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1 **Initial effects of forest N, Ca, Mg and B large-scale fertilization on surface water**

2 **chemistry and leaching from a catchment in central Sweden**

3

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9

10 **Highlights**

11 • Large scale forest fertilization resulted in considerable nitrogen and calcium leaching.

12 • High nitrate concentrations were reached in the first months after fertilization.

13 • Total nitrogen outflow in the first year was 14 % of applied fertilizer.

14 • Small pH decline with short-term duration occurred after the fertilization.

15 • Small amounts of boron (6 %) were leached after application.

16

17 *Abstract*

18 Highly increased use of biomass production is placing great demands on Swedish forests.

19 Several silvicultural measures can be implemented to increase forest production and

20 fertilization being addressed in this paper is one. Forest companies are now increasingly

21 applying fertilizer, with the main nutrient needed for high forest growth being nitrogen (N).

22 This study investigated how commercial N fertilization (150 kg N/ha, including also Ca, Mg

23 and B) of the 45 ha forest catchment Risfallet in central Sweden affected chemical

24 composition and runoff export in stream water during one year after the fertilization. This

25 well-defined and long-term monitored catchment proved very suitable for studies of water

26 quality and nutrient losses. The fertilizer consisted of ammonium nitrate (50/50 ammonium

27 and nitrate, respectively), plus calcium (Ca, 22 kg ha^{-1}) and magnesium (Mg, 12 kg ha^{-1}) to

28 mitigate acidification and boron (B 1.1 kg ha^{-1}) to compensate for decreased boron

29 availability. The study was carried out according to the paired catchment method using a

30 control area and a calibration period. Data from the after treatment period were compared

31 with previous 25-year monitoring data for the catchment and also data for a similar 83 ha

32 control catchment, Gusseltjärn, in the same region. During the first year after treatment, the

33 nitrate concentration in stream water increased from 0.05 mg L^{-1} to 3.3 mg L^{-1} on average.

34 Other elements showing increased concentrations were ammonium (300%), B (3-fold), Mg

35 (80%), Ca (60%), potassium (K) (50%) and sodium (Na) (40%). The pH decreased in the first

36 half-year by 0.2 pH-units. One year after treatment, 14% of the N applied had leached from

37 the catchment.

38

39 **Keywords:** fertilization, forest, catchment hydrology, nitrogen, boron, water chemistry

40

41

42   **1. Introduction**

43 There is a need for high biomass production to meet growing demand for wood products.

44 Higher forest biomass production can be achieved by better silvicultural measures, including

45 addition of nitrogen (N) being the main limiting nutrient in boreal forests (Nohrstedt, 2001).

46 Forty years ago, this was a widely used method to increase growth, but during a period of

47 high atmospheric N deposition its use had been fairly limited in Sweden in recent decades.

48 However, there is currently new interest in N fertilization together with small additions of

49 calcium (Ca), magnesium (Mg) and boron (B), despite elevated N deposition, being c. 5 kg

50 ha^{-1} year^{-1}, with no overall significant, clear trend for a decrease (Vuorenmaa et al., 2009).

51 Emissions have declined, but the effect on deposition is not clear (Nyiri et al., 2009).

52   Investigations on N deposition still show much higher inputs than outputs in surface waters

53   from catchments. Furthermore, there is a clear correlation between high N deposition and high

54   leaching to watercourses (LeGall, 2012). Additional N fertilization is thus likely to increase

55   leaching. Nitrogen is also stored in the catchment forest soils and this increasing accumulation

56   will probably also increase leaching. There are particularly high risks of leaching at sites with

57   low CN-ratios (Gundersen et al., 2006).

58

59   Despite these unwanted N load effects, the needs and production objectives of forestry are

60   considered more important and new attempts are being made to increase yields of timber,

61   energy biomass and other economically valuable forest by-products. Long-term research on

62   the effects of forest fertilization on biomass yield has shown that significant increases in

63   production can be achieved (Nohrstedt, 2001; Pettersson and Högbom, 2004). A great need

64   for increased future production is predicted (Bergh et al., 2008). However, the consequences

65   for environmental values are still being discussed, especially in light of changes in the

66   environment as regards elevated N deposition and climate change, which together may alter

67   nutrient turnover in soils and the total catchment. On the other hand, N fertilization could

68   mitigate higher atmospheric carbon dioxide (CO_2) content by increasing forest growth and

69   carbon (C) storage in organic material in the standing crop and in the soil compartment

70   (Nohrstedt, 2001). Consequently, N fertilization could increase C sequestration (Högberg,

71   2007; Hyvönen et al., 2008).

72

73   Nitrogen fertilization has multiple effects on soil, vegetation and water. Enhanced tree growth

74   has been reported and is of course the main reason for N fertilization. Adverse effects in terms

75   of altered ground vegetation composition, increased nitrification resulting in increased risks of

76   leaching and acidification have also been reported (Tamm, 1991; Nohrstedt, 2001).

77 Acidification is often mitigated by addition of Ca, but this promotes enhanced nitrification.

78 Boron deficiency can also occur, especially in ecosystems located far from the sea, but this

79 can be dealt with by adding B to the N fertilizer (Lehto & Mälkönen, 1994).

80

81 Studies on the effects of such forest fertilization on water quality could now be excellently

82 elucidated in a well-defined, long-term monitored catchment. The forest company Sveaskog

83 recently planned and carried out fertilization in June 2012 on c. 90% of the Risfallet (RF)

84 catchment, which had already been under monitoring for 25 years, especially regarding

85 discharge and stream water chemistry (Knutsson et al., 1995). This provided a great

86 opportunity to continue measurements in the new circumstances and obtain large-scale

87 information on the consequences of forest fertilization on surface water quality. In addition,

88 the RF catchment has a deep, unsaturated glacial till soil cover and deep, rather large

89 groundwater reservoirs, imposing rather small treatment effects on surface water chemistry

90 and leaching. This means that any changes in stream water chemistry, and therefore element

91 export, are likely to be the effect of forest fertilization.

92

93 This study examined the effects on outflow to surface waters of large scale application of

94 nitrogen and additional elements to almost a total catchment. This deviates from many studies

95 with plot or low shares of catchment area fertilization at stand level. The proportions of added

96 fertilizer constituents lost to downstream waters were estimated for the RF catchment. The

97 use of tractor application makes this study rather unique by more careful fertilization

98 compared to usual aerial methods and thereby have the possibility to avoid direct input to

99 surface waters mitigated unwanted leaching.

100

101

102   **2.   Material and methods**

103   *2.1 Catchment characteristics*

104   The study was based on the catchment concept and involved a fertilized catchment (RF) and a

105   control catchment 120 km NW in Dalecarlia, both in the boreal region of central Sweden (Fig.

106   1). Both catchments have been monitored on discharge and major chemical constituents for

107   long periods (~25 years). The fertilized catchment RF was part of a project studying

108   groundwater acidification and monitoring started in 1987 (Lundin, 1995). The control

109   catchment Gusseltjärn (GT) was established back in 1973 in the Siljansfors experimental

110   forest under the supervision of the Swedish University of Agricultural Sciences and can

111   mainly be considered protected from forestry operations (Bergqvist and Grip, 1975). Both

112   catchments are located in the northern boreal coniferous region of Sweden, on glacial till soils

113   above the highest coastline. The soil is rather coarse, mainly characterized by a sandy till

114   overlying granite bedrock at RF and porphyry bedrock at GT. Considerable parts of both

115   catchments have rather thick quaternary deposits and the groundwater level is often below 1-2

116   m depth. In RF this results in the dominant moisture class being fresh (Fig. 1). Besides the

117   dominating well-drained mineral soils, partly with slightly higher groundwater level and then

118   being moist, the catchments also contain small mires and wet areas being thin peatlands and,

119   in GT, even a small tarn, but for long periods the deep groundwater pathways prevail and

120   form discharging surface waters.

121

122   The catchment size is 83 ha for GT and 45 ha for RF (Table 1). Stand age differs, as GT is

123   dominated by over 100-year-old trees and with younger forest (approx. 60 years) on 20% of

124   the area with estimated average stand volume on c. 200 m^3 ha^{-1}. In RF the stand age is rather

125   uniformly ~35 years and is dominated by pine (*Pinus silvestris*). The ground vegetation class

126   is dominated by low grass types, a medium nutrient rich type deviating from rich herb types

127   and poor shrub types. The RF catchment is somewhat more fertile in slightly better climate

128   conditions, but the differences are not great (Table 1). The stand in RF was thinned in 2009,

129   with about 35% of the trees harvested and the estimated volume in 2006 being 184 m^3 ha^{-1}

130   and in 2012 144 m^3 ha^{-1}.

131

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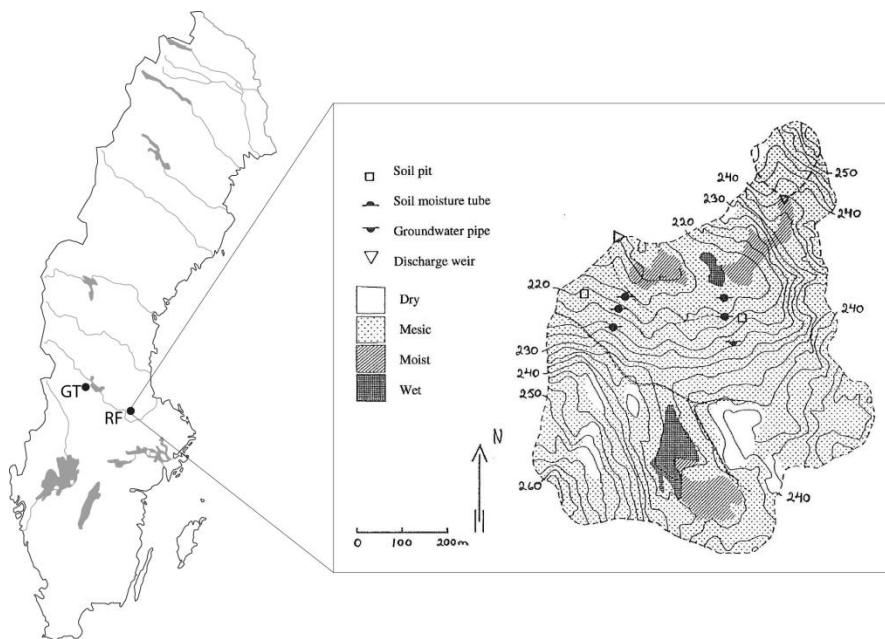
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134

135   Figure 1. Left: Map of Sweden showing geographical location of the Gusseltjärn (GT) and

136   Risfallet (RF) catchments. Right: Detailed map of the Risfallet catchment showing

137   hydrological installations, contour lines (m.a.m.s.l.) and distribution of moisture classes

138   (Lundin, 1995).

139

140

141

142

143

144 Table 1. Site characteristics of the Gusseltjärn (GT) and Risfallet (RF) catchments. Tree species

145 frequency given as 1/10 pine, spruce, birch (P/S/B). Climate data (1960-1990) Raab and Vedin (1995)

	Gusseltjärn, GT	Risfallet, RF
Location, Lat./Long.	N 60°35'; E 14°25'	N 60°21'; E 16°14'
Altitude, m a.m.s.l.	265-365	215-270
Area, ha	83	45
Temp. °C	+3.1	+4.0
Temperature sum (>5 °C)	1150	1200
Snow cover duration, days	160	140
Precipitation, mm	660	616
Runoff, mm	380	300
Tree species frequency, P/S/B, 1/10	9/1/0	8/1/1
Stand age, years	60 (17 ha), >130 (58 ha)	35
Stand stem volume, $m^3 ha^{-1}$	c. 200	184
Current stand increment, $m^3 ha^{-1} yr^{-1}$	4.0	4.6

146

147

148 The soil in the RF catchment is dominated by mineral quartz (approx. 60%) and also includes

149 K-Feldspar and Ca-Na Feldspar in about equal proportions (20%). Soil geochemistry analyses

150 showed pH values of around 4 in the H- and E-horizons, increasing with depth to 5 in the B-

151 horizon and 5.5 at about 1 m depth in the main matrix. Base saturation was approx. 75% in

152 the H-horizon, 20% in B and 30% below 1 m depth (Table 2).

153

154 Table 2. Geochemical properties of the glacial till soil in the Risfallet (RF) catchment. Exchangeable
155 cations and acidity extracted in 1 M NH_4Ac at pH 7, aluminium (Al) extracted in 1M KCl ($mmolc\ kg^{-1}$
156). Carbon, C and nitrogen, N analysed on LECO. CEC = cation exchange capacity, BS = base
157 saturation (%). (Lundin, 1995).

158

Horizon, depth, cm	pH H_2O	C %	N %	C/N	Ca	Mg	K	Na	Ac	Al	CEC	BS %
H, 3-5	3.9	43	1.34	32	101	19.6	13.6	1.0	49	11.4	185	73
E, 7-12	4.5	1.3	0.06	21	4.8	1.0	1.0	0.1	16.2	14.1	23	30
B, 12-17	4.9	2.8	0.13	22	2.9	0.7	1.0	0.2	22.7	25.6	28	17
C, 120-130	5.7	0.06	0.02	3	0.3	0.1	0.7	0.2	3.1	2.5	4	30

159

160   The fertilizer applied was 'SkogCAN', a currently commonly used fertilizer in Sweden which

161   is composed of ammonium nitrate. Nitrogen is the main growth element and Ca and Mg are

162   added to mitigate soil acidification. However, Ca and Mg influence the availability of B and

163   therefore a minor amount of B is also added. The amount of fertilizer applied was 550 kg ha^{-1},

164   supplying 150 kg N, 22 kg Ca, 12 kg Mg and ~1 kg B per hectare. The equipment used for

165   applying the fertilizer was a tractor equipped with GPS for positioning. When applying the

166   fertilizer a few small areas comprising mires and around installations were avoided, but of the

167   45 ha catchment more than 40 ha were fertilized.

168

169   *2.2 Investigation technique and analyses*

170   This study used the technique of calibration period and control area. Such technique has been

171   used in several studies, eg. Lundin and Bergquist (1990), (1995) and Löfgren et al. (2009).

172   This means pair-wise catchment area comparison first during a period with both catchment

173   without treatment (in this case 25 years) and from this comparison and the measured values at

174   the control being still in untreated condition, values for the treated catchment as untreated

175   could be calculated for the period after treatment. These values were then compared with the

176   values after treatment and the difference interpreted as the effects of the treatment; in this case

177   the fertilization. The fertilized RF catchment formed the impact area for which the effects of

178   fertilizer application were determined. The almost natural GT catchment area without forestry

179   operations was used as the control catchment from which un-treated values for the fertilized

180   RF catchment could be calculated using the relation between RF and GT for the 25-year

181   calibration period (1987-2011) and values for GT for the period just before and after

182   fertilization, i.e. January 2012 to June/July 2013. Fertilization was carried out during about

183   one week in the end of June 2012.

184

185   Water sampling was carried out monthly for almost the entire period and was intensified to up

186   to four samples per month during a five-month period following fertilization. Reference

187   values for the calibration period were calculated as monthly means for the period and used as

188   calibration values. Means of monthly values were calculated together with coefficients of

189   variation. Significance of changes were tested with confidence intervals (t-test). Calculations

190   of reference concentrations for the period after fertilization was mainly carried out based on a

191   quotient RF/GT from the calibration period and the measured value at the control GT for the

192   period after fertilization, i.e. July 2012 to July 2013. For most elements the mean and

193   variation for GT and RF during the calibration period didn't differ significantly. Nor did the

194   mean values of studied elements for GT in the period after fertilization differ from the values

195   in the calibration period. Deviating from this was only organic nitrogen.

196

197   Outflow of elements was calculated from the monthly concentrations and continuously

198   measured discharge at the catchment discharge station. The technique for element flow

199   calculations was based on interpolated daily concentrations and daily determined discharge at

200   the V-notch weir equipped with a water level chart recorder. The functioning of the weir and

201   the water level recorder was checked bi-weekly for most of the study period and was found to

202   be very good. However, for single years the monthly sampling and chemical content

203   determinations were somewhat sparse giving uncertainties at high flow periods. On the other

204   hand, the very long time record would partly compensate for this and also the fact that the

205   water flowpaths through the soil at both catchments were fairly long, partly levelling out the

206   large variations often occurring in catchments with upper soil layer flowpaths. Estimations of

207   element flows in the calibration period could be considered good and for the period after

208   fertilization, the sampling frequency was higher giving appropriate outflow values.

209

210 Chemical analyses were carried out by laboratories at SLU, Uppsala, using standardized

211 techniques according to SWEDAC (Swedish Board for Accreditation and Conformity

212 Assessment). For the elements presented in this paper, pH was measured with combination

213 electrodes, base cations with optical ICP OES (inductively coupled plasma-optical emission

214 spectrometry), anions with ion chromatography (Dionex ICS 1100) and total N mainly by

215 persulphate digestion and later by combustion (SS-EN 12260:2004). Boron was analysed with

216 digestion in 0.5% HNO_3 and measurement in ICP-MS (inductively coupled plasma-mass

217 spectrometry).

218

219 *2.3 Precipitation*

220 Daily precipitation values in the RF catchment were calculated from measured values at

221 Avesta national climate station, 23 km to the SSW. The precipitation regime (monthly and

222 annual sums) was classified according to Eriksson (1979) based on precipitation series from

223 1944 to June 2013.

224

225 Mean annual precipitation sum in the RF catchment during 1987-2012 was almost 690 mm

226 (range 520 mm in 1995 to 879 mm in 2000). In the year 2012 the precipitation was 858 mm.

227 During the one year period July 2012-June 2013, the precipitation sum was 782 mm, but in

228 March 2013 it was extremely low (1.6 mm), while in the period April-September 2012 it was

229 extremely high (560 mm).

230

231 *2.4 Discharge*

232 As the catchment area is rather small (45 ha), the average discharge is only a few litres per

233 second and there is commonly no flow at all during dry periods. Consequently, long periods

234   (1 week up to 4 months) of no stream flow were occasionally observed during summer and

235   early autumn.

236

237   After heavy rain or large snow-melt events, the peak flow sometimes exceeded 5 mm per day.

238   Discharge usually stayed low because of relatively great soil depth, large groundwater

239   reservoirs and a deep unsaturated soil water zone within most of the catchment area.

240   However, after heavy rainfall in July 2012, discharge reached 19.1 mm during one day.

241   The annual (January-December) discharge in the RF catchment during 1987-2012 varied from

242   98 mm to 457 mm (mean 231 mm). In the control GT catchment, annual discharge during

243   1987-2012 was on average about 50 mm higher than in the RF catchment, mainly due to very

244   high annual flow (583 mm) during the year 2000. However, after 2004 the annual discharge

245   pattern was very similar in the RF and GT catchments, with discharge values during the one

246   year period July-June of on average 228 mm (range 30-476 mm, the highest value between
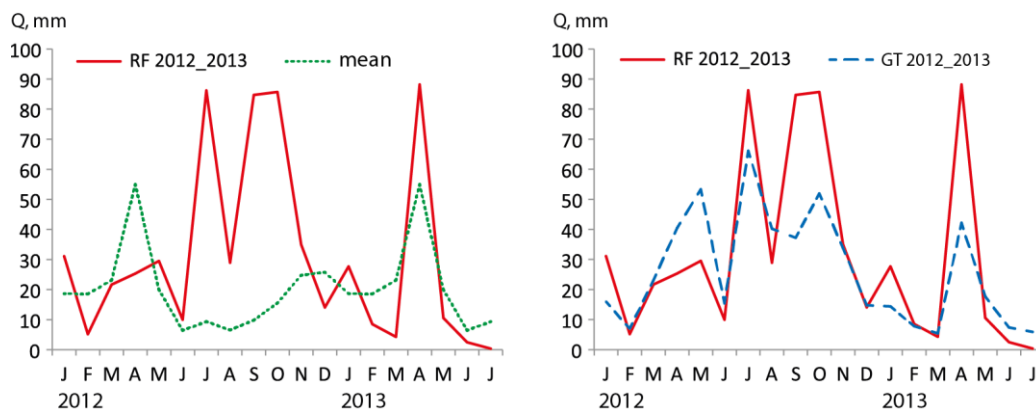
247   July 2012 and June 2013). Such high values should statistically occur only once every 100

248   years. Compared with mean monthly runoff discharge values, monthly discharge during July-

249   October 2012 was very high. The discharge pattern in the RF and GT catchments during this

250   period was rather similar (Fig. 2).

251

252

253

254 Figure 2. Monthly discharge (Q) January 2012-July 2013 in the Risfallet (RF) catchment

255 compared with: (Left) long-term mean monthly discharge 1987-2012 (green short dashed

256 line) in the RF catchment and (right) monthly discharge (2012-2013) in the Gusseltjärn (GT)

257 catchment (blue dashed line). Fertilization at end of June 2012 (↓).

258

259

260 **3. Results**

261 *3.1 Concentration of elements in surface water*

262 Estimations of background concentrations in the surface water of the RF catchment were

263 made from the correlations of the control GT catchment and the RF catchment for the

264 calibration period and the control GT values for the period January 2012 to July 2013. The

265 first half year in 2012 was before fertilization and the estimations could be compared to the

266 measured values for the RF catchment. Agreement between estimated and measured values

267 was good (Fig. 3 and 4). In July 2012, the effects of fertilization (June 2012) were obvious, as

268 could generally be seen (Fig. 3 and 4). The main focus of the results was on nitrogen but

269 additional elements, Ca, Mg and B, applied with the fertilizer also attracted considerable

270 interest.

271

272 *3.1.1 Nitrogen*

273 Fertilization was carried out with ammonium-nitrate, and nitrate (NO_3) in particular was

274 leached to surface waters since it is an easily moveable ion and may also be added from

275 oxidation of ammonium (NH_4). The highest nitrate concentration (one occasion 8.2 mg L^{-1})

276 was observed already in the first month after fertilization, in July 2013, compared with

277 summer values in the reference period of 0.05 mg L^{-1} and a highest value in the 25-year

278 period before fertilization of 0.3 mg L^{-1} on a few occasions, but generally below 0.1 mg L^{-1}.

279   For the full one-year period after fertilization, the mean concentration was 3.25 mg L^{-1},

280   compared with a calculated unfertilized value of 0.14 mg L^{-1} and a mean value for the total

281   25-year reference period of 0.055 mg L^{-1}, i.e. a 59-fold higher value (Table 3). High NO_3-N

282   concentrations occurred especially for the first six months after fertilization (Fig. 3).

283

284   The fertilizer applied contained equal amounts of the inorganic NO_3-N and NH_4-N, but NO_3

285   constituted the largest amount exported. In fact, NO_3 made up 91% of the total N leached and

286   the losses reached 19.8 kg ha^{-1} yr^{-1}, which is an increase for the one-year period of 19.5 kg ha^{-1}

287   yr^{-1}. It was the first five months after fertilization that dominated the excess outflow (Fig. 3).

288

289   Ammonium-nitrogen, NH_4-N, was also added with the fertilizer and the concentration in

290   stream water increased to 0.30 mg L^{-1}, but only during the first two months. However, there

291   was a significant over 10-fold increase in these two months, while for the year after

292   fertilization the mean increase was only 0.05 mg L^{-1}, i.e. 3-fold the unfertilized value (Table

293   3). In January 2013, there was a less high peak of 0.14 mg L^{-1} when actually the calculated

294   unfertilized concentration was 0 mg L^{-1} (Fig. 3). The very highest concentration observed on a

295   single sampling event was 0.84 mg L^{-1} in July 2012, when a value of 0.01 mg L^{-1} could be

296   expected in unfertilized conditions.

297

298   Leaching of NH_4-N was not as high as NO_3-N leaching, but reached a peak in the first month

299   after fertilization (Fig. 3). The total NH_4-N outflow for the first year was 0.6 kg ha^{-1} yr^{-1}, 15-

300   fold the background value (Table 4).

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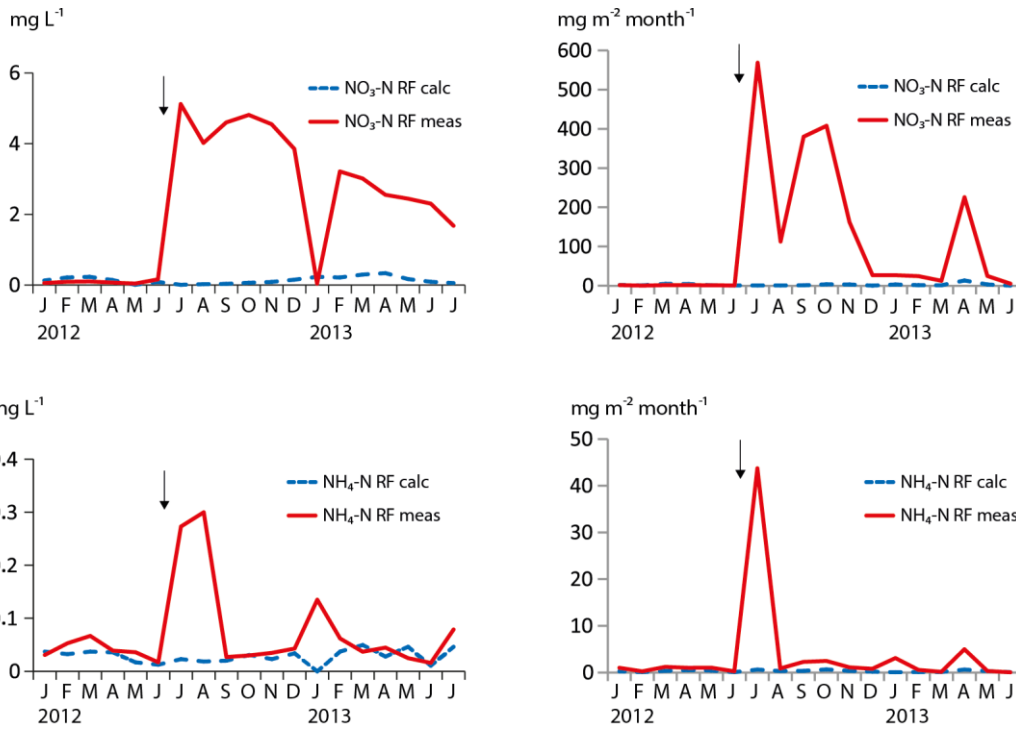
302

303

304   Figure 3. (Top row) Mean monthly stream water nitrate-nitrogen (NO_3-N) concentration (left)

305   and (right) NO_3-N outflow (mg m^{-2} month^{-1}) measured (meas, solid line) in the outlet from the

306   RF catchment in the period January 2012-July 2013 compared with calculated unfertilized

307   conditions (calc, broken line). Fertilization at end of June 2012 (↓). Second row,

308   corresponding graphs for ammonium-nitrogen (NH_4-N).

309

310   Total nitrogen is composed of organic and inorganic nitrogen. For Swedish waters in a

311   forested landscape such as the RF catchment, the organic form dominates, representing 75-

312   85% for the two catchments studied. In the reference GT catchment stream water, N_{org} was

313   83% for the 25-year calibration period and 68% in the one-year period after fertilization. In

314   the RF catchment stream water N_{org} made up 81% for the reference period, but reached only

315   slightly over 5% in the post-fertilization period. Instead NO_3-N dominated, with 94% of the

316   total nitrogen content (Table 3), while the N_{org} content remained on fairly stable levels (0.2-

317   0.3 mg L^{-1}).

318

319   Total nitrogen, N_{tot}, was on average 0.37 mg L^{-1} in unfertilized condition and the mean for the

320   first year after fertilization was 3.45 mg L^{-1}, i.e. an increase of 3.1 mg L^{-1} compared with the

321   calculated unfertilized concentration (Table 3). The very highest concentration observed in a

322   single sample was 9.5 mg L^{-1} in July and the calculated mean unfertilized value in that period

323   was 0.5 mg L^{-1}. However, the very highest concentration during the reference period was 2

324   mg L^{-1} but values over 0.7 mg L^{-1} only occurred three times in that 25-year long period and

325   could be considered uncertain. The N_{tot} peak was reached in July 2012 and from then the

326   concentration decreased in the rest of the one-year period to 2 mg L^{-1} in July 2013, with a

327   very low concentration (<1 mg L^{-1}) in January 2013 (Fig. 4).

328

329   Total nitrogen outflow in the first year after fertilization was 21.7 kg ha^{-1} and NO_3-N made up

330   91% and NH_4-N less than 3%, leaving about 6% as organic nitrogen (Table 4). The excess

331   amount of N exported reached 20.8 kg ha^{-1} for the first year, which represented 14% of the

332   amount of N applied. Nitrate showed similar patterns to N_{tot} as nitrate made up most of the

333   total nitrogen, while NH_4 only showed a short peak in the first month after fertilization (Fig.

334   3).

335

336   Table 3. Stream water pH and concentrations (mg L^{-1}) of elements in the control Gusseltjärn (GT)

337   catchment and the fertilized Risfallet (RF) catchment in the reference period 1987-2011 and after

338   fertilization in June 2012, from July 2012 to July 2013. Differences between measured and calculated

339   concentrations for RF presented as 'diff' together with significance level (sign.). CV = coefficient of

340   variation.

341

		GT before 1987-2011	GT after July2012-July 2013	RF before 1987-2011	RF calc July2012-July 2013	RF meas July2012-July 2013	RF diff	RF diff %	sign.
pH		5.78	5.96	5.77	5.95	5.71	-0.24		no
	CV	1.4	3.3	1.9	3.3	5.4			
Na		1.53	1.61	2.22	2.35	3.09	0.74	31	**
	CV	8	9	6	9	7			
K		0.35	0.39	0.38	0.42	0.63	0.21	50	*
	CV	14	52	17	52	17			
Ca		1.6	1.5	3.0	2.9	4.9	2.0	71	**
	CV	9	11	9	12	16			
Mg		0.33	0.34	0.59	0.59	1.07	0.48	81	**
	CV	10	10	11	10	14			
Cl		1.1	1.13	1.64	1.68	1.55	-0.13	-8	no
	CV	7	16	9	19	24			
NO_3-N		0.037	0.065	0.054	0.14	3.25	3.11	2221	***
	CV	71	22	78	78	45			
NH_4-N		0.011	0.018	0.013	0.028	0.07	0.042	154	no
	CV	54	47	80	47	114			
N_{org}		0.25	0.17	0.3	0.26	0.19	-0.07	-27	no
	CV	23	28	32	8	94			
N_{tot}		0.3	0.25	0.37	0.32	3.45	3.13	978	*
	CV	18	14	24	14	40			

342

343 *3.1.2 pH and base cations*

344 Fertilization had only a minor influence on pH, with an initial decrease of about 0.5 pH-units,

345 i.e. from pH ~6 to pH 5.5 (Fig. 4). For the full one-year period after fertilization, the pH was

346 0.2 units lower than calculated for the unfertilized conditions (Table 3), but with small and

347 insignificant changes in the last 6 months, i.e. January-June 2013.

348

349 Outflow of protons increased by 2.1 mg m^{-2} yr^{-1} in RF after fertilization (Table 4). There was

350 a strong initial peak during the first month after fertilization, which relates to several

351 processes, e.g. exchange of soil adsorbed protons, oxidation of NH_4, high groundwater levels

352   and high discharge (Fig. 2). Compared with the control, the increase in H^+ flow was

353   considerable, 1 mg m^{-2} $month^{-1}$, which was 10 times the calculated unfertilized flow (Table

354   4).

355

356   The fertilizer used included dolomite, furnishing additional Ca and Mg. Both elements

357   increased in stream water after fertilization. Mean Ca concentration during the 15 years before

358   fertilization was 3.0 mg L^{-1} and in the period after fertilization 4.9 mg L^{-1}. This can be

359   compared with the calculated unfertilized concentration of 2.9 mg L^{-1}, i.e. a mean increase of

360   2.0 mg L^{-1} (Table 3). In the short period July-October 2012, the four months after fertilization,

361   the Ca concentration was 5.7 mg L^{-1}, compared with the unfertilized value of 3.0 mg L^{-1}, i.e.

362   2.7 mg L^{-1} higher. Later, the difference was smaller (Fig. 4).

363

364   Fertilization increased the outflow of Ca from the RF catchment by 18 kg ha^{-1} yr^{-1} (224%),

365   compared with the calculated unfertilized runoff of 8 kg ha^{-1} yr^{-1} (Table 4). The increased Ca

366   outflow represented 82% of the amount of Ca applied in June 2012. The pattern with high

367   outflow during the first five months was similar to that observed for several other elements

368   (Fig 4).

369

370   The mean Mg concentration before fertilization was 0.59 mg L^{-1}, which was also the

371   calculated unfertilized value. In the first year after fertilization, the 1.5-year mean was 1.1 mg

372   L^{-1}, i.e. 0.5 mg L^{-1} higher (Table 3). The highest sample value was 1.7 mg L^{-1} in July 2012

373   compared with calculated unfertilized value of 0.6 mg L^{-1}, i.e. a 1.1 mg L^{-1} (1.8-fold) higher

374   value. As for Ca, the change decreased in the latter part of the study period (Fig. 4).

375

376   Mg was also applied with the fertilizer, at a rate of 12 kg ha^{-1}, and excess outflow of Mg was

377   observed. Background flow was ~1.5 kg ha^{-1} yr^{-1} but in the first full year after fertilization it

378   reached 5.6 kg ha^{-1} yr^{-1}, i.e. an increase of 4 kg ha^{-1} yr^{-1} or 255% (Table 4). The excess

379   outflow occurred during the whole year, but was most pronounced in the first five months

380   after fertilizer application and at spring flood in 2013.

381

382   The addition of elements by fertilization, especially Ca and Mg, influences other elements in

383   the soil. For example, the base cations sodium (Na) and potassium (K) enter into solution and

384   show higher values, and cause more export. The mean Na concentration in the period before

385   fertilization was 2.2 mg L^{-1} and after it was 3.1 mg L^{-1}, compared with a calculated

386   unfertilized value of 2.3 mg L^{-1}, i.e. an increase of 0.8 mg L^{-1} or 31% (Table 3). The largest

387   change occurred around three months after fertilization, in September, and reached 3.7 mg L^{-1}

388   ^{1}, compared with 2.3 mg L^{-1} as unfertilized (Fig. 4).

389

390   Sodium was not applied with the fertilizer but was still influenced by fertilizer application and

391   showed similar patterns to Ca and Mg, with excess outflow from the catchment. For Na, the

392   excess amount was 8 kg ha^{-1} yr^{-1} (Table 4).

393
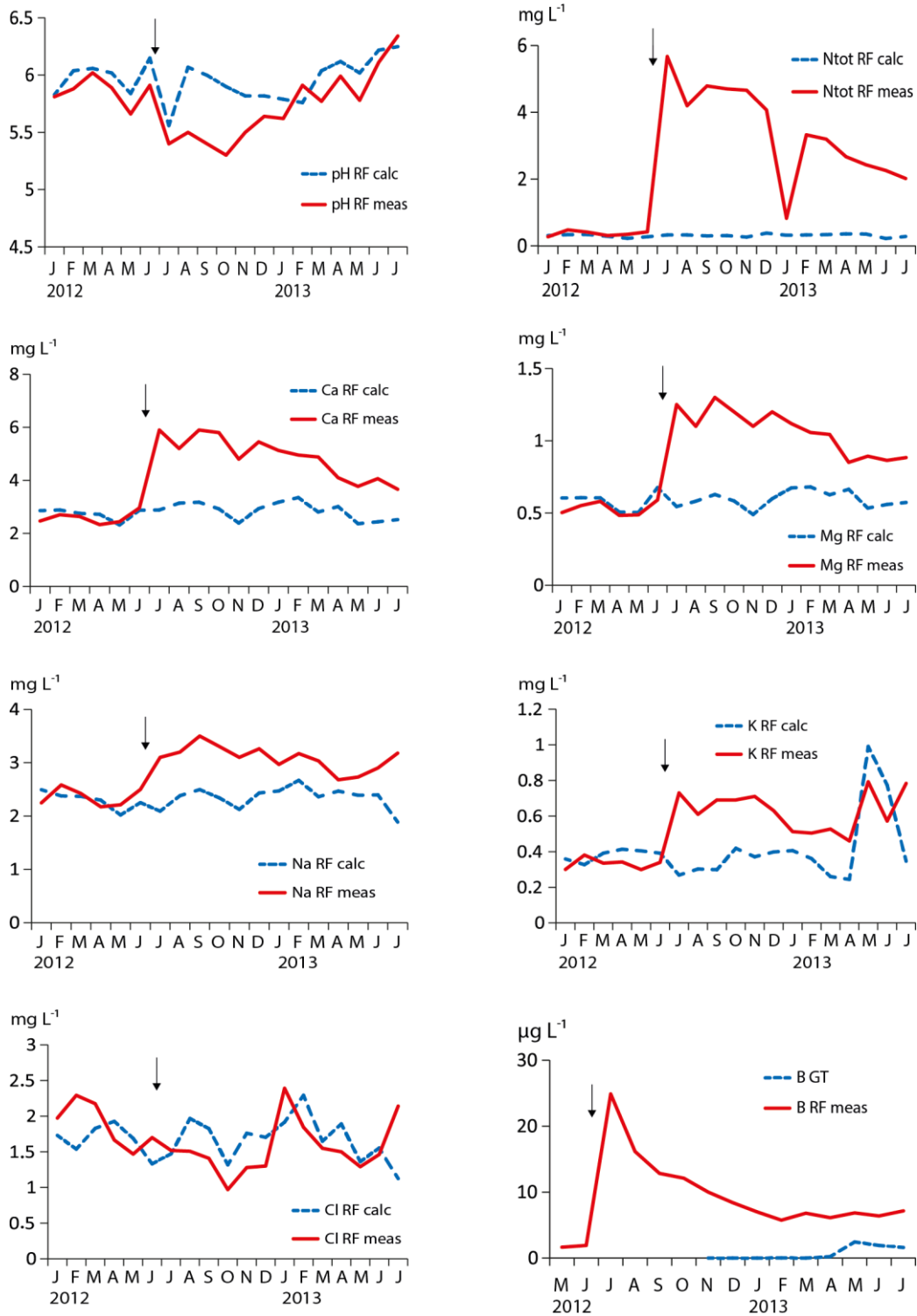
394

395

396   Figure 4. Mean monthly stream water pH and concentrations (mg L^{-1}) of total nitrogen (N$_{tot}$),

397   calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), chloride (Cl) and boron (B)

398   measured (meas) in the surface water outlet from the RF catchment in the period January

399   2012-July 2013 compared with calculated unfertilized conditions (calc). Fertilization at end

400   June 2012 (↓). Analyses of B in stream water samples from RF catchment started in May

401   2012 and from the control catchment (GT) in November 2013.

402

403   Potassium was also influenced by fertilization, with a mean value for the first year after

404   fertilization of 0.63 mg L^{-1}, compared with 0.4 mg L^{-1} for the reference period and also as

405   calculated for unfertilized conditions (Table 3). This represented a 50% increase in the K

406   concentration. For the first six months after fertilization, the changes in concentration were

407   fairly stable (0.3-0.4 mg L^{-1} higher values), but later the difference decreased (Fig 3). At the

408   end of the first year after fertilization, in May-June 2013, high concentrations were observed

409   both in the control area and in RF catchment stream water.

410

411   Potassium was not applied with the fertilizer but was still influenced by fertilizer application

412   and showed similar patterns to Ca and Mg, with excess outflow from the catchment. For K,

413   the excess amount was 2 kg ha^{-1} yr^{-1} (Table 4).

414

415   *3.1.3. Chloride, Cl and boron (B)*

416   Anions, such as chloride, are also influenced by increased concentrations of cations, but the

417   concentration of chloride (Cl) was 0.1 mg L^{-1} lower for the first year after fertilization.

418   However the monthly changes were very small and insignificant (Table 3) and actually for the

419   very first months the concentrations were up to 0.5 mg L^{-1} lower (Fig. 4).

420

421   Background outflow of Cl was somewhat higher from the RF catchment (3.6 kg ha^{-1} yr^{-1})

422   compared with the GT catchment (2.7 kg ha^{-1} yr^{-1}). The calculated unfertilized outflow was

423   2.8 kg ha^{-1} yr^{-1}, but reached 6.7 kg ha^{-1} yr^{-1} from the fertilized RF catchment. This was a

424 considerable increase (Table 4). It was mainly the first five months after fertilization and

425 April 2013 that showed high flows.

426

427 Concentration of B in the control (GT) catchment was low, 0-2.4 μg L^{-1} and for a few months

428 before fertilization in the RF catchment it was ~1.8 μg L^{-1}. After fertilization, a rapid change

429 in concentrations occurred and reached a maximum of 43 μg L^{-1} after one month. The mean

430 concentration for the first five months was 16 μg L^{-1}, after which the B concentration levelled

431 out at 5-6 μg L^{-1} (Fig. 4).

432

433 Estimated export of B during the first year after fertilization was 0.06 kg ha^{-1}, compared with

434 the 1 kg ha^{-1} applied, i.e. 6%. Background outflow of B was estimated to be 0.005 kg ha^{-1}.

435

436 *3.1.4. Element outflow*

437 Outflow of nitrogen, especially nitrate increased during the one-year period after fertilization,

438 i.e. July 2012-June 2013. Organic nitrogen decreased (Table 4). The outflow patterns for most

439 elements were fairly similar and strongly influenced by the discharge from the catchments as

440 NO_3-N outflow illustrates (Fig. 3). Outflow of other chemical elements from the two

441 catchments showed decreased acidity export and increased flow of base cations and Cl (Table

442 4).

443

444

445   Table 4. Outflow of elements (kg ha^{-1} yr^{-1}; for H$^+$ mg m^{-2} yr^{-1}) before and in the one-year period after

446   fertilization (July 2012-June 2013) from the control Gusseltjärn (GT) catchment and the fertilized

447   Risfallet (RF) catchment and change between measured outflow and calculated unfertilized outflow.

448

	GT before	GT after	RF before	RF calc after	RF meas after	Change	Change, %
H$^+$	0.74	0.47	0.55	0.34	2.45	2.10	605
Na	3.9	5.4	4.5	6.6	14.8	8.2	124
K	1.0	1.2	0.9	1.0	3.2	2.2	208
Ca	4.2	5.2	6.2	8.0	25.9	17.9	224
Mg	0.9	1.1	1.3	1.6	5.6	4.0	255
Cl	2.7	2.2	3.6	2.8	6.7	3.9	139
NO$_3$-N	0.07	0.16	0.12	0.36	19.8	19.5	5400
NH$_4$-N	0.036	0.057	0.025	0.039	0.61	0.57	1460
N$_{org}$	0.67	0.65	0.61	0.47	1.28	0.81	172
N$_{tot}$	0.77	0.87	0.76	0.87	21.7	20.8	2390

449

450

4. Discussion

452   Extraordinary circumstances allowed us to examine the effects of forest fertilization on

453   catchment waters and outflow of compounds to surface stream water in this study. The fact

454   that the fertilization was carried out over almost the whole catchment (~90%) and the

455   existence of long-term data series on hydrology and water chemistry provided excellent

456   opportunities for determining nutrient export to downstream surface waters. Nitrogen in

457   particular, but also other chemical compounds included in the fertilizer, such as Ca, Mg and

458   B, were studied.

459

460   Application of fertilizer by tractor, instead of earlier aerial application, protected streams and

461   other surface waters from direct inputs of fertilizer and the dominant freshwater hydrology in

462   the catchment resulted in little direct contact with groundwater. Instead, an unsaturated upper

463   soil profile provided storage possibilities for elements to become available later to plant and

464   tree roots. In contrast to many earlier studies of forest fertilization, where relatively small

465   parts of catchments were treated, the fact that around 90% of the Risfallet total catchment area

466   was fertilized made this a rather complete investigation.

467

468   Studies back in the early 1970s showed nitrogen outflow to downstream watercourses of up to

469   20% (Grip, 1982) after forest N fertilization by aerial application. High peaks of inorganic N

470   were observed in the first year after fertilization (Ehlert et al., 1974). Plot-wise investigations

471   showed leaching to groundwater of 0.6-2.7 kg N ha^{-1} yr^{-1} (Bergh et al., 2008). In ordinary

472   forest fertilization, the common nitrogen runoff has earlier been estimated to 5-10 % of

473   applied amount and export reaches 7-15 kg ha^{-1} N (Melin and Nômmik, 1988; Ring, 2007). In

474   a study of peatland aerial fertilization with 100 kg ha^{-1} N, the annual peak of N in the

475   discharge water reached 260 mg L^{-1} and the total loss of N during three months was 22% of

476   the amount applied (Lundin and Bergquist, 1985). Partly though, direct input to streams and

477   ditches occurred. However, in those studies fertilization mainly affected less than 50% of the

478   catchment area and the signal from only parts of the catchment treated would be minor as

479   compared to total catchment treatment. Reviews of earlier forest fertilization experiences

480   indicated the need for further investigations on nutritional management measures for forest

481   sustainability and treatment effects on the forest ecosystem and the surrounding environment

482   (Ingerslev et al., 2001). Best management practices (BMPs) based on that review showed the

483   potential to protect water quality following forest operations, but accurate assessments of the

484   overall effectiveness of BMPs are not possible because their benefits on different scales are

485   relatively unknown (Grace, 2005). Time scales have importance as well as share of catchment

486   treated. For the Risfallet site nitrogen deposition was in the range 5-6 kg N ha^{-1} yr^{-1}

487   (Vuorenmaa et al., 2012). Forest harvesting increased from 1.5 kg N ha^{-1} yr^{-1} in northern

488   Sweden (Löfgren et al., 2009) and was around 1990 estimated to 9.5 kg N ha^{-1} yr^{-1} for a

489   forested area and increased to 18 kg N ha^{-1} yr^{-1} in a four year period after cutting in southern

490   Sweden (Wiklander et al., 1990). In studies of cutting, drainage and shelterwood forestry in

491   central Sweden nitrogen outflow increased from 2.3 kg N ha^{-1} yr^{-1} to between 3.1 – and 3.5 kg

492   N ha^{-1} yr^{-1} during the first four years (Lundin, 1999). Hence, for this region, the runoff of

493   nitrogen during the first year after fertilization was high but the continuation in the following

494   year would show the duration in leaching.

495

496   A difference in fertilization between the RF catchment and earlier study areas was the use of

497   tractor compared with an aeroplane, which permitted fertilization directly into surface waters

498   to be avoided. The annual mean nitrate nitrogen concentration on 3.25 mg L^{-1} was almost as

499   high as the highest earlier reported concentration on 4 mg L^{-1} (Binkley et al., 1999). In the RF

500   catchment, 14% of the nitrogen applied was exported in the first year after fertilization, which

501   can be considered a rather large amount. One of the reasons for this was probably the high

502   water discharge during the first five months after application, 321 mm for the period

503   compared with a long-term average of 66 mm. This probably also influenced outflow of most

504   other elements reported.

505

506   Lowered pH was observed in the initial months after fertilization. There are several possible

507   reasons for this, one directly related to N fertilization being NH_4 exchange to protons in the

508   soil and nitrification of NH_4. Acidification effects of N fertilization were dealt with by

509   simultaneous addition of Ca and Mg and these elements were also included in exchange

510   processes in the soil, influencing pH and other cations such as Na and K. All base cations

511   increased in concentrations and leaching. Moreover, nitrification was probably enhanced by

512   the addition of Ca and Mg and these elements also contribute in proton exchange in the soil.

513   Nitrogen accumulation in soils tends to decrease Ca availability and lower pH (Perakis et al.,

514   2013).

515

516   Another circumstance that occurred with fertilization of the RF catchment was related to

517   hydrology. In the months following fertilization, heavy precipitation elevated the groundwater

518   level to surface soil horizons. In these soil layers, the pH was lower than in deeper soil layers

519   where water flow commonly occurred (Lundin, 1995). However, the lowered pH value

520   persisted for only a fairly short period and already in the beginning of 2013 it was similar to,

521   or even higher than, the 25-year reference value, probably influenced by added base cations.

522

523   Increases in other elements such as Na and K mainly resulted from soil exchange processes

524   and the fact that the NO_3 anion needs cation balance. The natural dolomite material, mainly as

525    $CaMg(CO_3)_2$ used in the fertilizer, could also have included small amounts of other minerals,

526   from e.g. clays, adding other elements. However, this probably did not have a major

527   influence.

528

529   During the first year after fertilization, rather high outflows of base cations of up to 82% (Ca)

530   and 46% (Mg) of applied amounts was observed. That the high outflow of Ca and Mg would

531   emanate directly from the fertilizer are be improbable with respect to water turnover time and

532   transport through the catchment soils. Instead, it is likely to be an effect of soil exchange

533   processes. The large export of mobile NO_3 ions carried away an equal amount of cations

534   originating mainly from the soil exchange pool, with a minor addition from the applied

535   fertilizer. Nitrate provided 1.4 kEq ha^{-1} in the first year and, together with Cl and SO_4 made

536   up 1.6 kEq ha^{-1}. These anions can be compared with the main cations exported, calculated to

537   be 1.68 kEq ha^{-1}, where Ca provided 0.9 kEq ha^{-1}, Na 0.36 kEq ha^{-1} and Mg 0.33 kEq ha^{-1}.

538   Anions and cations were fairly well balanced, indicating reasonable results.

539

540   Boron was added with the fertilizer to mitigate influences from Ca and Mg that might have

541   decreased B availability to the trees and caused B deficiency (Stone, 1990). Deposition of B

542   from the atmosphere is lower than that in outflow from Swedish catchments, meaning a net

543   loss of B (Ahl & Jönsson, 1972; Wikner, 1983). This is particularly the case in regions not

544   directly influenced by the sea, including the Risfallet catchment. However, information on B

545   turnover is limited and studies of B have been rather few. In addition, B requires fairly

546   complicated chemical analysis. However, a recent inventory of B in Swedish agricultural

547   fields and wastewater streams also included control values for semi-natural forests of 2.5 μg

548   B L^{-1}, compared with 22 μg L^{-1} from agricultural fields probably fertilized with B at some

549   time (Ahlgren et al., 2012). These values resemble those observed here in stream water from

550   the RF catchment after fertilization.

551

552

553   **5. Conclusions**

554   Despite heavy precipitation and considerable catchment discharge in the first five months

555   after forest fertilization, the first year losses of nitrogen were below 15% of the amount

556   applied. This could partly be related to the geophysiographical properties of the catchment

557   and partly to the use of ground (tractor) rather than aerial application, avoiding direct

558   spreading into watercourses. The high nitrate peak observed after fertilization did not lower

559   pH very substantially, perhaps because of the dolomite content of the fertilizer. However,

560   outflow of some elements, especially calcium, was high and soil acidity might have been

561   affected, even though the surface water was somewhat protected. Boron application was

562 followed by enhanced leaching, but concerned a minor fraction of the total boron applied. It

563 could be concluded that tractor fertilization has advantages mitigating direct input to surface

564 waters. Hydrological conditions could mean additional perquisites but could be difficult to

565 foresee. Considerable influence on base cation turnover was elucidated and low hazards

566 concerning boron loss were experienced.

567

568

569 **6. Acknowledgement**

578

579 **7. References**

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