Initial effects of forest N, Ca, Mg and B large-scale fertilization on surface water chemistry and leaching from a catchment in central Sweden

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Highlights

- Large scale forest fertilization resulted in considerable nitrogen and calcium leaching.
- High nitrate concentrations were reached in the first months after fertilization.
- Total nitrogen outflow in the first year was 14 % of applied fertilizer.
- Small pH decline with short-term duration occurred after the fertilization.
- Small amounts of boron (6 %) were leached after application.

Abstract

Highly increased use of biomass production is placing great demands on Swedish forests. Several silvicultural measures can be implemented to increase forest production and fertilization being addressed in this paper is one. Forest companies are now increasingly applying fertilizer, with the main nutrient needed for high forest growth being nitrogen (N). This study investigated how commercial N fertilization (150 kg N/ha, including also Ca, Mg and B) of the 45 ha forest catchment Risfallet in central Sweden affected chemical composition and runoff export in stream water during one year after the fertilization. This well-defined and long-term monitored catchment proved very suitable for studies of water quality and nutrient losses. The fertilizer consisted of ammonium nitrate (50/50 ammonium

and nitrate, respectively), plus calcium (Ca, 22 kg ha^{-1}) and magnesium (Mg, 12 kg ha^{-1}) to mitigate acidification and boron (B 1.1 kg ha^{-1}) to compensate for decreased boron availability. The study was carried out according to the paired catchment method using a control area and a calibration period. Data from the after treatment period were compared with previous 25-year monitoring data for the catchment and also data for a similar 83 ha control catchment, Gusseltjärn, in the same region. During the first year after treatment, the nitrate concentration in stream water increased from 0.05 mg L^{-1} to 3.3 mg L^{-1} on average. Other elements showing increased concentrations were ammonium (300%), B (3-fold), Mg (80%), Ca (60%), potassium (K) (50%) and sodium (Na) (40%). The pH decreased in the first half-year by 0.2 pH-units. One year after treatment, 14% of the N applied had leached from the catchment.

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

1. Introduction

There is a need for high biomass production to meet growing demand for wood products. Higher forest biomass production can be achieved by better silvicultural measures, including addition of nitrogen (N) being the main limiting nutrient in boreal forests (Nohrstedt, 2001). Forty years ago, this was a widely used method to increase growth, but during a period of high atmospheric N deposition its use had been fairly limited in Sweden in recent decades. However, there is currently new interest in N fertilization together with small additions of calcium (Ca), magnesium (Mg) and boron (B), despite elevated N deposition, being c. 5 kg ha^{-1} $year^{-1}$, with no overall significant, clear trend for a decrease (Vuorenmaa et al., 2009). Emissions have declined, but the effect on deposition is not clear (Nyiri et al., 2009).

Investigations on N deposition still show much higher inputs than outputs in surface waters from catchments. Furthermore, there is a clear correlation between high N deposition and high leaching to watercourses (LeGall, 2012). Additional N fertilization is thus likely to increase leaching. Nitrogen is also stored in the catchment forest soils and this increasing accumulation will probably also increase leaching. There are particularly high risks of leaching at sites with low CN-ratios (Gundersen et al., 2006).

Despite these unwanted N load effects, the needs and production objectives of forestry are considered more important and new attempts are being made to increase yields of timber, energy biomass and other economically valuable forest by-products. Long-term research on the effects of forest fertilization on biomass yield has shown that significant increases in production can be achieved (Nohrstedt, 2001; Pettersson and Högbom, 2004). A great need for increased future production is predicted (Bergh et al., 2008). However, the consequences for environmental values are still being discussed, especially in light of changes in the environment as regards elevated N deposition and climate change, which together may alter nutrient turnover in soils and the total catchment. On the other hand, N fertilization could mitigate higher atmospheric carbon dioxide (CO_2) content by increasing forest growth and carbon (C) storage in organic material in the standing crop and in the soil compartment (Nohrstedt, 2001). Consequently, N fertilization could increase C sequestration (Högberg, 2007; Hyvönen et al., 2008).

Nitrogen fertilization has multiple effects on soil, vegetation and water. Enhanced tree growth has been reported and is of course the main reason for N fertilization. Adverse effects in terms of altered ground vegetation composition, increased nitrification resulting in increased risks of 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

2. Material and methods

2.1 Catchment characteristics

The study was based on the catchment concept and involved a fertilized catchment (RF) and a control catchment 120 km NW in Dalecarlia, both in the boreal region of central Sweden (Fig. 1). Both catchments have been monitored on discharge and major chemical constituents for long periods (~25 years). The fertilized catchment RF was part of a project studying groundwater acidification and monitoring started in 1987 (Lundin, 1995). The control catchment Gusseltjärn (GT) was established back in 1973 in the Siljansfors experimental forest under the supervision of the Swedish University of Agricultural Sciences and can mainly be considered protected from forestry operations (Bergqvist and Grip, 1975). Both catchments are located in the northern boreal coniferous region of Sweden, on glacial till soils above the highest coastline. The soil is rather coarse, mainly characterized by a sandy till overlying granite bedrock at RF and porphyry bedrock at GT. Considerable parts of both catchments have rather thick quaternary deposits and the groundwater level is often below 1-2 m depth. In RF this results in the dominant moisture class being fresh (Fig. 1). Besides the dominating well-drained mineral soils, partly with slightly higher groundwater level and then being moist, the catchments also contain small mires and wet areas being thin peatlands and, in GT, even a small tarn, but for long periods the deep groundwater pathways prevail and form discharging surface waters.

The catchment size is 83 ha for GT and 45 ha for RF (Table 1). Stand age differs, as GT is dominated by over 100-year-old trees and with younger forest (approx. 60 years) on 20% of the area with estimated average stand volume on c. 200 m^3 ha^{-1}. In RF the stand age is rather uniformly ~35 years and is dominated by pine (*Pinus silvestris*). The ground vegetation class is dominated by low grass types, a medium nutrient rich type deviating from rich herb types

and poor shrub types. The RF catchment is somewhat more fertile in slightly better climate conditions, but the differences are not great (Table 1). The stand in RF was thinned in 2009, with about 35% of the trees harvested and the estimated volume in 2006 being 184 m^3 ha^{-1} and in 2012 144 m^3 ha^{-1}.

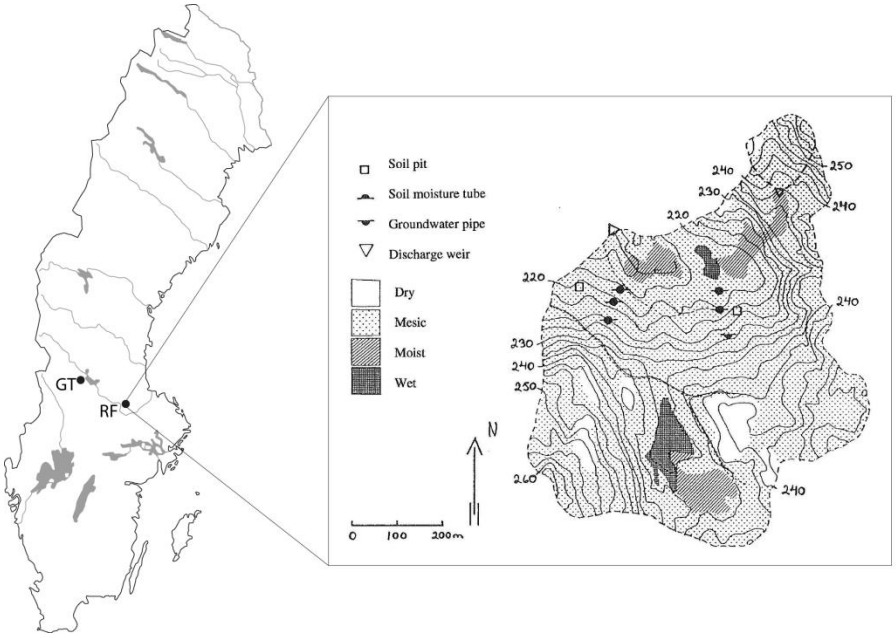

Figure 1. Left: Map of Sweden showing geographical location of the Gusseltjärn (GT) and Risfallet (RF) catchments. Right: Detailed map of the Risfallet catchment showing hydrological installations, contour lines (m.a.m.s.l.) and distribution of moisture classes (Lundin, 1995).

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

Water sampling was carried out monthly for almost the entire period and was intensified to up to four samples per month during a five-month period following fertilization. Reference values for the calibration period were calculated as monthly means for the period and used as calibration values. Means of monthly values were calculated together with coefficients of variation. Significance of changes were tested with confidence intervals (t-test). Calculations of reference concentrations for the period after fertilization was mainly carried out based on a quotient RF/GT from the calibration period and the measured value at the control GT for the period after fertilization, i.e. July 2012 to July 2013. For most elements the mean and variation for GT and RF during the calibration period didn't differ significantly. Nor did the mean values of studied elements for GT in the period after fertilization differ from the values in the calibration period. Deviating from this was only organic nitrogen.

Outflow of elements was calculated from the monthly concentrations and continuously measured discharge at the catchment discharge station. The technique for element flow calculations was based on interpolated daily concentrations and daily determined discharge at the V-notch weir equipped with a water level chart recorder. The functioning of the weir and the water level recorder was checked bi-weekly for most of the study period and was found to be very good. However, for single years the monthly sampling and chemical content determinations were somewhat sparse giving uncertainties at high flow periods. On the other hand, the very long time record would partly compensate for this and also the fact that the water flowpaths through the soil at both catchments were fairly long, partly levelling out the large variations often occurring in catchments with upper soil layer flowpaths. Estimations of element flows in the calibration period could be considered good and for the period after fertilization, the sampling frequency was higher giving appropriate outflow values.

Chemical analyses were carried out by laboratories at SLU, Uppsala, using standardized techniques according to SWEDAC (Swedish Board for Accreditation and Conformity Assessment). For the elements presented in this paper, pH was measured with combination electrodes, base cations with optical ICP OES (inductively coupled plasma-optical emission spectrometry), anions with ion chromatography (Dionex ICS 1100) and total N mainly by persulphate digestion and later by combustion (SS-EN 12260:2004). Boron was analysed with digestion in 0.5% HNO_3 and measurement in ICP-MS (inductively coupled plasma-mass spectrometry).

2.3 Precipitation

Daily precipitation values in the RF catchment were calculated from measured values at Avesta national climate station, 23 km to the SSW. The precipitation regime (monthly and annual sums) was classified according to Eriksson (1979) based on precipitation series from 1944 to June 2013.

Mean annual precipitation sum in the RF catchment during 1987-2012 was almost 690 mm (range 520 mm in 1995 to 879 mm in 2000). In the year 2012 the precipitation was 858 mm. During the one year period July 2012-June 2013, the precipitation sum was 782 mm, but in March 2013 it was extremely low (1.6 mm), while in the period April-September 2012 it was extremely high (560 mm).

2.4 Discharge

As the catchment area is rather small (45 ha), the average discharge is only a few litres per second and there is commonly no flow at all during dry periods. Consequently, long periods

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

After heavy rain or large snow-melt events, the peak flow sometimes exceeded 5 mm per day. Discharge usually stayed low because of relatively great soil depth, large groundwater reservoirs and a deep unsaturated soil water zone within most of the catchment area. However, after heavy rainfall in July 2012, discharge reached 19.1 mm during one day.

The annual (January-December) discharge in the RF catchment during 1987-2012 varied from 98 mm to 457 mm (mean 231 mm). In the control GT catchment, annual discharge during 1987-2012 was on average about 50 mm higher than in the RF catchment, mainly due to very high annual flow (583 mm) during the year 2000. However, after 2004 the annual discharge pattern was very similar in the RF and GT catchments, with discharge values during the one year period July-June of on average 228 mm (range 30-476 mm, the highest value between July 2012 and June 2013). Such high values should statistically occur only once every 100 years. Compared with mean monthly runoff discharge values, monthly discharge during July-October 2012 was very high. The discharge pattern in the RF and GT catchments during this period was rather similar (Fig. 2).

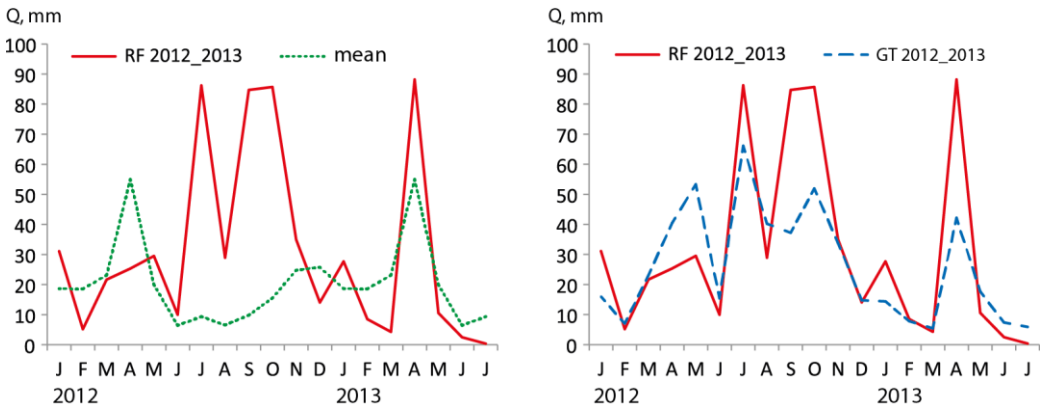

Figure 2. Monthly discharge (Q) January 2012-July 2013 in the Risfallet (RF) catchment compared with: (Left) long-term mean monthly discharge 1987-2012 (green short dashed line) in the RF catchment and (right) monthly discharge (2012-2013) in the Gusseltjärn (GT) catchment (blue dashed line). Fertilization at end of June 2012 (↓).

3. Results

3.1 Concentration of elements in surface water

Estimations of background concentrations in the surface water of the RF catchment were made from the correlations of the control GT catchment and the RF catchment for the calibration period and the control GT values for the period January 2012 to July 2013. The first half year in 2012 was before fertilization and the estimations could be compared to the measured values for the RF catchment. Agreement between estimated and measured values was good (Fig. 3 and 4). In July 2012, the effects of fertilization (June 2012) were obvious, as could generally be seen (Fig. 3 and 4). The main focus of the results was on nitrogen but additional elements, Ca, Mg and B, applied with the fertilizer also attracted considerable interest.

3.1.1 Nitrogen

Fertilization was carried out with ammonium-nitrate, and nitrate (NO_3) in particular was leached to surface waters since it is an easily moveable ion and may also be added from oxidation of ammonium (NH_4). The highest nitrate concentration (one occasion 8.2 mg L^{-1}) was observed already in the first month after fertilization, in July 2013, compared with summer values in the reference period of 0.05 mg L^{-1} and a highest value in the 25-year period before fertilization of 0.3 mg L^{-1} on a few occasions, but generally below 0.1 mg L^{-1}.

For the full one-year period after fertilization, the mean concentration was 3.25 mg L^{-1}, compared with a calculated unfertilized value of 0.14 mg L^{-1} and a mean value for the total 25-year reference period of 0.055 mg L^{-1}, i.e. a 59-fold higher value (Table 3). High NO_3-N concentrations occurred especially for the first six months after fertilization (Fig. 3).

The fertilizer applied contained equal amounts of the inorganic NO_3-N and NH_4-N, but NO_3 constituted the largest amount exported. In fact, NO_3 made up 91% of the total N leached and 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} yr^{-1}. It was the first five months after fertilization that dominated the excess outflow (Fig. 3).

Ammonium-nitrogen, NH_4-N, was also added with the fertilizer and the concentration in stream water increased to 0.30 mg L^{-1}, but only during the first two months. However, there was a significant over 10-fold increase in these two months, while for the year after fertilization the mean increase was only 0.05 mg L^{-1}, i.e. 3-fold the unfertilized value (Table 3). In January 2013, there was a less high peak of 0.14 mg L^{-1} when actually the calculated unfertilized concentration was 0 mg L^{-1} (Fig. 3). The very highest concentration observed on a single sampling event was 0.84 mg L^{-1} in July 2012, when a value of 0.01 mg L^{-1} could be expected in unfertilized conditions.

Leaching of NH_4-N was not as high as NO_3-N leaching, but reached a peak in the first month after fertilization (Fig. 3). The total NH_4-N outflow for the first year was 0.6 kg ha^{-1} yr^{-1}, 15-fold the background value (Table 4).

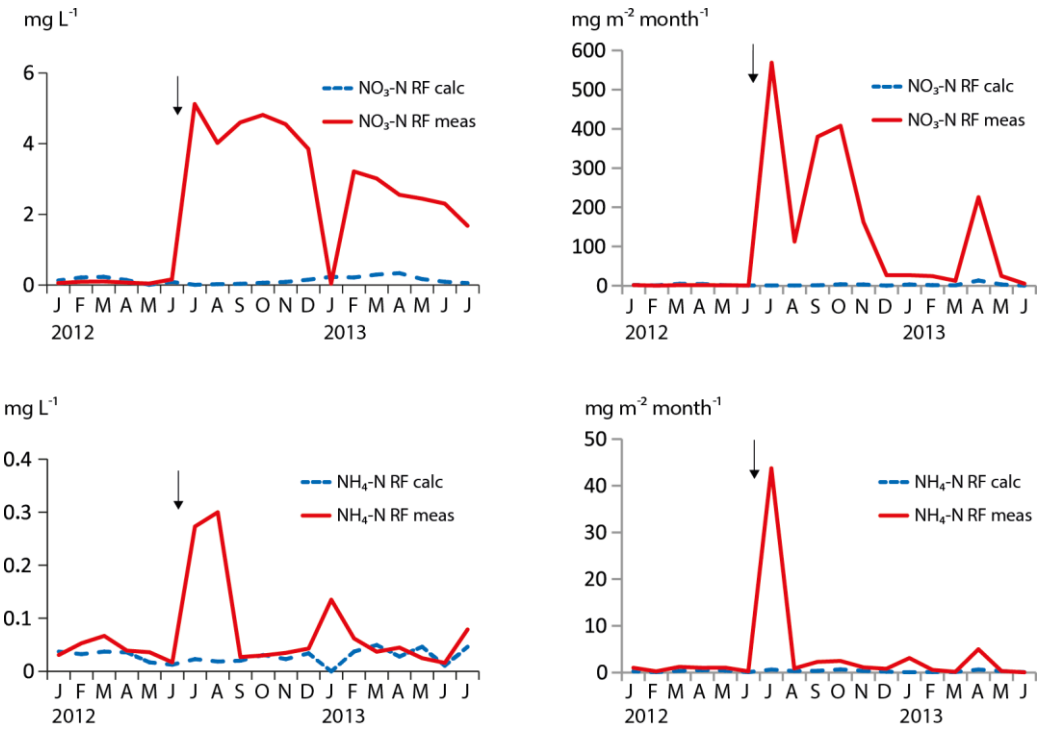

Figure 3. (Top row) Mean monthly stream water nitrate-nitrogen (NO_3-N) concentration (left) and (right) NO_3-N outflow (mg m^{-2} $month^{-1}$) measured (meas, solid line) in the outlet from the RF catchment in the period January 2012-July 2013 compared with calculated unfertilized conditions (calc, broken line). Fertilization at end of June 2012 (↓). Second row, corresponding graphs for ammonium-nitrogen (NH_4-N).

Total nitrogen is composed of organic and inorganic nitrogen. For Swedish waters in a forested landscape such as the RF catchment, the organic form dominates, representing 75-85% for the two catchments studied. In the reference GT catchment stream water, N_{org} was 83% for the 25-year calibration period and 68% in the one-year period after fertilization. In the RF catchment stream water N_{org} made up 81% for the reference period, but reached only slightly over 5% in the post-fertilization period. Instead NO_3-N dominated, with 94% of the total nitrogen content (Table 3), while the N_{org} content remained on fairly stable levels (0.2-0.3 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 , 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

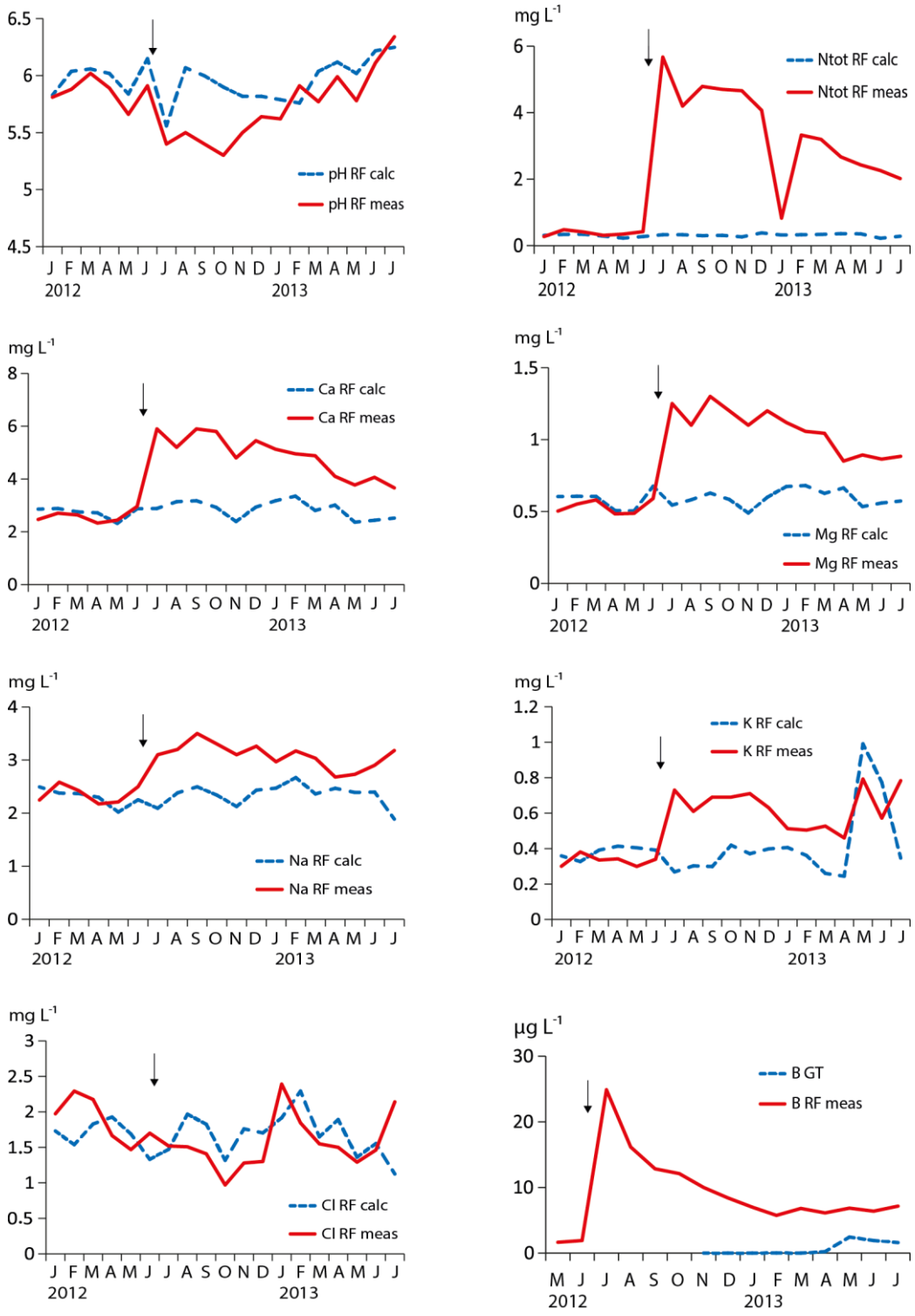

Figure 4. Mean monthly stream water pH and concentrations (mg L^{-1}) of total nitrogen (N_{tot}), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), chloride (Cl) and boron (B) measured (meas) in the surface water outlet from the RF catchment in the period January

2012-July 2013 compared with calculated unfertilized conditions (calc). Fertilization at end June 2012 (↓). Analyses of B in stream water samples from RF catchment started in May 2012 and from the control catchment (GT) in November 2013.

Potassium was also influenced by fertilization, with a mean value for the first year after fertilization of 0.63 mg L^{-1}, compared with 0.4 mg L^{-1} for the reference period and also as calculated for unfertilized conditions (Table 3). This represented a 50% increase in the K concentration. For the first six months after fertilization, the changes in concentration were fairly stable (0.3-0.4 mg L^{-1} higher values), but later the difference decreased (Fig 3). At the end of the first year after fertilization, in May-June 2013, high concentrations were observed both in the control area and in RF catchment stream water.

Potassium was not applied with the fertilizer but was still influenced by fertilizer application and showed similar patterns to Ca and Mg, with excess outflow from the catchment. For K, the excess amount was 2 kg ha^{-1} yr^{-1} (Table 4).

3.1.3. Chloride, Cl and boron (B)

Anions, such as chloride, are also influenced by increased concentrations of cations, but the concentration of chloride (Cl) was 0.1 mg L^{-1} lower for the first year after fertilization. However the monthly changes were very small and insignificant (Table 3) and actually for the very first months the concentrations were up to 0.5 mg L^{-1} lower (Fig. 4).

Background outflow of Cl was somewhat higher from the RF catchment (3.6 kg ha^{-1} yr^{-1}) compared with the GT catchment (2.7 kg ha^{-1} yr^{-1}). The calculated unfertilized outflow was 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
Nt_{ot}	0.77	0.87	0.76	0.87	21.7	20.8	2390

449

450

451 **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}

(Vuorenmaa et al., 2012). Forest harvesting increased from 1.5 kg N ha^{-1} yr^{-1} in northern Sweden (Löfgren et al., 2009) and was around 1990 estimated to 9.5 kg N ha^{-1} yr^{-1} for a forested area and increased to 18 kg N ha^{-1} yr^{-1} in a four year period after cutting in southern Sweden (Wiklander et al., 1990). In studies of cutting, drainage and shelterwood forestry in central Sweden nitrogen outflow increased from 2.3 kg N ha^{-1} yr^{-1} to between 3.1 – and 3.5 kg N ha^{-1} yr^{-1} during the first four years (Lundin, 1999). Hence, for this region, the runoff of nitrogen during the first year after fertilization was high but the continuation in the following year would show the duration in leaching.

A difference in fertilization between the RF catchment and earlier study areas was the use of tractor compared with an aeroplane, which permitted fertilization directly into surface waters to be avoided. The annual mean nitrate nitrogen concentration on 3.25 mg L^{-1} was almost as high as the highest earlier reported concentration on 4 mg L^{-1} (Binkley et al., 1999). In the RF catchment, 14% of the nitrogen applied was exported in the first year after fertilization, which can be considered a rather large amount. One of the reasons for this was probably the high water discharge during the first five months after application, 321 mm for the period compared with a long-term average of 66 mm. This probably also influenced outflow of most other elements reported.

Lowered pH was observed in the initial months after fertilization. There are several possible reasons for this, one directly related to N fertilization being NH_4 exchange to protons in the soil and nitrification of NH_4. Acidification effects of N fertilization were dealt with by simultaneous addition of Ca and Mg and these elements were also included in exchange processes in the soil, influencing pH and other cations such as Na and K. All base cations 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

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

Boron was added with the fertilizer to mitigate influences from Ca and Mg that might have decreased B availability to the trees and caused B deficiency (Stone, 1990). Deposition of B from the atmosphere is lower than that in outflow from Swedish catchments, meaning a net loss of B (Ahl & Jönsson, 1972; Wikner, 1983). This is particularly the case in regions not directly influenced by the sea, including the Risfallet catchment. However, information on B turnover is limited and studies of B have been rather few. In addition, B requires fairly complicated chemical analysis. However, a recent inventory of B in Swedish agricultural fields and wastewater streams also included control values for semi-natural forests of 2.5 μg B L^{-1}, compared with 22 μg L^{-1} from agricultural fields probably fertilized with B at some time (Ahlgren et al., 2012). These values resemble those observed here in stream water from the RF catchment after fertilization.

5. Conclusions

Despite heavy precipitation and considerable catchment discharge in the first five months after forest fertilization, the first year losses of nitrogen were below 15% of the amount applied. This could partly be related to the geophysiographical properties of the catchment and partly to the use of ground (tractor) rather than aerial application, avoiding direct spreading into watercourses. The high nitrate peak observed after fertilization did not lower pH very substantially, perhaps because of the dolomite content of the fertilizer. However, outflow of some elements, especially calcium, was high and soil acidity might have been 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

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576 Reference data from the GT site were available through collaboration with the SLU's
577 experimental forest in Siljansfors site.
578

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