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2 Experimental simulation of the effects of extreme climatic events
3 on major ions, acidity and dissolved organic carbon leaching from
4 a forested catchment, Gårdsjön, Sweden

5

6

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15 **Abstract**

16 Climate change is predicted to lead to an increase in extreme rainfall and, in coastal areas,
17 sea-salt deposition events. The impacts of these two climatic extremes on stream
18 hydrochemistry were separately evaluated via a novel watering manipulation at the
19 Gårdsjön experimental catchment, SW Sweden. In summer 2004, a 2000 m² hillslope
20 draining to a defined stream reach was brought to a high-flow hydrological steady state
21 for a nine day period by sustained addition of ‘clean’ water using a distributed sprinkler
22 system. Marine ions were then added, to generate a realistic ‘sea salt’ episode. A
23 remarkably well constrained hydrological response was observed, such that a simple two-

24 compartment mixing model could reasonably well reproduce observed conservative
25 tracer (chloride, Cl) measurements, and 78% of added water was recovered in runoff.
26 Stream base cation concentrations and acidity responded predictably to clean water and
27 sea-salt addition, with the former leading to an increase in pH and acid neutralising
28 capacity, and the latter to episodic acidification through hydrogen ion and aluminium
29 displacement from soil exchange sites by marine base cations. Anion responses were less
30 predictable: water addition caused a flush of nitrate, but this was apparently independent
31 of rainfall composition. Sulphate remained near-constant during clean water addition but
32 declined sharply during sea-salt addition, indicative of a strong, pH-dependent solubility
33 control on leaching, presumably adsorption/desorption in the mineral soil. Most
34 strikingly, dissolved organic carbon (DOC) concentrations were stable during clean water
35 addition but varied dramatically in response to sea-salt addition, exhibiting a strong
36 negative correlation with Cl concentrations in water draining the organic soil. These
37 observations provide a robust experimental verification of the hypothesis that deposition
38 chemistry, through its influence on acidity and/or ionic strength, has a major influence on
39 DOC leaching to surface waters.

40

41

42 **Key words**

43 Acidity, Climate Change, DOC, Ionic Strength, Hydrological Episodes, Nitrogen
44 Leaching, Sea Salt, Sulphate Adsorption, Gårdsjön.

45 **Introduction**

46

47 The ecological condition of running waters is, to a substantial extent, determined by the
48 severity of physical and chemical extremes. These, in turn, are controlled by climatic
49 factors, such as storm events and droughts. Among the potential consequences of climate
50 change, the frequency and severity of storm events is predicted to increase (IPCC, 2007;
51 Pinto et al. 2009). Storm events affect streams directly through increased discharge, and
52 indirectly through changes in water quality; in semi-natural catchments, storm events
53 typically lead to increased flow through surface soil horizons, diluting base cation inputs
54 from weathering and increasing inputs of dissolved organic carbon and/or nitrate from
55 shallow soils. These processes can lead to ecologically damaging episodic acidification,
56 particularly when superimposed on long-term catchment acidification associated with
57 anthropogenically-derived sulphur (S) and nitrogen (N) deposition (Davies et al., 1992;
58 Wigington et al., 1996; Evans et al., 2008a). Additionally, in coastal areas, heavy storms
59 can result in pulses of sea salt deposition, due to entrainment of marine aerosols from
60 breaking waves at high wind speeds. The major impact of marine ion deposition,
61 generally termed the “sea-salt effect”, is the alteration of cation-exchange equilibria
62 between soil and soil water. This is a transient process, in which episodic inputs of
63 marine base cations, primarily sodium (Na) and magnesium (Mg), cause the displacement
64 of adsorbed acid cations, protons (H) and inorganic Aluminium (Al_i). This in turn can
65 lead to the episodic acidification of runoff (e.g. Wright et al., 1988, Evans et al. 2001). In
66 many areas, the legacy of base saturation depletion due to historic acid deposition means
67 that soils, and therefore surface waters, are likely to remain highly susceptible to sea salt

68 episodes for many years to come (Evans, 2005). Climate change induced increases in the
69 future severity of high-flow events in general, and sea-salt episodes in particular,
70 therefore have the potential to reduce, or even negate, the benefits of reduced S and N
71 deposition for many aquatic ecosystems.

72

73 As acid deposition has decreased in many industrialised regions, widespread increases
74 have been observed in surface water DOC concentrations across many areas of Europe
75 and Northeastern North America (Erlandsson et al., 2008, Monteith et al., 2007, de Wit et
76 al., 2007, Driscoll et al., 2003, Hejzlar et al., 2003, Hruška et al. 2009). DOC production
77 by terrestrial ecosystems is intimately linked to biological activity, and therefore to
78 climatic and other factors influencing productivity including temperature (e.g. Freeman et
79 al., 2001; Clark et al., 2008); nitrogen deposition (e.g. Pregitzer et al., 2001; Braggazza et
80 al., 2006); and atmospheric CO₂ (Freeman et al., 2004) and drought-rewet cycles (e.g.
81 Worrall and Burt, 2004; Clark et al., 2005; Toberman et al., 2008). Transport of this DOC
82 to runoff is in turn influenced by hydrological factors, in particular the proportion of
83 streamflow routed through organic-rich surface horizons (McDowell and Likens, 1988),
84 such that DOC concentrations and (in particular) fluxes are in most cases positively
85 correlated with discharge (Worrall and Burt, 2007; Erlandsson et al., 2008, Hongve et al.
86 2004). Finally, there is growing evidence that observed rising DOC trends are causatively
87 linked to concurrent decreases in acid deposition (e.g. Monteith et al., 2007, Evans et al.,
88 2006, Clark et al., 2006; Erlandsson et al., 2008). The precise mechanism for this link has
89 not been fully resolved, but appears to be a solubility control on DOC mobility linked to
90 soil solution acidity, aluminium concentration and/or ionic strength (Hruška et al. 2009,

91 de Wit et al. 2007, Monteith et al. 2007). As well as anthropogenically-derived acid
92 deposition, sea-salt deposition also affects all of these variables, and long-term changes in
93 sea-salt deposition have been identified as a significant contributor to DOC variations in
94 long-term studies (Monteith et al., 2007; Evans et al., 2006). The impact of sea-salt
95 deposition on DOC leaching on an episodic timescale is, however, not well quantified.

96

97 For this study, we separately evaluated the impacts of episodic increases in a) water input
98 and b) sea-salt input on the runoff chemistry, utilising a unique catchment-scale
99 experimental facility at Gårdsjön, Sweden. A distributed watering system was used to
100 increase water inputs over a nine day period, first by adding clean water to generate a
101 high flow episode, and then (once the catchment was in hydrological steady state) by
102 adding water spiked with sea salt. Experimentally-induced hydrochemical changes,
103 including acidity, nitrate (NO_3), sulphate (SO_4) and DOC were measured in catchment
104 runoff, and in hillslope soil solution. The aim of the experiment was to distinguish
105 between the two main hypothesised drivers of event-scale runoff chemistry variations,
106 namely separate i) hydrological variation and ii) precipitation chemistry.

107 **Methods**

108

109 *Study site*

110

111 Lake Gårdsjön is located at 130 m elevation, 12 km inland on the Swedish west coast
112 ($58^\circ 04' \text{ N}$, $12^\circ 03' \text{ E}$), Figure 1. Since 1979 several small catchments around the lake
113 have been monitored and used for various manipulation experiments to investigate the

114 effects of air pollution, forestry practices and climate, on soils, waters and terrestrial and
115 aquatic organisms (e.g. Andersson and Olsson, 1985, Skeffington and Hultberg, 1998,
116 Moldan et al., 2006). The 6300 m² catchment G1 has been monitored since 1988. In 1991
117 the catchment was covered by a below-canopy plastic roof and for ten years all
118 precipitation intercepted by the roof was replaced by sprinkling of a “clean” precipitation
119 underneath the roof. The aim of the “roof” experiment was to study the rate and
120 mechanisms of recovery from soil and water acidification. The experiment was
121 completed and the roof removed in 2001, but the monitoring of the site has been
122 continued.

123

124 The G1 catchment is covered by a 90 year old conifer forest of Norway spruce (*Picea*
125 *abies* (L.) Karst.), with some Scots Pine (*Pinus sylvestris*) present. The bedrock is
126 gneissic with intermediate to acid chemical composition. Soils are podsollic, with a thick
127 LFH humus layer overlying an eluviated grey E horizon, and a lower mineral BC horizon
128 grading into unaltered compacted glacial till. Both the organic horizon and the B/C
129 horizons are thinner in hillslope areas, and deeper in valley areas (Table 1). Long term
130 annual precipitation measured at the nearby F1 reference catchment is 1140 mm yr⁻¹,
131 throughfall water input to forest floor is 750 mm, and runoff is 560 mm (1989 – 2007). A
132 detailed description of the experimental area is given by Andersson and Olsson (1985)
133 and by Hultberg and Skeffington (1998).

134

135 ***Experimental water addition***

136

137 Manipulation was undertaken on a hydrologically discrete area of hillslope in the
138 northwest of the catchment, which drains to the lower part of the stream channel (Figure
139 2). The experiment started on July 22nd, 2004 and water was added for nine days.
140 Because conditions were dry prior to the experiment, with near zero discharge, the
141 remainder of the catchment was hydrologically inactive throughout the experiment. To
142 apply artificial rainfall evenly across the hillslope, thirty four water sprinklers were
143 placed every 5 m over an area of about 1000m². In the valley bottom, an additional ca
144 1000m² of the catchment was watered indirectly by the water passing from the irrigated
145 slope towards the catchment outlet. Thus the total slope area affected by the irrigation
146 amounted to 2000 m². Ambient precipitation during the experiment amounted to 3.2 mm
147 on July 22nd and 2.6 mm on July 23rd – 25th. These rains were largely intercepted in the
148 canopy and the water amount reaching the forest floor was too small to cause a detectable
149 runoff response.

150

151 A similar experimental design has been repeatedly used at the site through the years for a
152 series of seven hydrological tracer experiments. In all seven campaigns the runoff rate
153 during the high flow 'steady state' part of the experiment was lower than irrigation rates
154 (Lange et al, 1996, Lischeid et al., 2000). On an annual basis, however, there has been
155 nearly perfect match between ten years of measured Cl input to the catchment from
156 deposition and sprinkling and Cl output by runoff (Moldan et al., 1998). It has been
157 concluded that under ambient conditions no measurable amount of water leaves
158 catchment to deep groundwater or bypasses the outlet by cracks in bedrock. However,
159 during the experiments the water table was strongly elevated in a part of catchment. As a

160 result, the catchment border repositioned and part of the water was drained across the
161 normal catchment border, and thus did not reach the catchment outlet. The amount of
162 water ‘leaking’ was estimated as a difference between sprinkling rate and discharge rate
163 in the mornings, when evapotranspiration could be assumed negligible (relative to
164 irrigation rate). In the hereby described 2004 experiment the steady state input amounted
165 to 0.68 L s^{-1} , and the output showed a diurnal pattern (Figure 3) due to the root water
166 uptake of transpiring trees. Discharge peaked in the mornings at values some 0.10 L s^{-1}
167 lower than the sprinkling rate. We assume that the difference of 0.10 L s^{-1} was water
168 drained outside the normal catchment border. Therefore the effective sprinkling rate, i.e.
169 the input of water which drained into the catchment, was estimated at 0.58 L s^{-1} .

170

171 Water pumped from nearby Lake Gårdsjön was used for the experiment. Lake water was
172 mechanically filtered and then de-ionised in cation and anion exchanger columns. For the
173 first phase of the experiment, this ‘clean’ water was used for irrigation. The objective of
174 the water addition was, firstly, to bring a part of the catchment to hydrological steady
175 state, such that artificial rain of constant intensity resulted in a constant discharge rate.
176 Hydrological pathways and residence times were then assumed to be in a steady state. A
177 constant rate of clean water addition was then maintained for a total of 5 days, with the
178 expectation that runoff chemistry would also stabilise to some extent (at least in relation
179 to flowpath changes) within this period.

180

181 In the second phase of the experiment, deionised water was mixed with a small quantity
182 of seawater, to simulate a sea-salt deposition event. 500 l of sea water were collected at

183 the coast of Skagerrak, about 20 km from the site. The salinity of the sea water was 22.2
184 g L⁻¹, equivalent to a chloride (Cl) concentration of 366 700 μmol_(c) L⁻¹. Since the
185 catchment was already at hydrological steady state and runoff chemistry had at least
186 partly stabilised, chemical changes during this phase of the experiment were considered
187 to be attributable primarily to the effects of the sea-salt addition. Addition was
188 undertaken in two steps: firstly a lower dose, simulating a common “normal” sea salt
189 input, was applied for a two day period (Tables 2 and 3). Subsequently, the dose was
190 tripled to simulate high sea salt input. Again, this dose was maintained for 2 days, after
191 which all water addition was halted. Both levels of sea salt addition were chosen based on
192 analysis of Cl concentrations in the long term records of throughfall precipitation at the
193 site (Hultberg and Skefington 1998).

194

195 *Sampling protocol*

196

197 Runoff at the G1 catchment outlet was sampled automatically at a frequency proportional
198 to the flow. Chemical analysis of runoff was performed at IVL Swedish Environmental
199 Research Institute using routine accredited methods: pH was determined by glass
200 electrode, Mg, Na, calcium (Ca), potassium (K), Cl, SO₄ and NO₃ by ion
201 chromatography. Aluminium was determined colourimetrically by flow injection
202 analysis. Al was speciated into organic (Al_o) and inorganic (Al_i) fractions using a method
203 adapted from Driscoll (1984). The charge for inorganic Al was assumed to be 3+
204 (Moldan et al., 1995). DOC was determined using platinum-catalyst, high temperature

205 oxidation using the non-purgeable organic C method. Ionic strength (IS) was calculated
206 from the chemistry of inorganic constituents (mol L^{-1}):

207

$$208 \quad \text{IS} = 1/2 \sum_i c_i Z_i^2 \quad (\text{Eq. 1})$$

209 where c is the concentration of element i and Z is the ionic charge.

210

211 Apart from runoff water, samples were also collected inside the catchment at the low
212 edge of the watered slope at the sampling point O6 (Figure 2). At this location a steep
213 outcrop of bare rock makes it possible to collect the dripping water draining the soils in
214 the slope above before it re-enters the soil at the foot of the rock. Four samples collected
215 at O6 were analysed for the full set of determinands above. The rest of the O6 samples
216 were only analysed for Cl.

217

218 *Mixing model construction*

219

220 A simple mixing model was constructed to test the assumption that Cl concentrations in
221 runoff could be adequately described by a mixing of pre-treatment soil water with water
222 added during the experiment. Two compartments were considered; the 1000m^2 slope to
223 which water was sprinkled and the 1000m^2 valley, to which the water from the slope
224 drained. The sampling point O6 was taken to represent water draining the hillslope, and
225 catchment runoff to represent the output from the valley. Initial Cl concentrations in pre-
226 experiment soil water were assumed to be $420 \mu\text{mol(c)}/\text{L}$, equal to measured
227 concentration in the first runoff collected after the start of the experiment. The amount of

228 soil water in each compartment was manually calibrated (90 mm in the slope and 135 mm
229 in the valley) to fit observed Cl variations in each compartment.

230

231 *Statistical significance of runoff chemistry changes*

232

233 Pearson correlation was used to evaluate statistical significance of relationships between
234 different solutes. Runoff chemistry time series were divided into three groups: 1.

235 Addition of clean water only; 2. Addition of a low concentration of sea salt; and 3.

236 Addition of a high concentration of sea salt. These groups were tested separately. All

237 statistical analysis was performed with NCSS 2001 (Hintze 2001) software.

238

239 **RESULTS AND DISCUSSION**

240

241 *Hydrological Response*

242

243 After initial tests and adjustments of the watering system, the watering of the catchment

244 slope resulted in a total water addition of 547 m³ (274 mm, Table 2) over the nine days,

245 equivalent to 274 mm of rainfall within 2000 m² of the irrigated area. Due to summer

246 drought, the catchment had near-zero discharge before the experiment. A day before the

247 start of the experiment a 12 mm rain event took place, which was insufficient to cause a

248 discharge response but which conveniently helped to wet the soils. Six hours after the

249 start of watering, discharge began to increase, and by 38 hours had reached 90% of the

250 sprinkling rate. At that point, the sprinkling rate was reduced from an initial 0.87 L s⁻¹ to

251 0.68 L s⁻¹. Thereafter, discharge was in an approximate balance with effective sprinkling
252 rate (Figure 3), and the catchment was hydrologically at steady state. The discharge rate
253 of between 0.5 and 0.6 L s⁻¹ (Figure 3) corresponds to the 98th percentile of long term
254 recorded discharge. At Gårdsjön, once stream discharge is initiated, the capacity of the
255 soil to store additional water is very limited and any additional water input results in rapid
256 discharge rate increase (Nyberg 1995). The change in soil water storage from near-zero
257 discharge at the beginning of the experiment and storage at peak discharge was about 15
258 mm. This was estimated from the discharge volume which left the catchment in the two
259 days between the end of experimental watering and the return of the system to near-zero
260 discharge (Figure 3). Of the 274 mm of sprinkled water between July 22nd and August
261 2nd, 31 mm (11%) was drained to outside the catchment, 213 mm (78%) was measured in
262 discharge and ca 30 mm (11%) was lost to evapotranspiration. This compared to
263 approximately 750 mm yr⁻¹ of annual average throughfall precipitation at the area, and an
264 annual discharge of 440 mm yr⁻¹. A distinct diurnal discharge pattern was observed, with
265 morning maxima and evening minima, due to transpiration by the trees (Figure 3).

266

267 *Chloride response and mixing model application*

268

269 Chloride concentrations in the stream gradually decreased during the clean water
270 addition, from the initial concentration of 402 µmol(c)/L to a minimum of 156 µmol(c)/L
271 (Figure 4). Concentrations were still gradually declining when sea salt addition was
272 initiated (Table 3). This reversed the decline, and Cl rose to a peak of 423 µmol(c)/L by
273 the end of the high sea-salt addition period. In runoff from the watered slope part of the

274 catchment (O6), Cl fell to 95 $\mu\text{mol(c)}/\text{L}$ during clean water steady state, and rose to 880
275 $\mu\text{mol(c)}/\text{L}$ at the end of high sea-salt addition. Observed Cl variations were reasonably
276 well reproduced by the simple two compartment mixing model (Figure 4), with calibrated
277 soil water storage of 90 mm in the hillslope and 135 mm in the valley bottom. The
278 correspondence between modelled and observed variations in Cl concentration in runoff
279 from the hillslope and runoff at the catchment outlet suggest that the hydrological
280 interpretation on which the mixing model was based is realistic. The thinner hillslope
281 soils, which received direct water addition from the sprinklers, responded rapidly to
282 changes in rainfall chemistry. Deeper valley soils, receiving water additions indirectly via
283 the hillslope, showed a slower and more damped chemical response (Figure 4).

284

285 *Sulphate response*

286

287 Sulphate concentrations remained stable during clean water addition, ranging between
288 120 and 140 $\mu\text{mol(c)}/\text{L}$ (Figure 5). This occurred despite the high water throughput, and a
289 zero concentration of SO_4 in added water, which would have led to substantial dilution if
290 SO_4 had behaved conservatively. Previous observations from the catchment also indicate
291 that SO_4 does not decline significantly during high flows (Moldan et al. 2004). The lack
292 of a decline strongly indicates that there must be large available pools of easily released
293 SO_4 in the soils. Mörth et al. (2005) estimated the amount of extractable SO_4 in the soil at
294 Gårdsjön to be 407 mmol/m^2 in 1990 and 354 mmol/m^2 in 1995 after 5 years of clean
295 precipitation treatment (Moldan et al. 2004). The amount of extractable SO_4 was not re-
296 measured since, but provided that the roof experiment continued for another 5 years after

297 1995 and that SO₄ deposition was in 2004 some 50-60% less than in 1990, the extractable
298 SO₄ pool could be expected to be in 2004 less than 354 mmol/m², perhaps less than 300
299 mmol/m². The amount of SO₄ leached to runoff during the nine days was 13 mmol/m²,
300 probably less than 5% of the extractable pool. Two possible sources are the desorption of
301 SO₄ from B horizon, and mineralization of organic S from the humus layer. As observed
302 for NO₃ (see below), the dry period prior to the experiment could have led to an
303 accumulation of mineralised S from the organic soils (Torssander and Mörth 1998).
304 However, the complete absence of any episodic SO₄ pulse comparable to that observed
305 for NO₃ argues against the flushing of a pool of mobile SO₄ accumulated through organic
306 S mineralisation, and in favour of an equilibrium-controlled release of SO₄ through
307 desorption. Higher observed pH during this phase of the experiment would favour SO₄
308 desorption from mineral soil surfaces (Johnson and Cole, 1980), increasing the strength
309 of this buffering process during the clean water addition period. Previous work at the
310 Gårdsjön catchment (Mörth et al., 2005) suggests that SO₄ desorption plays a relatively
311 modest role in delaying recovery from acidification over the long term as S deposition
312 declines; a conclusion which likely extends to similar glacial soils elsewhere in
313 Scandinavia. Our data suggest, however, that short-term adsorption-desorption of SO₄
314 may play a significant role in buffering runoff chemistry on an episodic timescale.

315

316 In marked contrast to the lack of a response to clean water addition, SO₄ declined sharply
317 following sea-salt addition, from 125 µmol(c)/L to 80 µmol(c)/L. This decline occurred
318 despite the fact that the sea-salt treatment solutions contained 55 µmol(c)/L and 165
319 µmol(c)/L of SO₄ in the low and high sea-salt rain solutions respectively. Concentrations

320 reached a minimum just at the end of the experiment, at which point they were less than
321 half the concentrations in the sprinkling solution. The response clearly cannot therefore
322 be explained by dilution, and the likeliest explanation is that the decrease was associated
323 with an acidity pulse triggered by sea-salt addition (discussed below); episodic soil
324 acidification has been shown to increase SO_4 adsorption in the Bs horizons of podzolized
325 soils (Gustafsson, 1995). Again, therefore, the observed response to sea-salt addition
326 supports the interpretation that mineral soil SO_4 adsorption/desorption has a strong
327 influence on runoff SO_4 concentrations at this site. As sea-salt addition was ceased, SO_4
328 slowly returned to pre-experiment level of ca. $120 \mu\text{mol}(\text{c})/\text{L}$ within three weeks after the
329 end of the experiment.

330

331 *Nitrate response*

332

333 Nitrate was not present in runoff at the first stage of watering (Figure 6), but it increased
334 steeply up to $25 \mu\text{mol}(\text{c})/\text{L}$ after two days of clean water treatment. Concentrations then
335 decreased gradually to $5 \mu\text{mol}(\text{c})/\text{L}$ at the end of the experiment, and finally returned to
336 non-detectable concentrations 5 days after the experiment ended (data not shown). NO_3
337 showed no visible response to the sea salt additions. Long-term yearly weighted NO_3
338 concentrations at the G1 catchment are very low ($1\text{-}2 \mu\text{mol}(\text{c})/\text{L}$, Hultberg et al. 1998),
339 but peaks are occasionally observed in response to intensive rain or snowmelt (maxima of
340 $40\text{-}70 \mu\text{mol}(\text{c})/\text{L}$ were observed during the winters of 2000 and 2002). The peak observed
341 in this experiment appears to represent a similar hydrologically-driven response, probably
342 enhanced by dry antecedent conditions leading to increased nitrification within catchment

343 soils. The increase of nitrate in runoff during heavy rains or snowmelt is a recognised
344 phenomenon reported in many regions (e.g. Kaste et al., 1997; Oulehle et al., 2008). In
345 normal conditions, NO₃ produced within upper soil layers is transported vertically
346 through the soil column by rainwater, and consumed by microbial or root uptake before
347 reaching the stream. Under the very high rate of experimental water input, the soil profile
348 was completely water saturated, near-surface lateral flow dominated, and water residence
349 times were reduced to a few hours, greatly reducing efficiency of NO₃ uptake. The
350 subsequent decline of NO₃ after 2 days of constant water input is indicative of exhaustion
351 of the soil NO₃ pool.

352

353 *Base cations response*

354

355 As for Cl and SO₄, base cations were removed from the sprinkling water by the ion
356 exchanger for the clean water addition, and added as part of the subsequent sea-salt
357 addition. The temporal response in runoff concentrations was consequently similar to Cl;
358 the sum of base cations (SBC = Ca+Mg+Na+K) decreased from ca. 550 μmol(c)/L to ca.
359 350 μmol(c)/L during the clean water sprinkling, and increased gradually to ca. 500
360 μmol(c)/L at the end of sea salt addition (Figure 5). The changes were most pronounced
361 for Na, and to a lesser extent for Mg, the two major base cations in sea-salt. K remained
362 stable at around 8 μmol(c)/L, while Ca increased slightly, from 20 to 26 μmol(c)/L,
363 during clean water addition. Ca is the main base cation derived from weathering in the
364 mineral soil, and this response appears to be associated with the peak in NO₃ leaching.

365

366 The overall increase in base cation concentration from the end of the clean water addition
367 to the end of the sea-salt addition (150 $\mu\text{mol}(\text{c})/\text{L}$) was smaller than the net increase in
368 $[\text{Cl} + \text{SO}_4]$ of 222 $\mu\text{mol}(\text{c})/\text{L}$. This provides clear evidence that sea-salt additions had the
369 anticipated effect of altering the cation exchange equilibrium through displacement of
370 non-marine acid and base cations by marine base cations (primarily Na and Mg). The
371 impacts of this process on Acid Neutralising Capacity, acidity and aluminium
372 concentrations is considered in the following section.

373

374 *Acidity, aluminium and ionic strength response*

375

376 During clean water addition, runoff pH increased from 4.22 to 4.47. This occurred as a
377 result of the more pronounced dilution of strong acid anions than base cations (Figure
378 7a). A similar response was manifested by acid neutralising capacity (ANC, calculated as
379 the sum of base cations minus the sum of acid anions) which increased gradually from –
380 24 $\mu\text{mol}(\text{c})/\text{L}$, and reached +25 $\mu\text{mol}(\text{c})/\text{L}$ immediately prior to sea salt addition (Figure
381 6). Al_i concentration decreased from 20 $\mu\text{mol}(\text{c})/\text{L}$ to 5 $\mu\text{mol}(\text{c})/\text{L}$ during clean water
382 treatment, and IS decreased from 0.44 to 0.23 (IS units*1000). Sea-salt addition
383 effectively reversed all these chemical changes: pH fell from 4.47 prior the sea-salt
384 addition to a minimum of 4.2, and ANC dropped to -60 $\mu\text{mol}(\text{c})/\text{L}$ (i.e. an overall
385 decrease of 100 $\mu\text{mol}(\text{c})/\text{L}$ during a 4 day period with no hydrological change). This was
386 associated with an increase in Al_i from 3 to 39 $\mu\text{mol}(\text{c})/\text{L}$ and with an increase in H^+
387 from 33 to 59 $\mu\text{mol}(\text{c})/\text{L}$ at the end of sea-salt addition (Figure 7b). IS increased to 0.45
388 at the end of the sea-salt addition.

389

390 Over the full experimental period, IS and H^+ concentration were both strongly correlated
391 with Cl concentration (Figure 8). Correlations with ANC and Al_i were weaker, but still
392 significant (all at $p < 0.001$). Al_i was positively correlated to H^+ over the full course of
393 the experiment ($p < 0.001$), but during sea-salt addition a more statistically significant
394 correlation for Al_i was observed with IS ($p < 0.001$) than for H^+ ($p < 0.01$). This suggests
395 that during the clean water addition, Al_i was governed by standard Al-H equilibria, but
396 that during sea-salt addition (for the high dose in particular) incoming Na and Mg
397 effectively displaced Al_i from soil cation exchange sites, resulting in the observed Al-IS
398 correlation.

399

400 Changes in ANC did not correspond directly to those in hydrogen ion concentration, due
401 to the presence of DOC in the stream. According to dissociation model of Hruška et al.
402 (2003), there were ca. 30-55 $\mu\text{mol(c)}/\text{L}$ of organic anions (A^- , Figure 7b) present in the
403 stream (with dissociation ranging between 42 and 47 %) at the level of DOC 7.5-12 mg
404 L^{-1} . This organic acidity contributes significantly to stream acidity, but has a positive
405 influence on ANC, as reflected in an alternative definition of ANC (units: $\mu\text{mol(c)}/\text{L}$):

406

$$407 \quad \text{ANC} = \text{SBC} - \text{SAA} = \text{HCO}_3^- + A^- - H^+ - Al_i^{n+} \quad (\text{Eq. 2}).$$

408

409 Since pH stayed below 4.47 during the experiment (i.e. hydrogen ion concentration
410 always exceeded 35 $\mu\text{mol(c)}/\text{L}$), Al_i always exceeded 5 $\mu\text{mol(c)}/\text{L}$, and since HCO_3^-

411 concentration is zero at low pH, ANC would have been continuously negative through
412 the experiment in the absence of organic acids.

413

414 *Dissolved organic carbon response*

415

416 DOC concentrations of 5-10 mg L⁻¹ are typically observed in G1 stream water during
417 base flow conditions (0.1-0.2 L s⁻¹). During high discharge events (about 4 L s⁻¹) DOC
418 commonly increases, up to around 20 mg L⁻¹. In this experiment, DOC showed highly
419 contrasting responses to the two phases of treatment (as noted earlier, due to the summer
420 drought there was no runoff before the start of the experiment). At the onset of clean
421 water addition, runoff DOC concentration was relatively high (14.2 mg L⁻¹). DOC
422 concentrations then stabilised at around 12 mg L⁻¹ for the remainder of the clean water
423 addition. Several days of constant watering effectively saturated the soil. Hydrological
424 flowpaths shifted from mineral soil horizons to more organic-rich upper organic layers
425 and enhanced DOC leaching (e.g. McDowell and Likens 1988). The amount of DOC
426 leached out over the five days before the onset of sea salt addition was 1.5 g/m². This
427 compares to an estimated 2-3 g/m² of potential DOC in shallow upland soils (Haaland
428 and Mulder 2010). The markedly stable DOC concentrations during clean water addition
429 suggests that (like SO₄, but unlike NO₃), the watering did not simply flush out an
430 accumulated DOC pool out of the soil, as observed in some other studies of similar
431 systems (Haaland and Mulder, 2010), but rather that a solubility control was in operation.
432 On the other hand streamwater Cl, and consequently IS, declined by about 50% over the
433 same period, while pH increased from 4.2 to 4.35 (Figures 5 and 6). These observations

434 are seemingly at odds with studies suggesting that DOC solubility is controlled by acidity
435 or IS (Monteith 2007, de Wit et al. 2007, Evans et al. 2006, Hruška et al. 2009).
436 However, streamwater IS, pH and Al_i concentrations probably do not fully reflect
437 conditions in the organic horizons from which DOC was predominantly derived (e.g.
438 Oulehle and Hruška 2005, Giesler et al. 1996). Whereas runoff chemistry was strongly
439 influenced by the deeper mineral horizon in the valley soils, seepage data from the thin,
440 organic-dominated hillslope soils sampled at the sampling point O6 (Figure 2) may be a
441 better proxy for organic horizon soil solution. Full chemical characterisation was not
442 undertaken on all O6 samples, but Cl measurements (Figure 4) suggest that organic
443 horizon soil water chemistry may have stabilised relatively quickly (within 2 days) in
444 response to clean water addition, leading to stable stream DOC over the same period. In
445 addition, any DOC passing through the mineral soil may be affected by anion adsorption-
446 desorption; higher pH may favour desorption of DOC, as was noted earlier for SO_4 . On
447 the other hand, because DOC and SO_4 compete for adsorption sites, desorption of SO_4
448 from the soil during clean rain treatment could have enhanced DOC retention (Zech et al.,
449 1994; Kalbitz et al., 2000). A similar response has been noted over the longer term at the
450 Solling acidity manipulation study in Germany (Evans et al., 2008b). While anion
451 adsorption-desorption provides long-term buffering in older, unglaciated soils, the results
452 of the clean rain addition at Gårdsjön suggest that it can also play a significant short-term
453 buffering role in glaciated catchments, for both SO_4 and DOC.

454

455 Following the onset of sea-salt addition, DOC began a steady decline, reaching 10 mg L^{-1}
456 during the period of low sea-salt addition, and falling further to a minimum of 7.5 mg L^{-1}

457 during high sea-salt addition. Overall, this represents a ca. 40% decline in DOC during 4
458 days of sea salt addition at a constant discharge rate, and a total runoff DOC flux of 0.9
459 g/m². In contrast to the period of clean water addition, hillslope seepage data suggest that
460 organic horizon water chemistry was changing substantially, and continuously, through
461 the sea-salt addition period (Figure 6). Taking the entire period of hydrological steady
462 state conditions (i.e. from 24 July onwards, including both clean water and sea-salt
463 addition periods) there is a very strong correlation between stream water DOC, and the Cl
464 concentration in hillslope seepage water ($p < 0.001$, $r^2 = 0.96$, Figure 9). This strongly
465 supports the hypothesis that organic horizon acid-base chemistry is controlling DOC
466 leaching.

467

468 The results of this study provide some insights regarding the drivers of recent, widely-
469 observed increases in surface water DOC concentrations across Northern Europe and
470 parts of North America. The stable DOC concentrations over the period of clean water
471 addition suggest that, at least over the timescale and water flux magnitude of the
472 experiment, DOC concentrations in runoff are not constrained by limitations on DOC
473 supply. On the other hand, the rapid DOC response to changes in precipitation chemistry
474 supports the conclusion of various studies (e.g. Evans et al., 2006; Monteith et al., 2007;
475 de Wit et al., 2007; Hruška et al., 2009; Oulehle and Hruška, 2009) that DOC increases
476 are driven by solubility changes, driven by reductions in acid deposition. Our results also
477 clearly demonstrate that runoff DOC concentrations are affected by changes in sea-salt
478 deposition, as proposed by Monteith et al (2007).

479

480 With regard to the mechanisms by which such changes occur, most previous studies have
481 been based on observations of long-term change under ambient conditions, and were thus
482 unable to differentiate between specific mechanisms determining organic matter
483 solubility, in particular the relative importance of pH, Al concentrations and IS. A
484 number of relevant experimental studies have been undertaken, however. The HUMEX
485 field experiment in Norway, in which strong acid loadings were increased, showed a
486 decrease in soil water DOC, associated with a decrease in pH (Vogt et al. 1994). Clark et
487 al (2006) found that peat pore water DOC decreased along with pH during laboratory
488 simulated drought experiments. It is likely that (at least in mineral soils), increases in
489 acidity are accompanied by increases in inorganic Al concentration, which acts as a
490 coagulant for DOC (Tipping and Woof, 1991, De Wit et al, 2001). A few studies have
491 also specifically shown that increasing IS reduces DOC concentrations (Tipping and
492 Hurley 1988, Evans et al. 1988). Our data show a high correlation between DOC and Cl
493 concentration in the hillslope organic horizon (Figure 9), and a strong correlation between
494 Cl and IS at the catchment outflow (Figure 8). However, runoff Cl concentration was also
495 strongly correlated with H^+ , and to a lesser extent with Al_i , and it is thus not possible to
496 definitively distinguish between these proposed controls on DOC solubility. In reality, the
497 three proposed drivers are highly interlinked in acidic, mineral soil catchments, and it is
498 perhaps spurious to attempt to distinguish between them in these systems. A different
499 situation might be expected in peats (where Al_i is not present) or in more alkaline
500 catchments, where IS can change without concurrent changes in pH or Al_i (Hruška et al.,
501 2009). In this study, our clear conclusion is that alterations in precipitation chemistry can
502 result in near-instantaneous changes in runoff DOC concentrations, and that these

503 changes appear to be mediated through solubility controls within the organic horizon.
504 This is consistent with the hypothesis that long-term DOC increases are attributable to
505 reducing levels of acid deposition, and that DOC is also affected on an inter-annual
506 timescale by variations in sea-salt deposition.

507

508 **Conclusions**

509

510 Sustained, hillslope-scale water addition generated a remarkably well constrained
511 hydrological response, which could be explained by a simple mixing model comprising
512 hillslope and valley soil compartments. Adding ‘clean’ water at a constant rate had a
513 positive effect on the runoff chemistry: over four days pH increased from 4.3 to 4.5, Al_i
514 decreased from 20 to 5 $\mu\text{mol(c)/L}$, and ANC increased from -24 to $+25$ $\mu\text{mol(c)/L}$. A
515 flush of NO_3 was observed, but DOC and SO_4 both remained remarkably constant once
516 hydrological steady state was achieved. Sea-salt addition, on the other hand, led to a
517 rapid, and prolonged, deterioration of the runoff quality, to biologically toxic levels: Al_i
518 increased to 80 $\mu\text{mol(c)/L}$, pH decreased to 4.2 and ANC fell to -60 $\mu\text{mol(c)/L}$. Sea-salt
519 addition also led to large reductions in both SO_4 and DOC concentrations. The behaviour
520 of these solutes suggests strong solubility controls on leaching. SO_4 leaching appears to
521 be controlled by pH-dependent adsorption and desorption in the mineral soil, and DOC
522 leaching by acidity and/or ionic strength in the organic soil.

523

524 The results of this study have a number of wider implications for understanding and
525 prediction of surface water quality under changing climate and deposition. They confirm

526 that biologically critical chemical extremes are highly sensitive to climate events, but
527 indicate that this sensitivity is not simply related to the magnitude of precipitation inputs.
528 For example, increased water fluxes will increase DOC leaching to surface waters, but
529 increased sea-salt inputs will have the opposite effect. Acidity, Al and SO₄ responses are
530 also highly influenced by rainfall composition. Nevertheless, all of the responses
531 observed appear explicable in terms of current mechanistic understanding, providing
532 encouragement that future hydrochemical extremes may be accurately predicted, and
533 quantitatively modelled, from the magnitude and composition of precipitation inputs.

534

535 Finally, we argue that large-scale manipulation experiments such as the one described in
536 this study provide a uniquely valuable means for improving understanding the
537 biogeochemical response of natural ecosystems. Compared to laboratory and even plot-
538 scale experiments, which tend to minimise heterogeneity within small, replicated and
539 often carefully selected soil units (Schindler 1998), hillslope-scale manipulations capture
540 more of the inherent complexity and heterogeneity of real ecosystems. On the other hand,
541 they can control for some of the multiple sources of variability (in this case short-term
542 hydrological fluctuation) that can confound interpretation of ambient monitoring data.
543 While challenging to maintain, particularly for extended periods, large-scale experimental
544 catchments remain a vital tool for biogeochemical research.

545

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552

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777 **Figure legends**

778 Figure 1. Map of Sweden with location of the Gårdsjön lake research area

779

780 Figure 2. Map of G1 catchment with watered slope and part of valley affected by
781 watering marked by dots. O6 – sampling point for surface runoff of water coming from
782 the watered slope, catchment runoff sampled at the catchment outlet.

783

784 Figure 3. Discharge and effective sprinkling rate during the experiment at Gårdsjön.

785

786 Figure 4. Concentration of Cl in the sprinkling water (dashed line), in the water draining
787 the irrigated slope (open circles) and in runoff (closed circles) and theoretical
788 concentrations Cl produced by a mixing of sprinkling water with pre-event water in the
789 slope and water draining the slope with soil water in the valley (solid lines).

790

791 Figure 5. Concentration of Cl, SO₄ and sum of base cations measured during the
792 experiment. Line with circles represented streamwater, bold line appropriate solute
793 concentration in sprinkling water.

794

795 Figure 6. Concentration of DOC, ANC, Al_i , NO_3 , IS and pH measured during the
796 experiment. Line with circles represented streamwater, bold line appropriate Cl
797 concentration in sprinkling water.

798

799 Figure 7a. Sum of base cations ($BC=Ca+Mg+Na+K$) and sum of the strong acids
800 ($SAA=Cl+NO_3+SO_4$) observed in the stream during the experiment.

801

802 Figure 7b. Sum of Al_i (calculated with charge 3^+) and H^+ and organic acids anions (A^-)
803 observed/modelled in stream during experiment.

804

805 Figure 8. Runoff concentrations of chloride (Cl) plotted against ionic strength (IS),
806 hydrogen ion (H^+) Acid Neutralising Capacity (ANC) and inorganic aluminium (Al_i).

807

808 Figure 9. DOC in runoff in comparison with Cl leaving catchment slope (O6). Samples
809 prior reaching the hydrological steady state and after the end of the watering excluded.

810

811 **Table legends**

812 Table 1. Thickness of the soil horizons (cm) at experimental G1 catchment

813

814 Table 2. The amount of water and sea water added during the watering experiment at

815 Gårdsjön G1 catchment in July- August 2004.

816

817 Table 3. Sprinkling water concentrations ($\mu\text{mol(c)}/\text{L}$) of Cl, SO_4 and base cations during
818 the sea salt addition to the G1 catchment.
819

1 **Figures**

2

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4



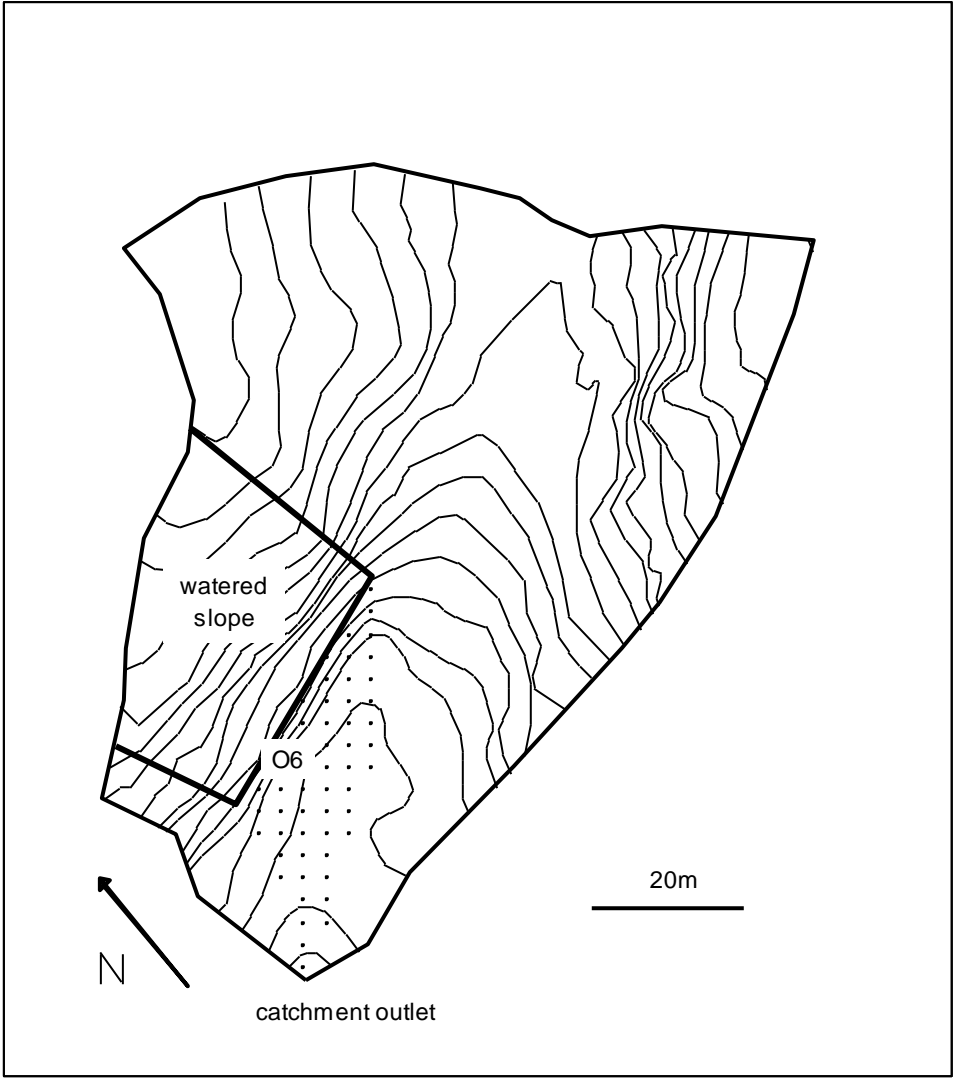
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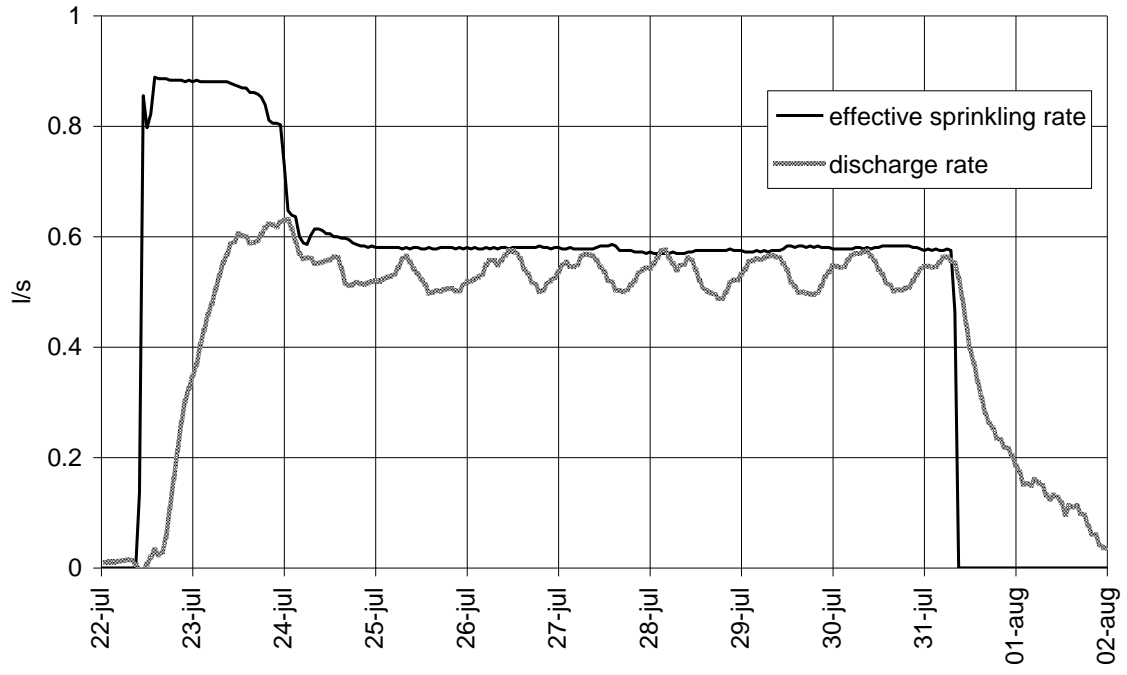
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Figure 1.

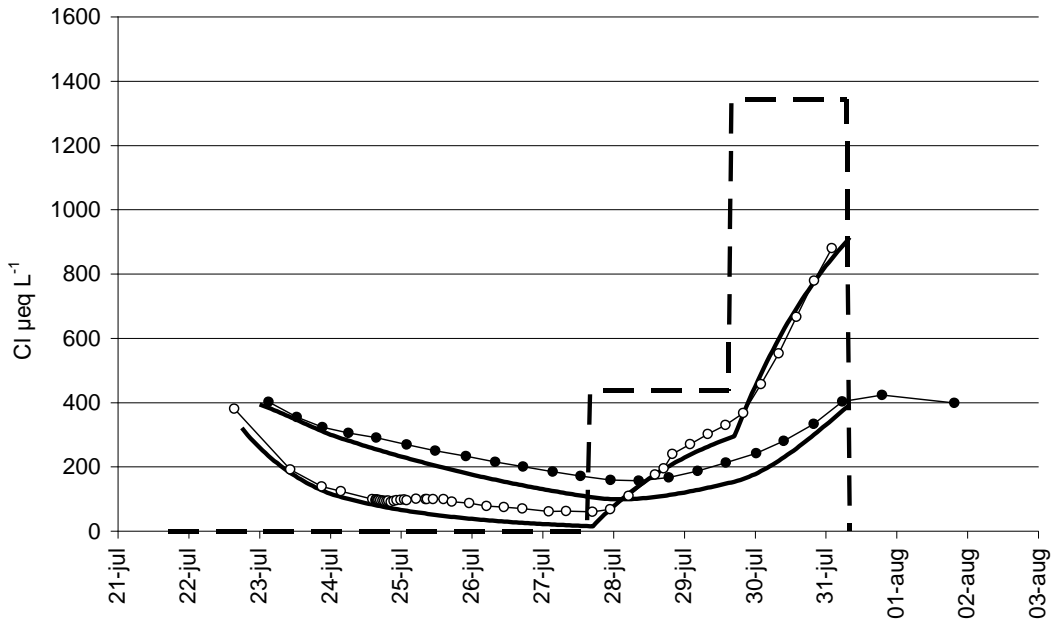


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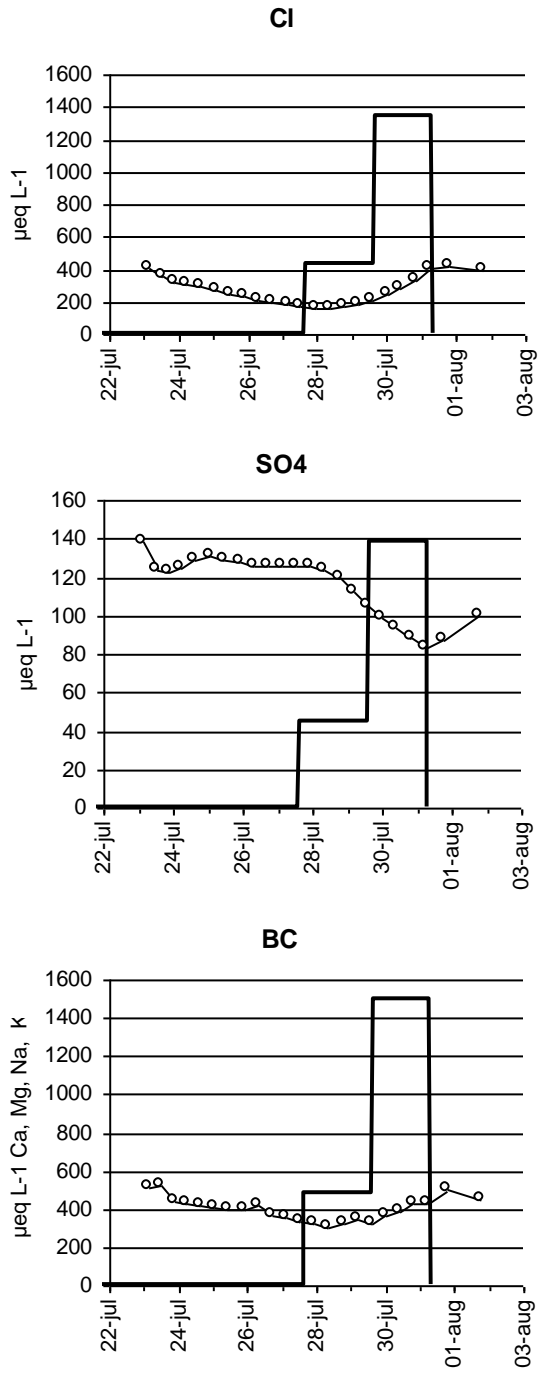
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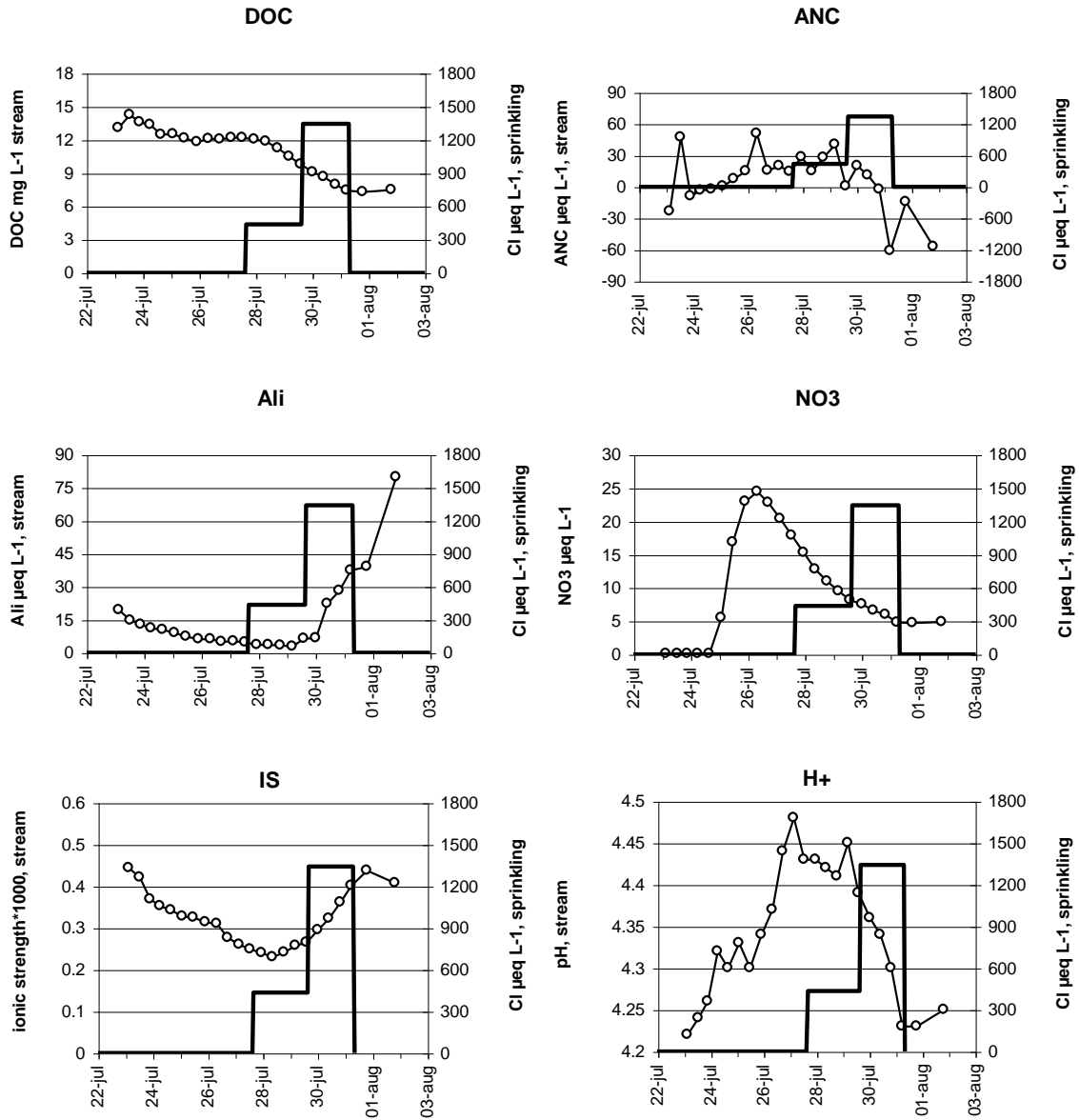
15
16 Figure 3.
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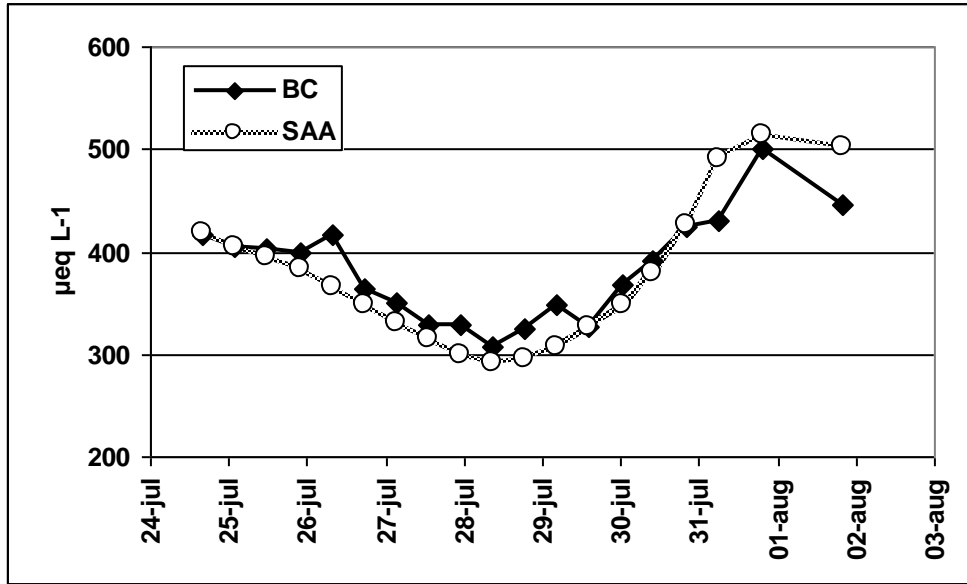
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19 Figure 4.



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21 Figure 5.
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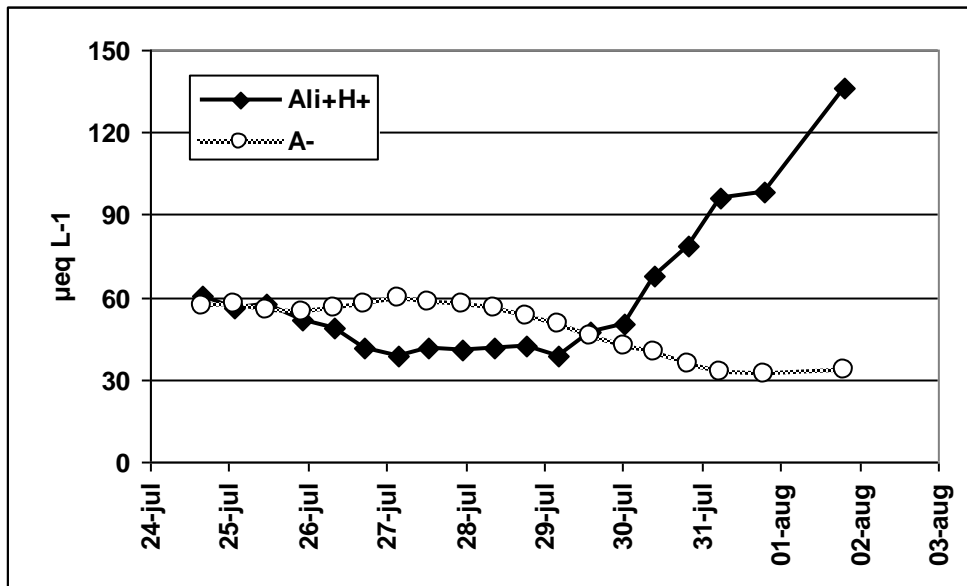


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24 Figure 6.



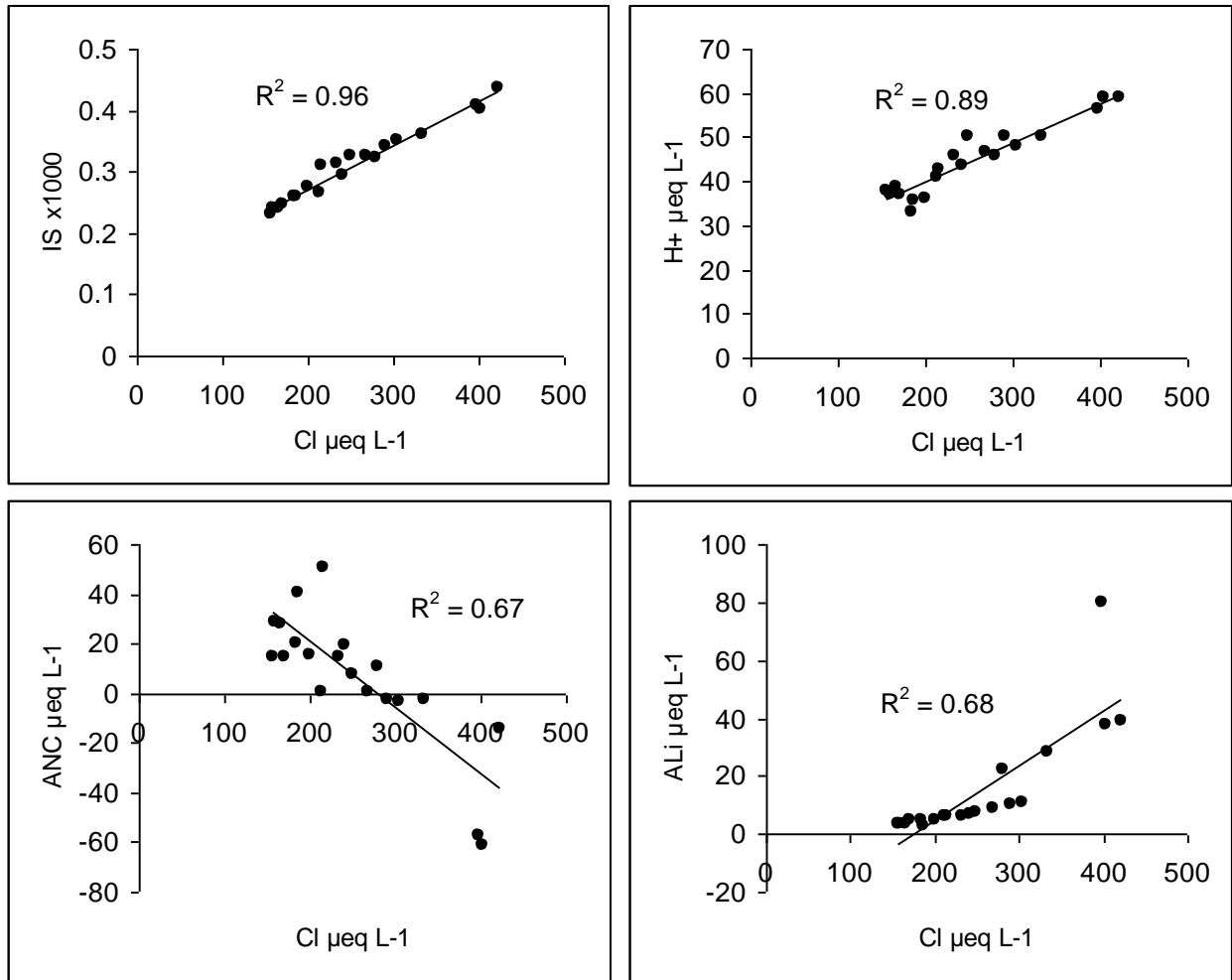
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Figure 7a.



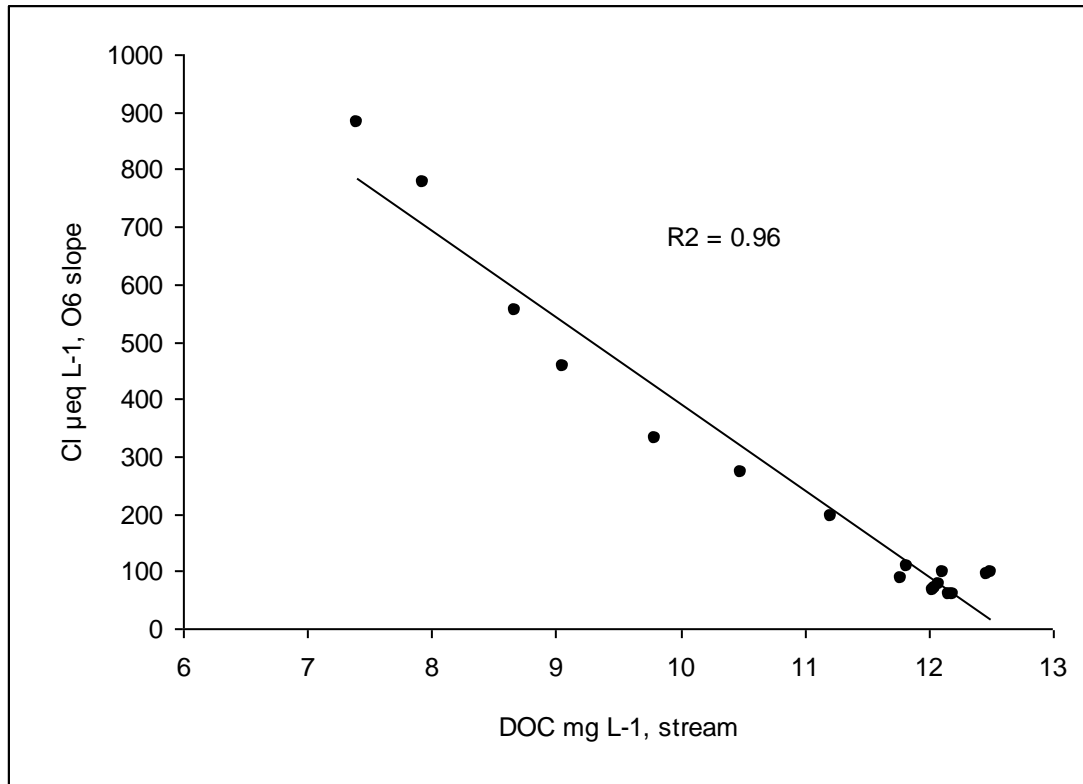
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Figure 7b.



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Figure 8.



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Figure 9.

38 **Tables**

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Table 1.

	Organic layer	E horizon	B/C horizon
Catchment slope	8.2	4.7	3.3
Catchment valley	16.8	4.1	25.1

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Table 2.

	Duration [hours]	Water [m ³]	Water [mm] (2000 m ² irrigated area)	total seawater added [l]
Water (de-ionised)	127	336.3	168	0
Water + low sea salt	48	116.0	58	138.4
Water + high sea salt	39	94.6	47	347.0

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Table 3.

	Cl	SO ₄	Na	Mg	Ca	K
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Low addition	437	45	375	87	16	8
High addition	1344	139	1153	266	50	24

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