ICP-OES (base cations), ion chromatography (Dionex, anions) and a
182 Bran and Luebbe AutoAnalyser 3 (N-species). Prior to analysis freshwater samples
183 were filtered using Whatman no. 42 filter papers, whilst soil solutions were filtered by
184 the 0.1 µm Rhizon membrane. Performance of all instrumental methods was checked
185 using synthetic standard reference materials. Nitrate concentrations obtained by ion
186 chromatography and automated colorimetry did not differ significantly.

187

188 2.5 Statistical analysis

189 For soil data, an one-way ANOVA non-parametric alternative test was utilised, the
190 Kruskal-Wallis test, as there is debate and scepticism about whether two-way
191 ANOVA extension of the identically named test is valid (Dytham, 2003 p.145). The
192 non-parametric test will not indicate whether there is an interaction between site and
193 distance, as this portion is not computed. For all statistical tests, significance was
194 accepted at $\alpha \leq 0.05$. Statistical analyses were performed using SPSS version 11.0.1
195 (2001).

196

197 **3 Results**

198 3.1 Road drainage and bulk precipitation chemistry

199 Sodium ion concentration in the control site bulk precipitation ranged between 1.21
200 and 4.37 mg l⁻¹, in comparison to bulk precipitation at 4 m from the wall where
201 concentrations ranged from 0.03 and 40.51 mg l⁻¹. The lowest sodium and chloride
202 concentrations being detected before the winter maintenance season had commenced
203 (02/11/2005). Sodium and chloride concentrations were significantly higher (at the
204 1% level) at 4 m than those of the controls after the salting-runs had been initiated.
205 Spray data from the bulk precipitators is incomplete as a proportion of the samples
206 were lost (i.e. bags dislodged, ripped or removed by on-site sheep/cattle), especially
207 for the 27/01/2006. 9/12/2005 and 03/01/2006 are the only dates for which a
208 complete set of data for the five bulk precipitators is available, both indicate a
209 reduction in sodium and chloride concentration as the distance from the road is
210 increased. There was no significant difference between water from the control and
211 that from the salt-affected bulk precipitation collections for ammonium-N and nitrate-
212 N, and no apparent distance affect for these N species.

213 All heavy metals (Ba, Cd, Cu, Mn, Pb, Zn) concentrations were below the
214 detection limits of ICP-OES (< 0.02 mg l⁻¹) for both bulk precipitation and drainage
215 water (T1 & T2) samples.

216 Road drain water samples contained higher concentrations of sodium and
217 chloride in July (31.2 and 45.8 mg l⁻¹, respectively) as compared to October (1.5 and
218 0.93 mg l⁻¹, respectively). The ammonium and nitrate concentrations observed in the

219 drainage water were 0.76 and 0.44 mg l⁻¹, respectively. The samples are not from the
220 salt application period.

221

222 3.2 Base cation and hydrogen ion occupation of the CEC

223 Table 2 shows mean values of ammonium acetate-extractable base cations and KCl-
224 extractable ammonium as a percentage occupation of CEC for T1/T2, T3/T4 and
225 T5/T6 transects. These means are across all 6 distances. Table 3 shows the data
226 disaggregated by distance (2, 4, 8, 16, 32 and 64 m) and transect type. The mean Na
227 % occupancy of CEC (across all distances: Table 2) for T1/T2, T3/T4 and T5/T6
228 transects differ significantly at the 1% level (direct > indirect > control). Percentage
229 occupation by sodium on the CEC never exceeds 0.65 % for T5/ T6, compared to
230 maximum values of 3.5 and 34 % for T3/T4 and T1/T2, respectively. The percentage
231 contribution for T1/T2 of sodium to the CEC declines to 16 m, and converges towards
232 the control values thereafter. The spray-affected transects (T3/T4) do not follow a
233 significant spatial pattern (Table 3) but always exceed the control soil values.

234 In October (data not shown) there was a reduction in Na % of CEC close to
235 the road on the salt-affected transects, especially for the T1/T2 (34 to 5% at 2 m).
236 Below 32 m there was no significant difference between the two sampling dates.

237 Ca % occupation of CEC for both sets of salt-affected transects is significantly
238 above that for the control (1% level, Table 2). The Ca % of CEC for all salt-affected
239 transects declines consistently with distance from the highway (Table 3), but results
240 for T3/T4 again show a irregular spatial trend.

241 The Mg % of CEC at 2 m follows the order T3/T4 > T5/T6 > T1/T2 (Table 3).
242 Differences between transect types are much smaller at 4 m, and Mg % of CEC
243 generally increases further down slope for T1/T2 and T3/T4. Spatial variation is
244 much less for T5/T6 than for salt-impacted transects, as would be expected where
245 there is no salt impact.

246 For Ca and Mg % of CEC (data not shown) there was a general decline
247 between April and October for all three transect scenarios at 2 and 8 m. However, Ca
248 % of CEC for T1/T2 increases from less than 5% in April to more than 10% in
249 October.

250 The H⁺ % of CEC values, calculated by subtracting Σ base cations from CEC
251 for the three scenarios show significant differences, with T5/T6 > T3/T4 = T1/T2 (1%

252 level). At 2 m the H⁺ % of CEC for T1/T2 falls to 49%, compared to 72 and 89% for
253 T3/T4 and T5/T6, respectively. Acidity increases down the salt-affected transects
254 from 2 to 16 m, to ~ 88%. T5/T6 maintain a constant acidity at ~ 92% (Table 3).
255 Below 16 m T1/T2 give values approaching control levels (64 m = 91%), while H⁺ %
256 of CEC for T3/T4 declines to 67% at 64 m reflecting the higher Ca % and Mg %
257 values. H⁺ % of CEC generally showed an increase for all transects in October (data
258 not shown), indicating partial reversibility of the neutralizing effect of high sodium
259 inputs over winter.

260 The CEC % occupation by base cations and hydrogen ions are also reflected in
261 the soil pH (H₂O).

262

263 3.3 Soil pH

264 Soil pH (H₂O) at 2-4 m during April 2005 for the T1/T2 transects was higher by more
265 than two units than that for the T3/T4 transects, and two and a half to three units
266 higher than that for the T5/T6 transects (Fig. 2, 1% level). This corresponds to the
267 high sodium dominance and low hydrogen occupancy of the CEC in the soils of the
268 T1/T2 transect (Tables 2 & 3).

269 The T1/T2 soils at 2 m maintain a pH above 7 in October (Fig. 2), whilst for
270 the T3/T4 soils pH has increased by over half a unit compared with the April value,
271 almost certainly due to a lower mobile anion (Cl⁻) effect in October. At 8 m all the
272 soils still have a pH after summer at ~ 4.5 units, but the T5/T6 soils are still most
273 acidic in October. Over time, the T5/T6 soil pH remains constant at ~ 4. All three
274 scenarios are statistically significantly different from each other, in both April and
275 October at the 1% level with T1/T2 > T3/T4 > T5/T6.

276

277 3.4 Soil extractable ammonium-N

278 Figure 3 shows KCl-extractable ammonium in April, at the end of the salting period,
279 as a percentage occupation of CEC at 2, 4, 8, 16, 32 and 64 m for each transect type.
280 It is immediately obvious that the T5/T6 transects contain significantly more
281 extractable ammonium (on average 0.99%, Table 2) than either of the transects for
282 other pollution scenarios (0.25 and 0.36% on average for T1/T2 and T3/T4,
283 respectively) (1% level). In the most salt-impacted soils (T1/T2) the proportion of

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

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

298

299 3.5 Soil extractable nitrate-N

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

314 Seasonally, soil nitrate-N concentration for T5/T6 was overall statistically
315 significantly higher in October (3.35 mg kg⁻¹) than in April (0.01 mg kg⁻¹) (1% level).

316 However, there was no significant difference between October and April for either of
317 the salt-affected transects.

318

319 3.6 Soil loss-on-ignition and C:N

320 Table 4 shows soil loss of ignition for T1/T2, T3/T4, and T5/T6 from 2-16 m from the
321 wall. It clearly shows a significant difference between T1/T2, T3/T4 and T5/T6 at 2,
322 4 and 8 m (5% level). At 2 m, LOI (%) is significantly lower for the T1/T2 and T3/T4
323 than for T5/T6. Further from the road LOI% in T3/T4 soils converges to the T5/T6
324 soil LOI (%) content, with the T3/T4 soils differing significantly from the T1/T2 soils
325 up to 8 m. By 16 m the difference is not significant.

326 Figure 5 shows the C:N disaggregated by pollution exposure scenario and
327 distance from the wall for April 2005. It is immediately obvious that the C:N is
328 consistently and significantly lower across all distances for the control transects (T5/
329 T6) than either salt-impacted scenarios (1% level). Ratios for T1/T2 significantly
330 change with distance (1% level). As the distance from the highway increases the C:N
331 declines from 24.3 at 2 m to 14.4 at 64 m. Neither T3/ T4 nor T5/ T6 show
332 significant changes in soil C:N ratio down slope from the road.

333

334 3.7 Soil solution sodium

335 Soil solutions from impacted soils from 12th October 2005 to the 8th July 2006
336 highlighted high concentrations of sodium ions, declining with distance from the road.
337 Concentrations as high as 5800 mg Na l⁻¹ were observed 2 m from the road for T1/T2.
338 In comparison, soil solutions for T3/T4 contained < 200 mg Na l⁻¹ at 2 m, declining to
339 21-48 mg Na l⁻¹ at 64 m; the controls had background concentrations of 2-2.5 mg Na
340 l⁻¹ across all distances on the 03/01/2006. The trends in sodium ion concentration in
341 the soil solution were reflected in chloride data, although chloride concentrations were
342 higher due to the nature of the two elements, with some sodium tending to be retained
343 within the soil due to its cationic properties. The large episodic increases in both
344 sodium and chloride concentrations were closely associated with road salt application
345 dates throughout the winter period, while data from 12/10/2005 and 03/11/2006
346 provide background soil solution concentrations prior to initiation of salt application
347 for winter maintenance.

348

349 3.8 Soil solution nitrate-N

350 Figure 6 shows the soil solution nitrate-N concentrations for T1-T6 at distances 2, 4,
351 8, 16, 32 and 64 m from the wall on eight sampling occasions. The T5/T6 soil
352 solutions very consistently contain minimal ($< 0.14 \text{ mg l}^{-1}$) amounts of nitrate-N (note
353 change of scale Fig. 6), whilst the salt-affected transects have dramatically increased,
354 but spatially and temporally variable, concentrations. Nitrate-N concentrations for
355 T1/T2 below the drains were consistently relatively low from 2 to 8 m, peaking at 16
356 to 32 m (with a maximum concentration of 25 mg l^{-1} on 09/12/2005), and thereafter
357 declining (but still much higher than control concentrations) by 64 m. In T3/T4,
358 nitrate-N concentration declined from 2 to 4 m, and thereafter peaked at 8-32 m,
359 before declining at 64 m. Nitrate concentrations in salt-impacted soils were greatest
360 generally in December and January.

361

362 3.9 Soil solution ammonium-N

363 If ammonium starts to accumulate slowly in soil during autumn months as a result of
364 reduction in utilization by microbes and vegetation, high ammonium-N concentrations
365 in soil solution would be expected where chloride concentration rises sharply in
366 response to road salting (the mobile anion effect). Such an effect would be
367 particularly great close to the road, and this can be clearly seen for T1, T2 and T4
368 (Fig. 7). It was noted that T4 had higher Cl^- concentrations than T3, so the mobile
369 anion effect would be less for T3. However high ammonium-N occupancy of
370 exchange sites was seen on salt impacted sites at 32 m (Fig. 1) and this is also
371 reflected in soil solution ammonium-N concentration at these distances in Fig. 7. The
372 apparently anomalously high ammonium-N concentration down much of the T6
373 transect in July 2006 could possibly reflect a localized high input from animal
374 defecation during a wet (10.6 mm of rainfall over 24-h) sampling period, as on the
375 other sampling dates T5 and T6 displayed generally similar values (note differences in
376 scales for T5 and T6).

377

378 3.10 Crookdale Brook

379 Water pH and concentrations of the base cations Ca, Mg and Na in the river increased
380 as the road (Fig. 8) and Crookdale Brook converged (Fig. 1). However base cation
381 concentrations varied over time too, and were especially high during periods when
382 winter maintenance was prominent (22/11/2005- 27/01/2006). This suggests
383 relationships between the quantities of base cations observed in Crookdale Brook and
384 road salt application.

385 The sampling sites ranged over 1.5 km of the water course from S1, where
386 there was no road salt effect, to S7, with a progressive increase in the road effect (Fig.
387 1). Site S7 might be expected to have the greatest potential affect as it is closest to the
388 road, with a drainage pipe entering the system up slope, just prior to the river
389 sampling point. However, the concentration of sodium ions at S7 is diluted by the
390 introduction of additional unpolluted water (S6) from the Borrowdale Brook tributary
391 prior to the sampling point. Up stream of S1, the catchment area spans over ca. 7
392 km²; hence, the enhancements in base cation concentrations depicted in Fig. 8 are
393 very significant, bearing in mind the relative area of unaffected catchment upstream of
394 S2. A considerable road impact occurs within a few hundred metres. This trend is
395 also apparent in chloride concentration, and there were positive significant
396 relationships between the concentrations of base cations (Na, Mg and Ca) and
397 chloride (all at the 1% level). S7 data was excluded in drawing up the correlation
398 matrix for reasons discussed earlier.

399 Figure 8 shows that nitrate-N in the river increased as the road and Crookdale
400 Brook converged, especially during periods when winter maintenance was prominent
401 (22/11/2005- 27/01/2006). There is a relationship between the concentrations of
402 nitrate and sodium observed (5% level). There does not appear to be a spatial trend
403 with respect to the river ammonium concentrations (Fig. 8), although the high
404 ammonium concentrations in autumn reflect temporal trends also observed in
405 October/November in upland streams in Scotland (Clark *et al.*, 2004).

406

407 **4 Discussion**

408 Organic matter is mobilized as a result of a high pH desorption process as well as via
409 a loss of soil aggregate stability following displacement of calcium and magnesium
410 ions from soil organic matter cation exchange sites by sodium ions. From Table 4 it is

411 clear that organic matter loss from salt-impacted soils has occurred between 2 and 8
412 m, which correspond to dominance of the base cations by sodium (Tables 2 & 3), but
413 also higher pH (Fig. 2). Organic matter within 2-8 m has probably shifted down slope
414 due to the sodium dispersal effects on organic matter. This mobilization would be
415 facilitated by the higher soil pH in the salt-affected soils (Fig. 2), especially at 2-4 m,
416 which would also favour loss of organic matter by mineralization. There would be
417 less organic matter input near drain-affected areas too which, coupled to past heavy
418 leaching losses, could lead to the apparent accumulation down slope. Lower organic
419 matter input is a likely result of lower root density and/or faunal activity (Peinemann
420 *et al.*, 2005). Visual examination of the soil profiles clearly showed reduced organic
421 horizon depths at salt-affected sites at 2-8 m, which is indicative of a degenerative
422 long-term process. This would make less organic N available for mineralization. The
423 reduced organic matter depth is unlikely to be a result of pedological processes as the
424 trend depicted between the salt-exposure scenarios close to the road has been
425 consistently replicated in several studies completed by the authors at 4 m from the
426 wall (Green *et al.*, 2007, under revision). In addition the C:N ratio for the control
427 transect (2-32 m) is significantly and consistently lower than ratios for either of the
428 salt-impacted transects (Fig. 5). The C:N ratio provides some evidence towards a
429 greater mineralization as a result of a higher pH at salt-impacted transects (Fig. 2),
430 although this is not unequivocally proven here.

431 A high negative charge is essential in the bonding of soil organic matter to the
432 layered clay minerals by cation bridges (calcium and magnesium ions) and to iron and
433 aluminium oxides. Steric changes of the organic matter associated with this bonding
434 and the formation of the cross linkages between polymers by polyvalent cations
435 stabilize the organic molecules against both chemical and biological attack
436 (Peinemann *et al.*, 2005). If the calcium and magnesium ions are displaced from the
437 organic matter cation exchange sites, the organic fraction becomes vulnerable to
438 mobilization. However, it is clear from Tables 3 & 4 that there are elevated calcium
439 contents in salt-affected transects close to the highway over and above the control
440 values. This is a product of the road salt itself containing a portion of calcium ions, as
441 well as sparing soluble residues (i.e. 7.5% by mass, which includes gypsum) (Kay
442 Monaghan, Salt Union, Pers. Comm). Hence, the organic matter loss at this site is
443 more likely to be controlled by pH.

444 It must be noted that most of the organic matter that was potentially mobile
445 has already been dispersed close to the road (Green *et al.*, under revision), so evidence
446 of such facilitated movement of organic matter in soil solution now is unlikely as road
447 salting has been conducted in this region for several decades. The freshwater data
448 (Fig. 8) illustrate a sudden increase in both calcium and magnesium concentrations for
449 the first salting event sampled (22/11/2006). However, this was not reflected in the
450 soil solution data for the soils upslope where no sudden increase in concentration of
451 either cation was detected (results not shown). The effect is due to the higher chloride
452 input acting as a mobile anion on soils further down slope, with calcium and
453 magnesium being displaced from soils in the riparian zone.

454 Ammonium will be competitively displaced through cationic exchange
455 processes. Duckworth & Cresser (1991) noted that environments receiving salt inputs
456 from marine sources (although episodic in nature) may experience greater mobility of
457 NH_4^+ in the soil system, due to competitive ion-exchange effects from the weak
458 neutral soluble salts. The proportion of ammonium on the CEC is also markedly
459 lower than that of the control for both T1/T2 and T3/T4 (Fig. 3); this is as
460 hypothesised. Such displacement may lead to ammonium limitation, which may also
461 generate plant stress and growth suppression. It could be made worse by faster
462 nitrification (Fig. 4) at the higher pH in salt-affected soils, coupled to nitrate leaching.

463 The interpretation of the possible influence of road salting on the nitrogen
464 cycle is complex due to the number of possible drivers involved which may be
465 affected by salting. Soil pH (Fig. 2), salinity and the displacement of organic matter
466 (including organic-N) and cation exchange effects all influence key processes in the
467 nitrogen cycle such as ammonification and nitrification. It is very clear though that
468 ammonium % occupancy of the soil CEC has been reduced over time in the salt-
469 affected transects, by displacement and/or enhanced nitrification at higher soil pH.
470 Therefore no major displacement flush would necessarily be expected in the soil
471 solution data in this study. However, there is an initial increase in ammonium-N in
472 soil solution at 2 m after December; thus some displacement may be occurring at very
473 high mobile anion concentrations or a direct road runoff influence is present (Fig. 7,
474 T1/T2). The ammonium and nitrate concentrations observed in the drainage water
475 (0.76 and 0.44 mg l^{-1} , respectively) and road salt analysis (0.02 and 0.05 mg l^{-1} per
476 200 mg NaCl l^{-1} , respectively) could explain a portion of this observation, but is a

477 small contribution compared to concentrations in soil solution detected at 2 m from
478 the highway for T1/T2.

479 The sodium and chloride concentrations observed at the A6 are likely to be
480 typical of A roads in the UK. The heavier traffic loads tend to be on trunk routes and
481 motorways, which will tend to have a greater number of applications within the winter
482 maintenance period.

483 The reduction in CEC (Table 2) has a knock-on effect on bioavailability of
484 ammonium for further microbial transformation processes or direct plant uptake.
485 What also needs to be considered is the role of salinity and pH shifts on the microbial
486 population as well as effects upon soil structure stability and the enhanced organic
487 matter mobility; these together ultimately affect microbial functioning. Heavy metal
488 contamination from spray or road drainage, and hence interfering with microbial
489 processes in the soil are unlikely due to the concentrations of manganese, copper,
490 lead, cadmium, zinc and barium all being below $< 0.02 \text{ mg l}^{-1}$.

491 There are clear spatial variations between and within transects with respect to
492 pH (Fig. 2) which will enhance or suppress nitrification within the study area.
493 Elevated nitrate-N concentrations above control levels are evident in both drainage-
494 and spray-affected soils, suggesting that nitrification has been enhanced by the
495 elevated pH. The decline in KCl-extractable nitrate-N below 32 m (Fig. 4)
496 corresponds with the start of ammonium-N build up in soil solution (Fig. 7) in salt-
497 affected soils, probably as a result of less nitrification due to more acidic conditions at
498 16-32 m and beyond, and increasingly organic soils as the distance from the highway
499 increases. The elevated nitrate-N concentrations in soil solution along polluted
500 transects also indicate an enhanced potential for leaching to surface waters (Fig. 7).

501 Green *et al.* (2007) showed that the concentration of ammonium-N was much
502 greater in unpolluted control soils. As well as the ammonium leaching from salt-
503 impacted soils, this probably reflects the lower organic matter content, and hence
504 lower CEC (Tables 2 & 3), that has evolved in impacted soils, leading to a reduced
505 pool of mineralizable N and lower content of stored ammonium. However, it can
506 only be speculated about the extent to which this reflects enhanced leaching losses of
507 organic C and N over many years, enhanced decomposition of organic matter at the
508 higher soil pH that is a consequence of the salting impact over several decades, or
509 reduced input of plant litter as a consequence of salt impacts upon vegetation growth.

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

516

517 **5 Conclusion**

518 There is clear evidence that a number of effects on the nitrogen cycle are induced by
519 highway winter maintenance activities. There is evidence indicative of high sodium
520 inputs flushing ammonium from soils and a reduction in the extent of ammonium
521 retention on exchange sites close to the highway (Fig. 3 and Table 2), while with
522 increasing distance from the highway down slope ammonium retention increases (Fig.
523 3). In addition there is evidence to support the hypothesis that organic matter content,
524 and hence the pool of mineralizable-N, of roadside soils is lowered, with a possible
525 increase down slope. Evidence to support the theory that enhanced mineralization of
526 organic-N, especially nitrification, is promoted by the increase in soil pH on soil
527 processes is provided in this paper, along with evidence of increased soil solution
528 nitrate-N in rivers and soil solutions.

529 Multiple drivers are involved in the processes, but their relative importance is
530 difficult to establish unequivocally. The experiments performed by Green *et al.*
531 (2007; under revision) complement the field study discussed above. The influence of
532 road salt declines as the distance from the highway increases; however, the impacts on
533 the Crookdale Brook, many tens of metres from the road, are still prominent.

534

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540

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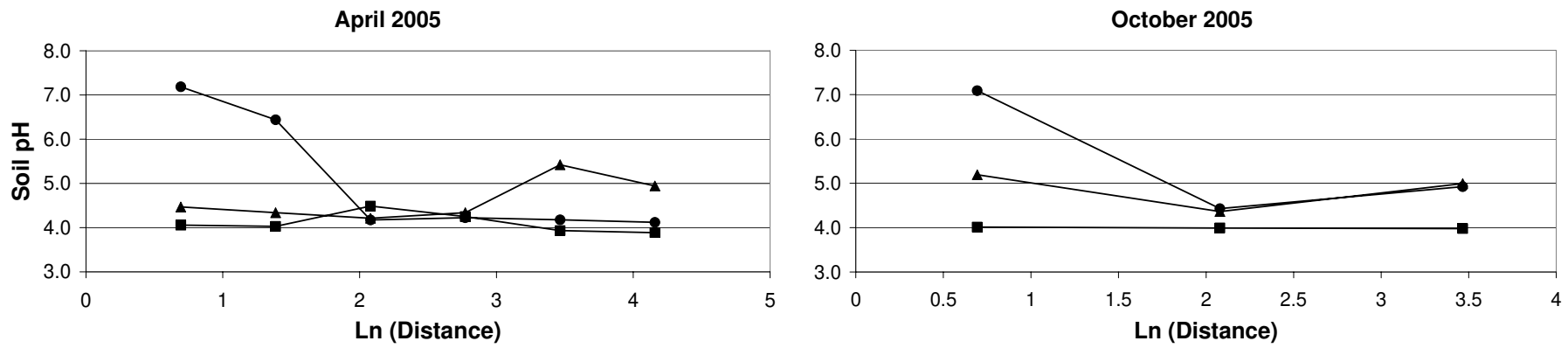
582 Figure 1: Map showing the location of the field Site, UK. The A6 road runs due north

583 across the centre of the insert map; S1 – S7 indicate the river sampling points. (C)

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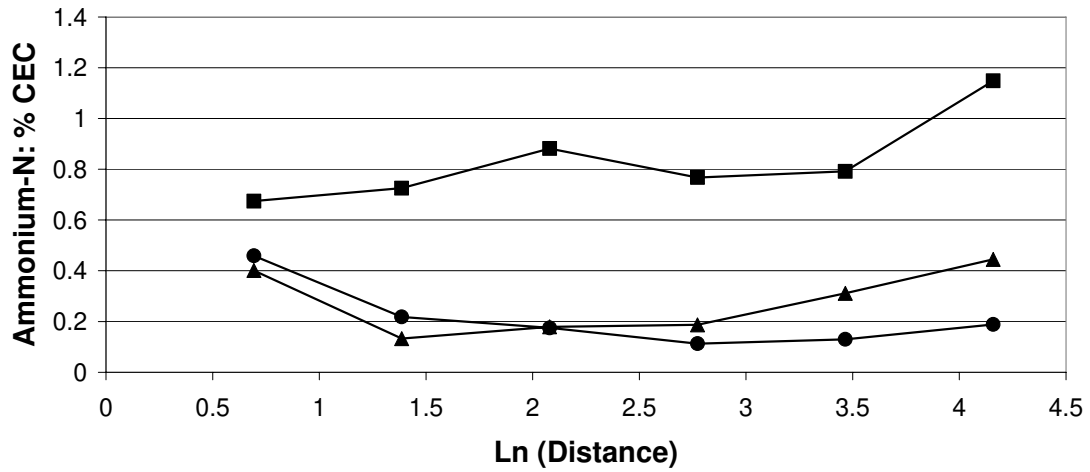


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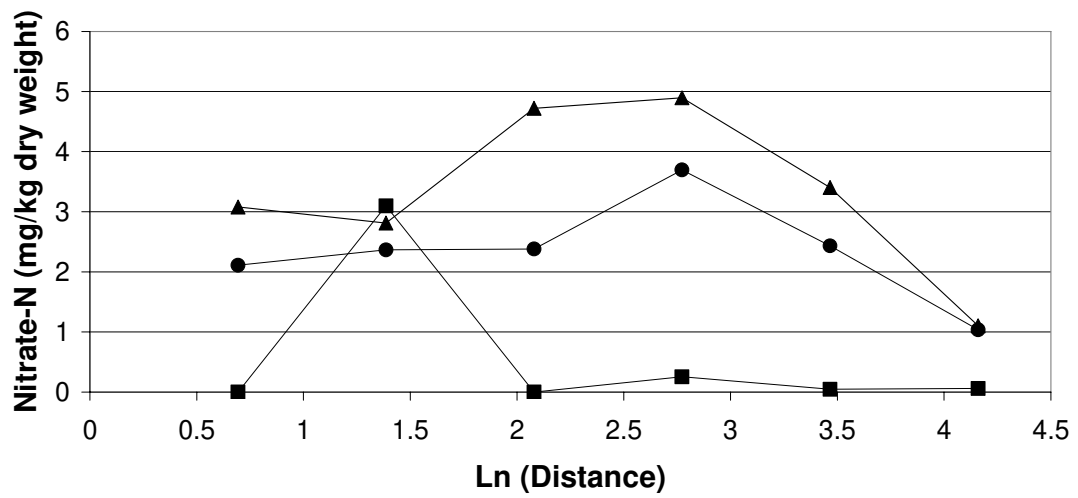
Figure 2: Soil pH (H₂O) for April and October 2005 for soil samples at 2, 4, 8, 16, 32 and 64 m from the wall for the controls (T5 & T6: squares), drain-impacted soils (T1 & T2: circles) and indirectly affected soils (T3 & T4: triangles).



590

591 Figure 3: Mean percentage ammonium-N occupation of the CEC for April 2005 for 2,
 592 4, 8, 16, 32 and 64 m from the wall for the controls (T5 & T6: squares), drain-
 593 impacted soils (T1 & T2: circles) and indirectly affected soils (T3 & T4: triangles).

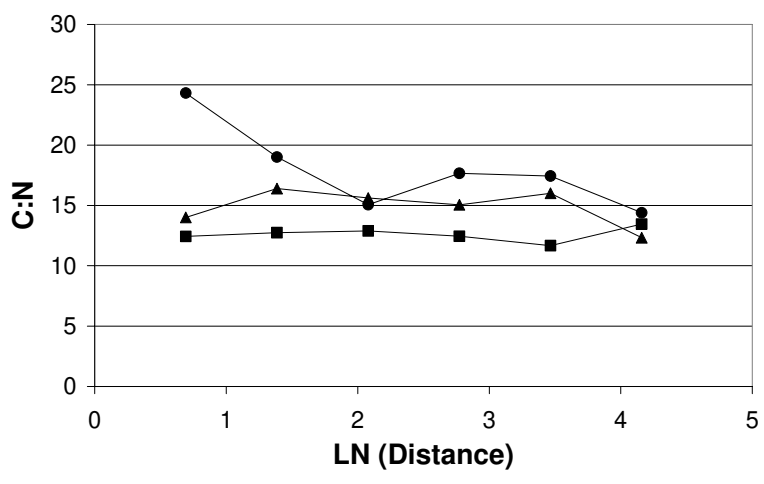
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596 Figure 4: KCl-extractable nitrate-N concentration (mg/kg) for April 2005 for soils
597 sampled at 2, 4, 8, 16, 32 and 64 m from the wall for the controls (T5 & T6: squares),
598 drain-impacted soils (T1 & T2: circles) and indirectly affected soils (T3 & T4:
599 triangles).

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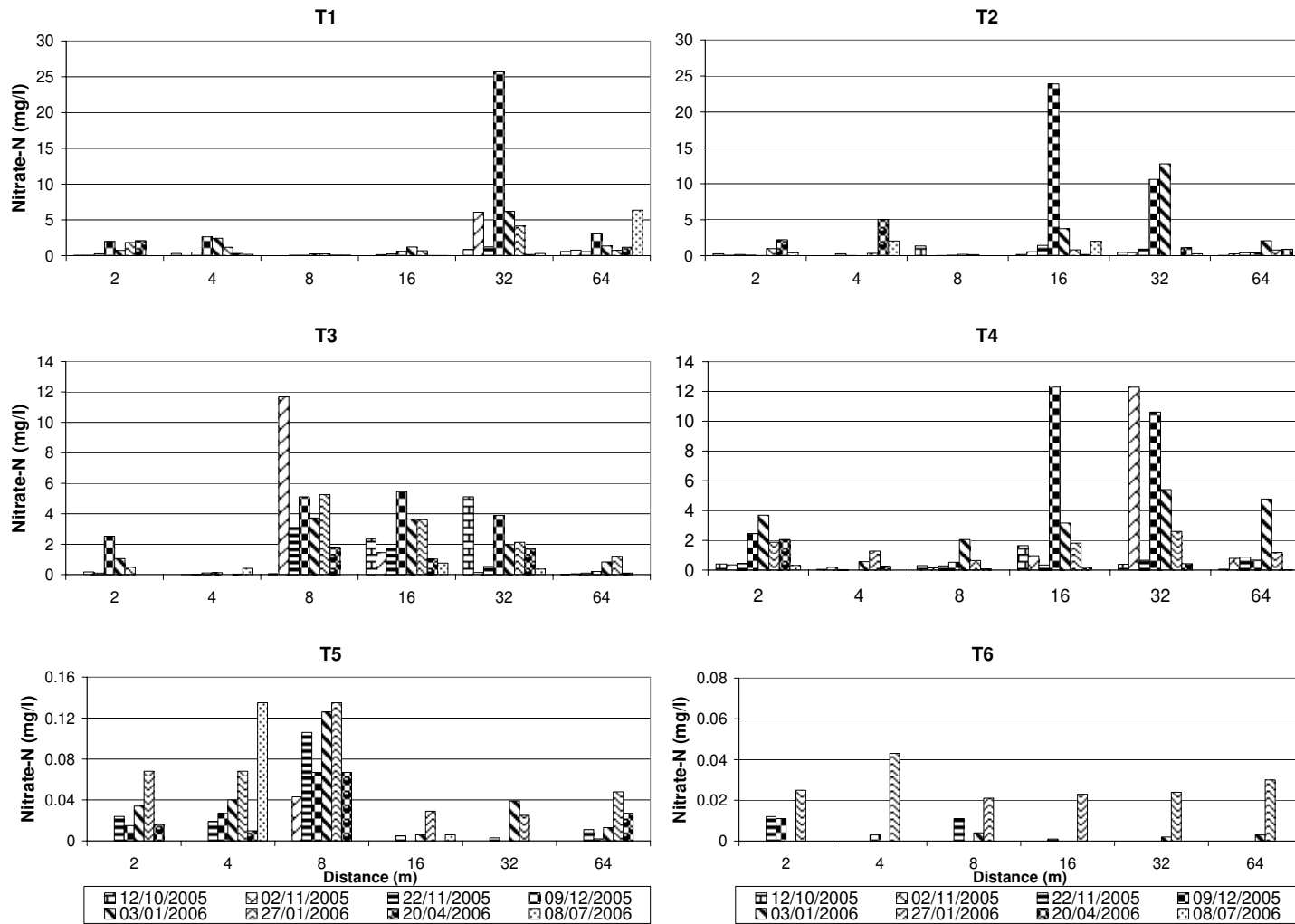
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602 Figure 5: C:N for April 2005 for soil samples at 2, 4, 8, 16, 32 and 64 m from the wall

603 for the controls (T5 & T6: squares), drain-impacted soils (T1 & T2: circles) and

604 indirectly affected soils (T3 & T4: triangles).

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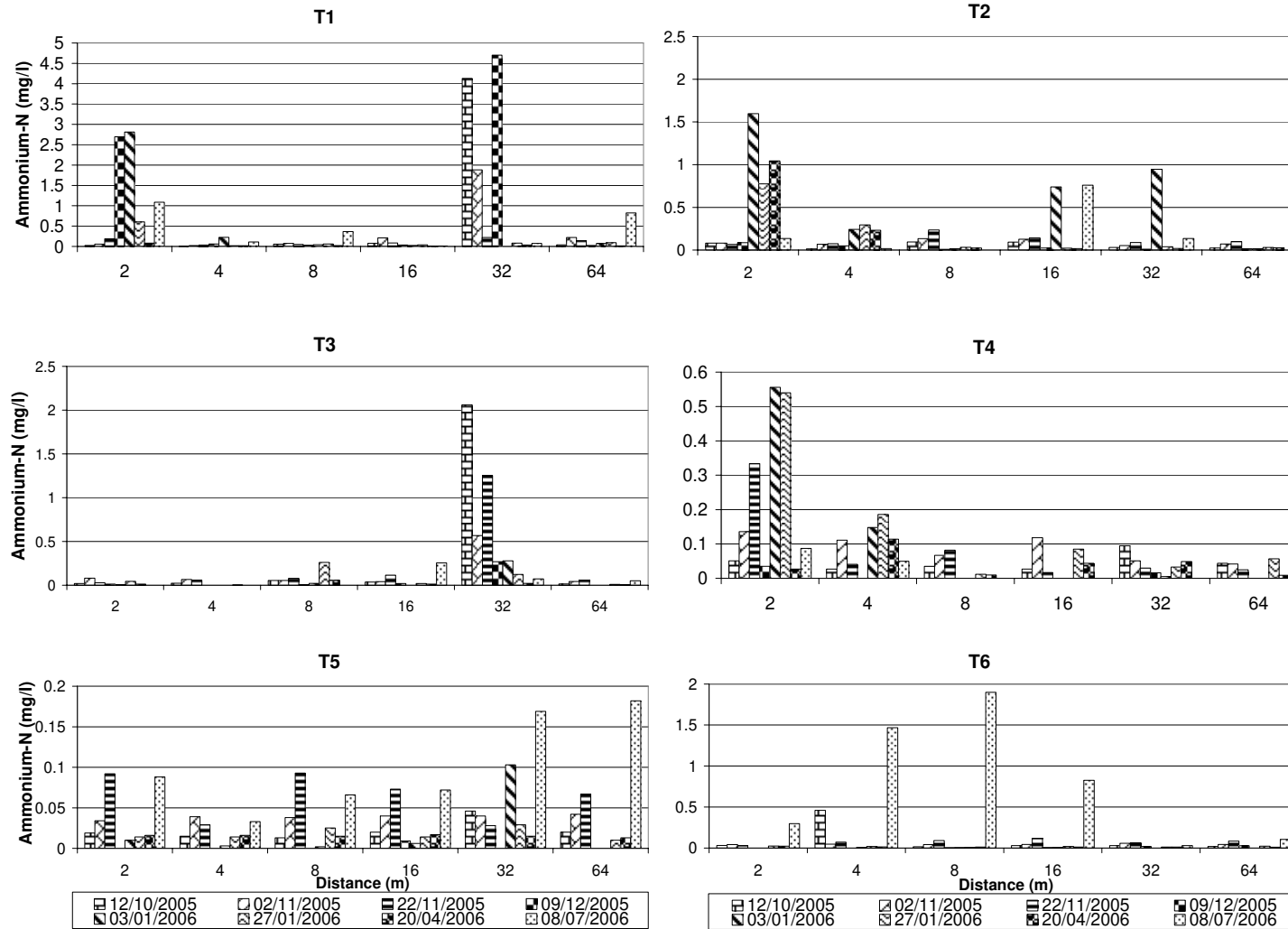
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Figure 6: Nitrate-N concentration for soil solutions at 2, 4, 8, 16, 32 and 64 m for drain-affected soils (T1 & T2), spray-affected soils (T3 & T4) and control soils (T5 & T6).

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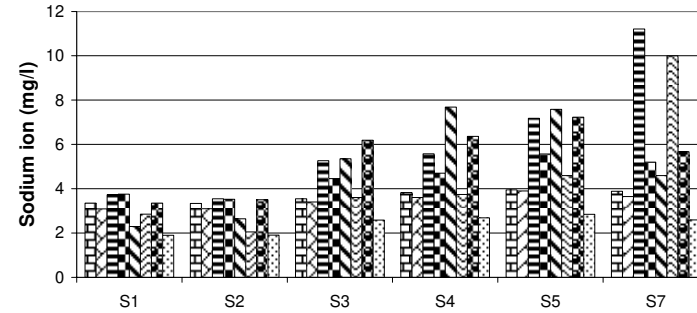
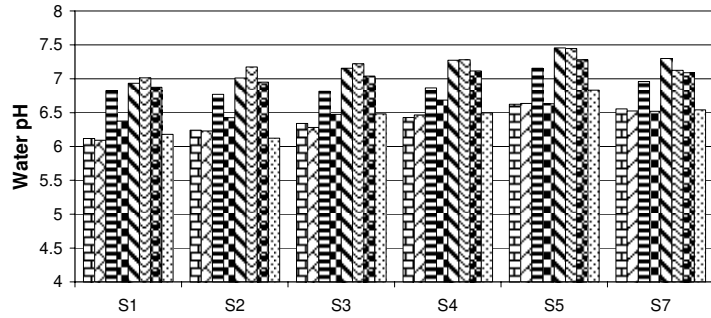
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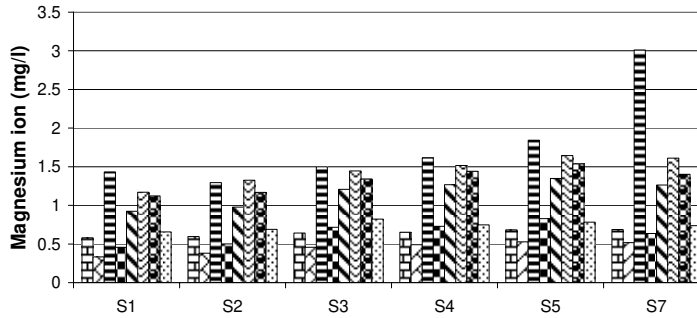
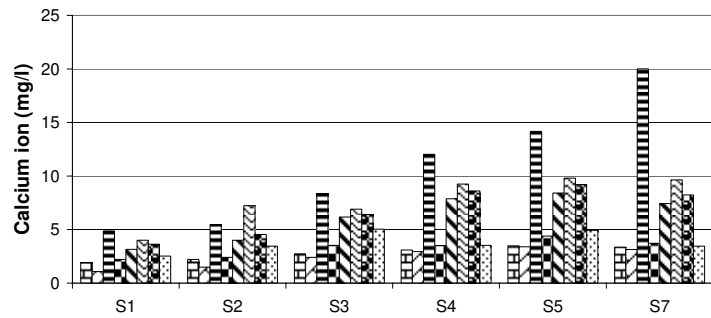
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Figure 7: Ammonium-N concentration for soil solutions at 2, 4, 8, 16, 32 and 64 m for drain-affected soils (T1 & T2), spray-affected soils (T3 & T4) and control soils (T5 & T6).

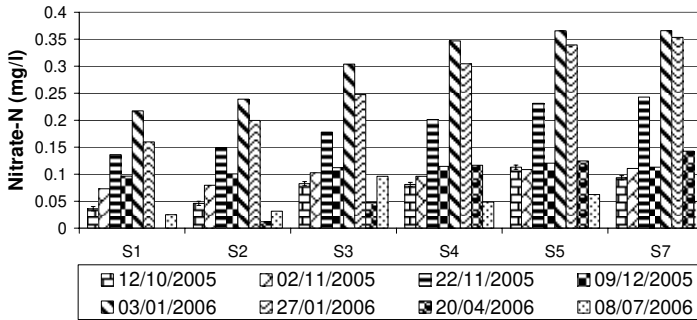
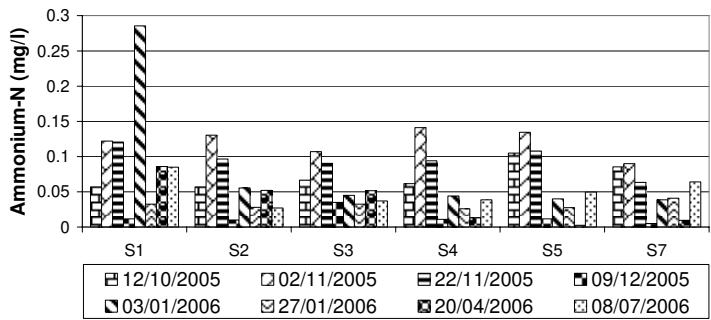
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Figure 8: The change in (a) pH, (b) sodium (c) calcium (d) magnesium (e) ammonium-N and (f) nitrate-N concentration (mg l^{-1}) with time and distance along Crookdale Brook for the period 12/10/2005 – 08/07/2006.

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

OCTOBER		NOVEMBER		DECEMBER		JANUARY		FEBRUARY		MARCH		APRIL	
2005		2005		2005		2006		2006		2006		2006	
01-10-05		01-11-05		01-12-05		01-01-06	Y	01-02-06	Y	01-03-06	Y	01-04-06	
02-10-05		02-11-05		02-12-05		02-01-06	Y	02-02-06		02-03-06	Y	02-04-06	
03-10-05		03-11-05		03-12-05		03-01-06	Y	03-02-06	Y	03-03-06	Y	03-04-06	
04-10-05		04-11-05		04-12-05		04-01-06	Y	04-02-06		04-03-06	Y	04-04-06	
05-10-05		05-11-05		05-12-05	Y	05-01-06	Y	05-02-06		05-03-06	Y	05-04-06	
06-10-05		06-11-05		06-12-05	Y	06-01-06	Y	06-02-06		06-03-06	Y	06-04-06	
07-10-05		07-11-05		07-12-05	Y	07-01-06		07-02-06	Y	07-03-06	Y	07-04-06	
08-10-05		08-11-05		08-12-05	Y	08-01-06	Y	08-02-06	Y	08-03-06		08-04-06	
09-10-05		09-11-05	Y	09-12-05		09-01-06		09-02-06		09-03-06		09-04-06	
10-10-05		10-11-05	Y	10-12-05		10-01-06		10-02-06	Y	10-03-06	Y	10-04-06	
11-10-05		11-11-05		11-12-05	Y	11-01-06	Y	11-02-06	Y	11-03-06	Y	11-04-06	
12-10-05		12-11-05	Y	12-12-05	Y	12-01-06		12-02-06		12-03-06	Y	12-04-06	
13-10-05		13-11-05	Y	13-12-05	Y	13-01-06		13-02-06		13-03-06	Y	13-04-06	
14-10-05		14-11-05		14-12-05	Y	14-01-06	Y	14-02-06		14-03-06	Y	14-04-06	
15-10-05		15-11-05	Y	15-12-05		15-01-06	Y	15-02-06	Y	15-03-06	Y	15-04-06	
16-10-05		16-11-05	Y	16-12-05	Y	16-01-06	Y	16-02-06	Y	16-03-06	Y	16-04-06	
17-10-05		17-11-05	Y	17-12-05	Y	17-01-06	Y	17-02-06	Y	17-03-06	Y	17-04-06	
18-10-05		18-11-05	Y	18-12-05	Y	18-01-06		18-02-06	Y	18-03-06		18-04-06	
19-10-05		19-11-05	Y	19-12-05	Y	19-01-06		19-02-06	Y	19-03-06		19-04-06	
20-10-05		20-11-05	Y	20-12-05		20-01-06	Y	20-02-06	Y	20-03-06		20-04-06	
21-10-05		21-11-05	Y	21-12-05	Y	21-01-06	Y	21-02-06	Y	21-03-06		21-04-06	
22-10-05		22-11-05	Y	22-12-05		22-01-06	Y	22-02-06	Y	22-03-06		22-04-06	
23-10-05		23-11-05	Y	23-12-05	Y	23-01-06	Y	23-02-06	Y	23-03-06		23-04-06	
24-10-05		24-11-05	Y	24-12-05	Y	24-01-06	Y	24-02-06	Y	24-03-06		24-04-06	
25-10-05		25-11-05	Y	25-12-05	Y	25-01-06	Y	25-02-06	Y	25-03-06		25-04-06	
26-10-05		26-11-05	Y	26-12-05	Y	26-01-06	Y	26-02-06	Y	26-03-06		26-04-06	
27-10-05		27-11-05	Y	27-12-05	Y	27-01-06	Y	27-02-06	Y	27-03-06		27-04-06	
28-10-05		28-11-05	Y	28-12-05	Y	28-01-06	Y	28-02-06	Y	28-03-06	Y	28-04-06	
29-10-05		29-11-05	Y	29-12-05	Y	29-01-06	Y			29-03-06		29-04-06	
30-10-05		30-11-05	Y	30-12-05	Y	30-01-06	Y			30-03-06		30-04-05	
31-10-05				31-12-05	Y	31-01-06	Y			31-03-06			

624 Table 2: Mean cation exchange capacity and % Na⁺, Ca²⁺, Mg²⁺, K⁺, NH₄⁺ and H⁺ of
 625 CEC for April 2005, with standard errors in parentheses. ** denotes significant
 626 difference in mean for direct, spray and control transects at the 1%, * at the 5 % level.
 627 Similar superscript letters indicate no significant difference for post-hoc.

Parameter	Mean (SE)		
	Direct (T1 & T2)	Indirect (T3 & T4)	Control (T5 & T6)
CEC (mmol _c kg ⁻¹)	306.67 (36.95)	257.45 (27.94)	396.18 (45.68)
Na ⁺ (%)**	9.97 ^a (3.23)	2.47 ^a (0.38)	0.51 ^b (0.03)
Ca ²⁺ (%)**	9.32 ^a (1.69)	15.16 ^b (2.11)	3.74 ^c (0.62)
Mg ²⁺ (%)*	2.41 ^a (0.30)	4.03 ^{ab} (0.57)	2.84 ^b (0.15)
H ⁺ (%) **	77.78 ^a (4.53)	77.53 ^a (2.91)	92.28 ^b (0.73)
NH ₄ ⁺ (%)**	0.25 ^a (0.05)	0.36 ^a (0.07)	0.99 ^b (0.10)

628 Table 3: Mean cation exchange capacity and % Na⁺, Ca²⁺, Mg²⁺, NH₄⁺ and H⁺ of CEC for April 2005 for soils sampled at 2, 4, 8, 16, 32 ad 64 m from
 629 the wall, with standard errors in parentheses. ** denotes significant difference in mean for direct, spray and control transects at the 1%, * at the 5 %
 630 level. Similar superscript letters indicate no significant difference for post-hoc.

Dist. (m)	CEC (mmol _c kg ⁻¹)			Na ⁺ (% CEC)			Ca ²⁺ (% CEC)			Mg ²⁺ (% CEC)			H (% CEC)		
	Direct (T1 & T2)*	Indirect (T3 & T4)	Control (T5 & T6)	Direct (T1 & T2)**	Indirect (T3 & T4)	Control (T5 & T6)	Direct (T1 & T2)	Indirect (T3 & T4)	Control (T5 & T6)	Direct (T1 & T2)	Indirect (T3 & T4)	Control (T5 & T6)	Direct (T1 & T2)*	Indirect (T3 & T4)	Control (T5 & T6)
2	170 (43.6) ^a	119 (43.3)	452 (172)	34.3 (12.4) ^a	3.41 (1.62)	0.62 (0.12)	14.8 (4.87)	17.7 (7.68)	6.27 (3.25)	1.21 (0.40)	5.51 (2.49)	3.17 (0.55)	49.4 (17.3) ^a	71.6 (12.2)	89.4 (3.74)
4	167 (29.46) ^a	305 (19.8)	524 (139)	14.3 (5.32) ^a	1.40 (0.21)	0.49 (0.7)	16.8 (3.08)	12.1 (2.70)	3.39 (0.72)	1.67 (0.30)	2.36 (0.19)	2.93 (0.39)	66.8 (8.02) ^a	83.3 (3.16)	92.7 (0.91)
8	203 (53.8) ^a	279 (41.8)	277 (65.2)	7.31 (3.95) ^{ab}	1.69 (0.76)	0.52 (0.10)	8.48 (5.67)	14.6 (6.64)	5.08 (0.91)	2.43 (0.58)	3.18 (1.06)	2.96 (0.40)	81.5 (9.43) ^{ab}	80.0 (8.46)	90.8 (0.64)
16	490 (90.8) ^b	367 (100)	376 (75.1)	1.38 (0.41) ^{bc}	1.59 (0.64)	0.45 (0.68)	6.98 (3.55)	6.81 (3.01)	3.50 (0.96)	2.70 (0.54)	2.43 (0.29)	2.35 (0.31)	88.3 (3.73) ^{ab}	88.7 (3.87)	93.4 (1.46)
32	468 (84.6) ^b	287 (85.6)	326 (69.6)	1.38 (0.35) ^{bc}	3.32 (0.82)	0.45 (0.48)	4.94 (1.41)	18.2 (2.40)	2.14 (0.57)	3.54 (1.37)	4.54 (0.60)	2.90 (0.20)	89.6 (3.17) ^b	73.6 (3.19)	93.8 (0.61)
64	339 (72.6) ^{ab}	184 (33.4)	419 (138)	1.05 (0.22) ^c	3.44 (0.79)	0.54 (0.10)	3.94 (2.14)	21.6 (5.84)	2.04 (0.43)	2.92 (0.40)	6.19 (1.58)	2.71 (0.35)	91.2 (2.67) ^b	67.9 (5.54)	93.7 (1.24)

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632 Table 4: Mean loss-on-ignition (%) for April 2005 for soils sampled at 2, 4, 8, 16, 32 ad 64 m from the wall, with standard errors in parentheses. *
 633 denotes significant difference in mean LOI (%) for direct, spray and control transects at the 5 % level for the defined distance. Similar superscript letters
 634 indicate no significant difference for post-hoc.

Distance (m)	Mean LOI (%)		
	Direct (T1& T2)	Spray (T3 & T4)	Control (T5 & T6)
2*	14.7 (1.0) ^a	11.4 (0.8) ^a	37.7 (11.0) ^b
4*	12.1 (1.7) ^a	24.2 (0.7) ^{ab}	38.1 (9.5) ^b
8*	12.6 (2.0) ^a	21.9 (0.6) ^b	21.4 (2.8) ^b
16	29.4 (4.4)	26.9 (5.5)	20.5 (3.6)

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