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**Ecosystems**

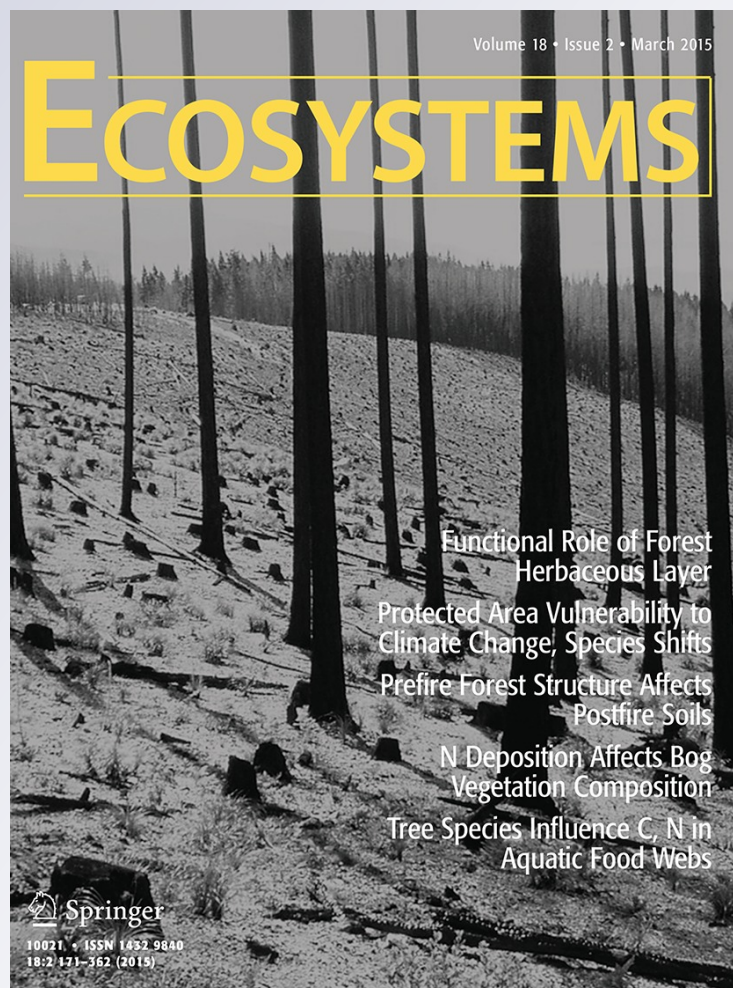
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# Land Cover Controls the Export of Terminal Electron Acceptors from Boreal Catchments

Marjo Palviainen,<sup>1\*</sup> Jouni Lehtoranta,<sup>2</sup> Petri Ekholm,<sup>2</sup> Tuija Ruoho-Airola,<sup>3</sup> and Pirkko Kortelainen<sup>2</sup>

<sup>1</sup>Department of Forest Sciences, University of Helsinki, P.O. Box 27, 00014 Helsinki, Finland; <sup>2</sup>Finnish Environment Institute (SYKE), P.O. Box 140, 00251 Helsinki, Finland; <sup>3</sup>Finnish Meteorological Institute, P.O. Box 503, 00101 Helsinki, Finland

## ABSTRACT

NO<sub>3</sub>, Mn, Fe, and SO<sub>4</sub> act as terminal electron acceptors (TEAs), modifying mineralization pathways and coupling biogeochemical cycles. Although single TEA concentrations and fluxes have been intensively studied, the factors regulating the simultaneous fluxes and molar ratios of TEAs are poorly elucidated. We studied the mean concentrations, exports, and molar ratios of TEAs from 27 boreal catchments differing in land cover (percentage of agricultural land, peatland, forest, and built-up area) during the years 2000–2011. TEA exports and molar ratios were strongly controlled by land cover and only a little by atmospheric deposition. Fields produced the highest export of TEAs, particularly NO<sub>3</sub>. Peatland was linked to low NO<sub>3</sub> and SO<sub>4</sub>, but high Fe exports. NO<sub>3</sub>, Mn, and Fe

exports from forests were low, SO<sub>4</sub> having proportionally the highest export. Together, the percentages of field and peatland predicted 93, 80, 75, and 67% of the variation in the export of NO<sub>3</sub>, Mn, Fe, and SO<sub>4</sub>, respectively. The variable export of TEAs having different availability and physical behavior may create different premises for anaerobic mineralization in downstream systems, which adds a new dimension to the link between terrestrial system, land use, and environmental problems, such as eutrophication and climate change.

**Key words:** atmospheric deposition; climate change; eutrophication; iron; land cover; manganese; nitrate; organic carbon; sulfate.

## INTRODUCTION

Only linking the ecological status of surface waters to the load of nutrients and organic C may prove to be too narrow a perspective toward understanding and managing aquatic ecosystems. The export of terrestrial organic C and primary production

determine the potential for mineralization in a body of water. Microbial redox reactions consuming terminal electron acceptors (TEAs) are central in mineralization processes. TEAs include a set of common compounds, for example, O<sub>2</sub>, NO<sub>3</sub>, Mn and Fe oxides, and SO<sub>4</sub>. Through the primary and secondary redox reactions, TEAs contribute to (i) the availability of nutrients (Rysgaard and others 2001; Smolders and others 2006, 2010; Lehtoranta and others 2009; Burgin and others 2011; Hall and Silver 2013), (ii) the fluxes of greenhouse gases (Conrad 1996; Dise and Verry 2001; Davidson and Seitzinger 2006; Raghoebarsing and others 2006; Beal and others 2009; Knittel and Boetius

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\*Corresponding author; e-mail: marjo.palviainen@helsinki.fi

2009; Cai and others 2012; Bridgham and others 2013; Kortelainen and others 2013), and (iii) the mobilization of harmful substances (Islam and others 2004; Burgin and others 2011). For example, a generation of toxic sulfides (Wang and Chapman 1999) may block Fe cycling and enhance the release of P from bottom sediments into water (Smolders and others 2006, 2010; Lehtoranta and others 2009). Therefore, the ecological status of an aquatic system is also a function of TEAs, as they partly control mineralization processes and pathways. Yet, the fluxes of TEAs and the factors regulating them at the catchment level have remained poorly quantified.

Depending on the availability of organic C and TEAs, and the morphological features of the system, TEAs and their end products may escape an aquatic system (i) untouched, (ii) in a more reduced or oxidized, yet dissolved form, (iii) in a gaseous form ( $N_2$ ,  $N_2O$ ,  $H_2S$ ) after the reduction process, or (iv) through burial of solid compounds (N, Mn, Fe, S) in bottom sediments. Owing to such losses, an external source of TEAs or their precursors is needed to maintain TEA concentrations in the system, although endogenous oxidation processes may sustain a specific mineralization pathway in surface sediments for significant periods (that is, reductive and oxidative cycles of Fe or S; Urban and others 1994; Holmer and Storkholm 2001; Thomsen and others 2004).

Atmosphere, soil, and bedrock form the primary sources of TEAs, while land cover may markedly modify the TEA export from the catchment into aquatic systems (Figure 1). In agricultural fields, fertilization increases the fluxes of  $NO_3$  and  $SO_4$  (Korkman 1973; Mattsson and others 2007) and tillage those of Fe oxides by accelerating soil erosion (Ekholm and Lehtoranta 2012). In peatland,

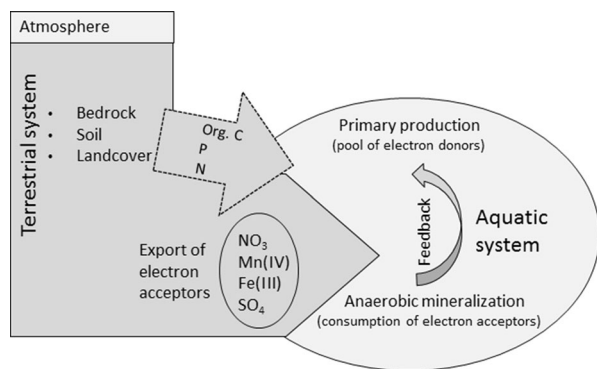
the export of TEAs may be governed by the peat itself and by soil underneath through anaerobic microbial redox processes, driven by natural or man-made fluctuation of the water level (Martikainen and others 1993; Regina and others 1996; Mörth and others 1999; Eimers and others 2004; Kane and others 2013). In contrast to water-logged peatland, the prevailing oxic conditions in forests may maintain the ability of soil to retain TEAs (MacDonald and others 2002; Fuss and others 2011).  $NO_3$  may also be retained through the assimilation of biota to long-term organic pools, which reduces the flux of  $NO_3$  from boreal forests (Tamm 1991; Kortelainen and others 2006). In addition to land cover, atmospheric deposition may be an important driver affecting TEA export (Dise and Wright 1995; Gundersen and others 2006; Mattsson and others 2007), but the separate and mutual importance of these two factors regulating TEA export is largely unknown in boreal catchments. Moreover, most of the studies on TEAs have not recognized the inherent connection of TEAs, but have looked at specific TEAs separately from the viewpoint of acidification, erosion, eutrophication, and pollution (Henriksen and others 1992; Curtis and others 2005; Lehtoranta and others 2009; Ekholm and Lehtoranta 2012; Kopáček and others 2013).

The objective of this study was to investigate the export and molar share of TEAs ( $NO_3$ , Mn, Fe, and  $SO_4$ ) and how they vary in relation to the catchment land cover. To this aim, we examined numerous boreal catchments differing in land cover, hypothesizing that land cover and atmospheric deposition control the average annual export and the molar proportion of TEAs from the catchments.

## MATERIALS AND METHODS

### Study Areas

The analysis was made for 27 catchments differing in land cover (Figure 2; Table 1). The catchments were located all over boreal Finland, between latitudes 60 and 68°N, and their areas ranged from 0.1 to 4,283 km<sup>2</sup>. Land cover was divided into five percentual classes: peatland (open and forested peatlands, Peat%), forests on mineral soils (Forest%), agricultural fields (Field%), built-up areas (Built-up%), and water (Water%). The land-cover data were derived from the national CORINE land-cover (CLC2006) database (25 × 25 m grids), except for Field% and Built-up%. In the national CORINE database, Peat% was based on the topographical



**Figure 1.** Factors controlling the export of major electron acceptors from terrestrial systems affecting mineralization and the coupling of element cycles in aquatic systems.

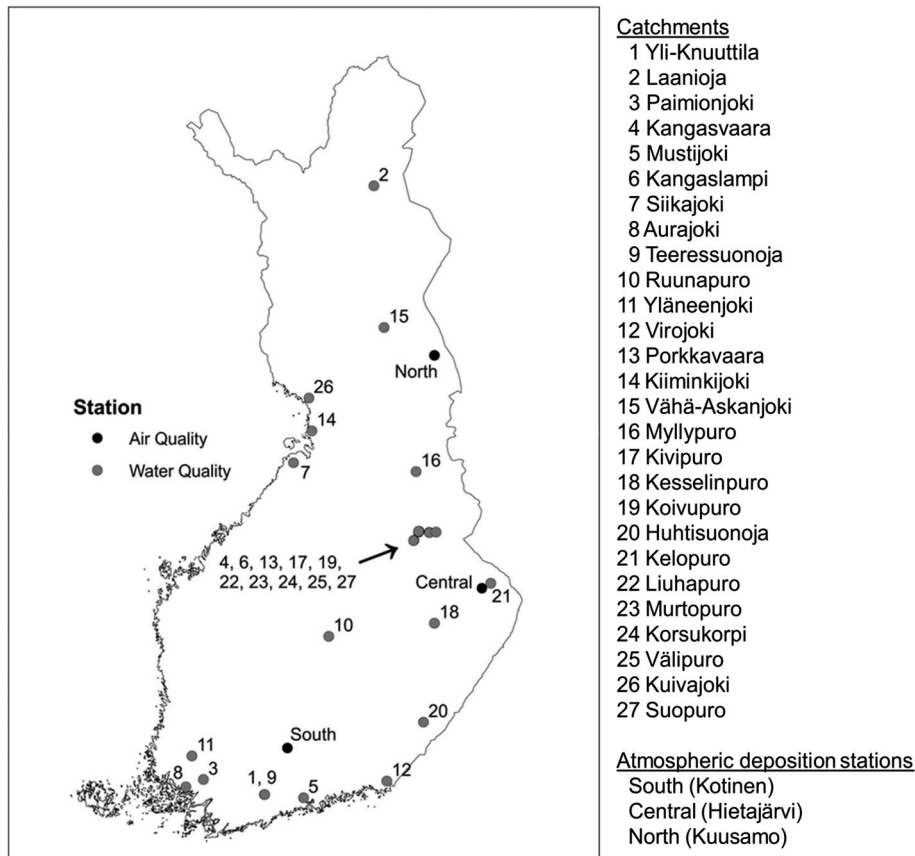


Figure 2. Location of the catchments and atmospheric deposition stations.

database of the National Land Survey of Finland. Peat% includes areas in which peatland vegetation dominates and the thickness of the peat layer is at least 30 cm. Field% was obtained from the field plot register owned by Mavi (Agency for Rural Affairs), in which all the field plots receiving area-based subsidies in 2010 were digitized. Built-up% was derived from the Urban layer database (25 × 25 m grids) of the Finnish Environment Institute. Land-cover data for small forested catchments (4, 6, 13, 17, 19, 22, 23, 24, 25, 27) were derived from field inventories.

Forest% ranged from 30 to 92 (average 62, Table 1) and was dominated by coniferous species, mainly Norway spruce (*Picea abies* Karsten) and Scots pine (*Pinus sylvestris* L.). Field% varied between 0 and 42 (average 6.7) and Peat% between 0 and 70 (average 28). Water areas, mainly small lakes, covered only 0–4% (average 1%) of the catchments. Built-up% included paved surfaces, such as urban or industrial areas, road networks, and aggregate extraction sites, and accounted for 0–6.9 (average 1.3). All the catchments were sparsely populated and point-source loading was negligible. Thus, the main human impacts in these catchments were due to agriculture, forestry, and

atmospheric deposition. The forestry practices, when present, consisted of thinning, clear-cutting, ditching, and/or soil scarification. Three catchments (22 Liuhapuro, 25 Välipuro, and 13 Porkkavaara) represented natural-state forests, where no forestry operations had been carried out during recent decades. Agricultural practices consisted of cereal crop and grass cultivation, with some poultry, pig, and cattle animal husbandry.

Bedrock was formed of granitic rocks, migmatites, and schists. Till and fine late-glacial minerogenic sediment covered the bedrock. Extensive fine-sediment deposits were mainly found in southern and western Finland. The soils in forested areas were Podzols or Dystric and Eutric Histosols. The soils not covered by forest were Leptosols, Cambisols, and Gleysols. The mean annual temperature was about 6°C in the southernmost catchments and about 0°C in the northernmost catchments. The mean annual precipitation ranged from 400 to 700 mm and the mean annual runoff from 203 to 440 mm during the study period (Table 1). The catchments have been described in more detail by Seuna (1983), Finér and others (1997), Vuorenmaa and others (2002), and Kortelainen and others (2006).

**Table 1.** Area, the Proportion of Peatlands, Forests on Mineral Soils, Agricultural Fields, Built-up Areas and Water as Percentage of the Catchment Area, Mean Annual Runoff and the Export of Total Nitrogen, Total Phosphorus, Total Organic Carbon (TOC), and Total Suspended Solids (TSS) in the Catchments. Catchments were arranged according to Peat% in ascending order

Catchment	Area (km <sup>2</sup> )	Peatland (%)	Forest (%)	Field (%)	Built-up (%)	Water (%)	Runoff (mm a <sup>-1</sup> )	Total N (mol km <sup>-2</sup> a <sup>-1</sup> )	Total P (mol km <sup>-2</sup> a <sup>-1</sup> )	TOC (mol km <sup>-2</sup> a <sup>-1</sup> )	TSS (kg km <sup>-2</sup> a <sup>-1</sup> )
1	0.1	0	92.3	0.01	0.9	0	254 (147)	20,440 (8,130)	320 (190)	337,230 (23,520)	5,000 (2,990)
2	14	4.6	91.5	0	3.0	0	440 (87)	4,050 (1,260)	80 (30)	89,840 (26,740)	550 (360)
3	988	6.6	39.7	42.3	4.2	2.0	270 (114)	58,000 (24,710)	2,130 (1,170)	335,540 (158,440)	36,610 (22,430)
4	0.6	8.0	92.0	0	0	0	329 (94)	3,650 (950)	50 (10)	178,060 (50,740)	120 (70)
5	770	8.3	49.6	29.2	4.6	1.6	257 (79)	57,520 (23,570)	1,120 (460)	347,540 (146,310)	19,670 (9,090)
6	0.3	9.0	91.0	0	0	0	231 (61)	4,920 (1,370)	60 (20)	336,260 (98,960)	60 (30)
7	4,283	10.2	75.6	9.7	1.2	2.3	283 (71)	25,030 (6,530)	660 (140)	499,320 (161,970)	5,450 (2,230)
8	727	11.0	41.2	36.9	4.5	0.3	289 (117)	60,370 (24,860)	2,310 (1,320)	388,480 (170,300)	31,710 (20,150)
9	0.6	12.1	77.3	0	6.9	0	204 (81)	16,430 (6,250)	110 (60)	346,300 (154,340)	1,480 (830)
10	5.5	12.9	63.8	17.2	2.3	0	203 (37)	24,240 (5,580)	560 (160)	308,690 (84,570)	8,040 (5,470)
11	199	14.7	49.8	29.3	3.2	0.1	290 (129)	55,760 (26,550)	1,160 (630)	431,110 (214,030)	13,430 (8,930)
12	356	15.0	62.7	12.4	2.5	3.3	379 (93)	38,000 (11,090)	640 (200)	564,060 (193,100)	6,100 (2,740)
13	0.7	16.0	84.0	0	0	0	357 (114)	5,720 (1,650)	60 (20)	351,350 (122,560)	190 (160)
14	3,814	20.7	71.5	2.4	1.0	3.3	353 (89)	15,300 (4,170)	380 (90)	493,640 (154,010)	3,000 (1,140)
15	16	26.0	73.9	0	0	0.1	386 (82)	7,270 (1,660)	170 (50)	306,110 (72,890)	1,710 (820)
16	11	31.9	66.8	0.3	0.2	0.5	353 (98)	13,520 (3,680)	280 (60)	570,490 (205,410)	1,290 (580)
17	0.5	32.0	68.0	0	0	0	331 (101)	13,080 (3,800)	220 (60)	823,920 (286,270)	220 (100)
18	20	36.1	60.6	1.0	0.3	0.8	253 (56)	15,410 (3,820)	340 (90)	646,760 (219,440)	1,220 (280)
19	1.2	43.0	57.0	0	0	0	385 (90)	12,720 (2,800)	160 (30)	729,710 (188,360)	280 (110)
20	4.9	45.3	54.7	0	0	0	204 (61)	14,570 (4,190)	190 (60)	512,670 (177,630)	1,960 (750)
21	0.7	47.7	48.6	0	0	3.5	294 (84)	5,480 (1,540)	70 (20)	290,400 (110,630)	nd
22	1.7	48.0	52.0	0	0	0	351 (114)	14,620 (5,210)	240 (80)	950,880 (363,610)	210 (160)
23	4.9	50.0	50.0	0	0	0	428 (151)	17,300 (5,900)	280 (100)	1034,290 (402,090)	350 (150)
24	0.7	56.0	40.0	0	0	4.0	393 (78)	10,000 (2,100)	110 (30)	735,680 (197,200)	410 (250)
25	0.9	56.0	44.0	0	0	0	353 (92)	14,000 (3,370)	190 (50)	100,460 (263,410)	200 (110)
26	1,350	57.8	36.7	1.2	0.6	2.7	414 (130)	20,620 (6,620)	490 (150)	626,070 (245,320)	4,080 (2530)
27	1.1	70.0	30.0	0	0	0	359 (91)	9,660 (2,470)	100 (20)	648,280 (187,620)	320 (180)

Standard Deviation in the Parenthesis.  
nd = not determined.

## Sampling and Determinations

The study period covered the years 2000–2011. Daily runoff from the catchments was monitored for, predominantly, 11 or 12 years, except Yli-Knuuttila (1), where the runoff data was only available for 4 years. Daily runoff was determined by the rating curve method, using continuous water level data, or in the case of some rivers, from data obtained from hydro-power plants. Water samples were taken, on average, 9–41 times per year, concentrating on spring and autumn high-flow periods (Table 2). The samples were analyzed with accredited methods in the laboratories of Regional Environment Centres and the Finnish Environment Institute.  $\text{NO}_3$  was analyzed by the Cd method and  $\text{SO}_4$  by ion-chromatography. Concentrations of total Fe, total Mn, total N, and total P were determined colorimetrically after digestion with  $\text{K}_2\text{S}_2\text{O}_8$  in an autoclave. The digestion transforms analyte to a reactive form, oxidizes organic matter, and reduces inferring color, but may not attack all element forms, for example, those strongly bound in mineral particles. In Fe and Mn determinations, digestion is performed at low pH to form reactive forms of Fe and Mn. Fe(III) is reduced to Fe(II) by hydroxylammonium chloride, and Fe(II) is stained by TPTZ. Mn(II) is stained by formaldoxime. According to a validation performed on natural waters by the Finnish Environment Institute, the total Fe determined with the above method differed less than 10% from total Fe determined with ICP-OES after digestion with nitric acid in a microwave oven. However, the colorimetrically analyzed total Mn gave somewhat higher and more variable results than ICP-OES, which may indicate that the Mn values are overestimates. In our catchments, Fe and Mn have probably been in various chemical and physical forms, such as attached to inorganic particles in agricultural runoff and to organic colloids in humic waters. In such a setting, total concentrations include a variable fraction of bioavailable forms. The concentrations of total suspended solids (TSS) were determined as the portion retained on the 0.4  $\mu\text{m}$  polycarbonate or glass fiber filter. TOC concentrations were determined using high-temperature oxidation followed by infrared gas measurements. We excluded  $\text{O}_2$ , as its supply is determined by water–air interactions, rather than land cover or atmospheric deposition.

The annual  $\text{SO}_4$ ,  $\text{NO}_3$ , Fe, and Mn bulk deposition values for southern, central, and northern Finland were derived from three deposition stations (Kotinen, Hietajärvi, and Kuusamo, Figure 2) run by the Finnish Meteorological Institute. The bulk deposition was measured continuously, using weekly or monthly sampling, according to the

EMEP manual (EMEP 2001). The samples were analyzed with accredited methods in the laboratory of the Finnish Meteorological Institute.

## Calculations and Statistical Analyses

Daily concentrations for non-sampled days were linearly interpolated from sequential determined values. The daily loads were calculated by multiplying daily concentrations with daily runoff and annual exports were obtained by summing up the daily values. The limited frequency of the sampling and interpolation of concentrations may cause uncertainties in the calculated exports. The estimated exports may differ from the true exports, as the concentrations do not change linearly over time and there can be a short-term variation in water quality related to flow paths, transit times and discharge, and temporal variability in the biological activity (Barco and others 2013). In our study, the sampling frequency was higher during the high-flow periods in spring and autumn, which improved the accuracy of the element export estimates (Rekolainen and others 1991). To estimate the reliability of the linear interpolation method, annual exports were also estimated, using flow-weighted mean concentrations for a few catchments and the results given by these two methods were at the same level.

The relationship between land-use patterns and the export of TEAs was examined with principal component analysis (PCA) and multiple regression analysis. The five land-cover classes (field, built-up area, forest, peatland, and water) were used as predictors of mean annual concentrations and exports of TEAs. In the regression analysis, we entered the land-cover classes one by one in the model, built separately for each TEA, and then selected the models on the basis of explanation power and mutual correlation between the explaining variables, excluding models with a variance inflation factor exceeding five. The regression models were validated using an independent dataset: catchments were arranged, according to Peat% in ascending order and every second, that is, 14 catchments were included in the model and the remaining 13 catchments were used in the model validation. The statistical analyses were performed with CANOCO and SAS softwares.

## RESULTS

### TEA Concentrations, Export, and Proportions

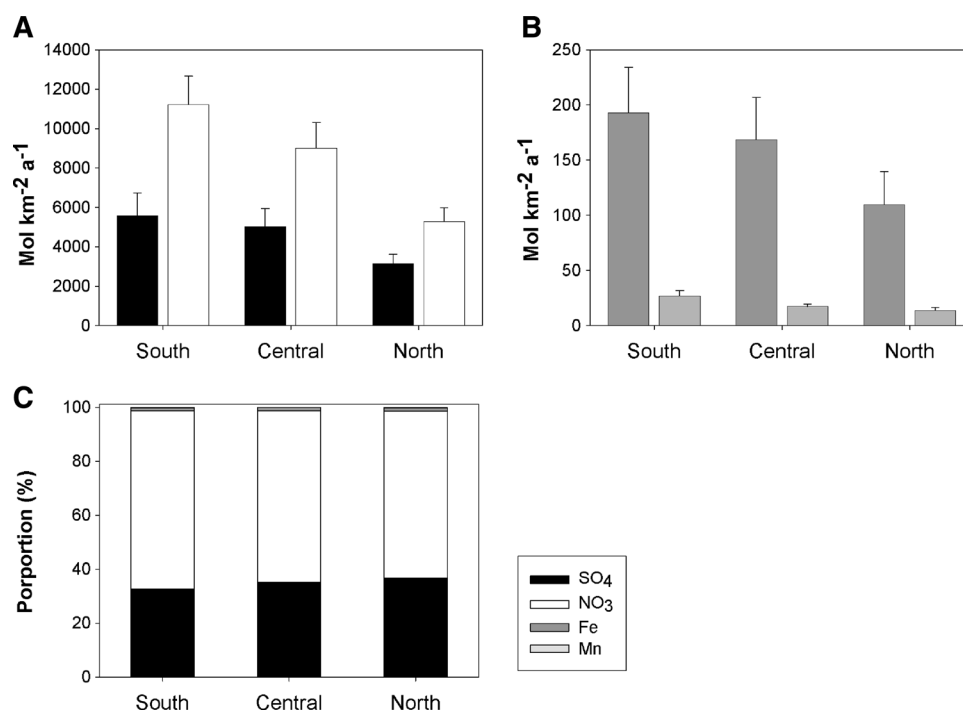
The atmospheric deposition of all the TEAs decreased from south to north (Figure 3A, B), but the

**Table 2.** Length of the Study Period, Number of Water Samples per Year, and Mean Annual Nitrate, Manganese, Iron, Sulfate, Total Nitrogen, Total Phosphorus, Total Organic Carbon (TOC), and Total Suspended Solids (TSS) Concentrations in Stream Water During the Study Period

Catchment	Study period	Samples/ year	NO <sub>3</sub> ( $\mu\text{mol l}^{-1}$ )	Mn ( $\mu\text{mol l}^{-1}$ )	Fe ( $\mu\text{mol l}^{-1}$ )	SO <sub>4</sub> ( $\mu\text{mol l}^{-1}$ )	Total N ( $\mu\text{mol l}^{-1}$ )	Total P ( $\mu\text{mol l}^{-1}$ )	TOC ( $\mu\text{mol l}^{-1}$ )	TSS ( $\text{mg l}^{-1}$ )
1	2000–2003	16	45.8 (2.6)	1.1 (0.2)	29 (8)	130 (50)	86 (25)	1.2 (0.3)	1,150 (168)	20.1 (5.8)
2	2000–2010	14	1.5 (0.4)	0.2 (0.1)	2 (0.5)	28 (1)	8 (1)	0.2 (0.03)	180 (29)	1.0 (0.8)
3	2000–2003, 2005–2011	24	129.6 (37)	4.7 (1.9)	122 (44)	122 (19)	190 (37)	6.6 (1.2)	1,120 (129)	104.0 (36)
4	2000–2010	9	1.2 (1.1)	0.4 (0.1)	5 (1)	19 (1)	12 (2)	0.2 (0.03)	590 (101)	0.4 (0.2)
5	2000–2011	13	121.9 (23)	2.7 (0.5)	57 (18)	189 (37)	182 (30)	3.4 (0.6)	1,230 (147)	47.3 (14)
6	2000–2010	10	0.3 (0.3)	0.3 (0.03)	8 (1)	16 (2)	20 (2)	0.3 (0.05)	1,240 (150)	0.4 (0.2)
7	2000–2011	16	26.9 (5.4)	2.7 (0.5)	60 (5)	118 (38)	81 (7)	2.3 (0.2)	1,660 (178)	16.4 (4.0)
8	2000–2011	41	121.6 (35)	4.2 (0.4)	85 (9)	150 (8)	180 (34)	5.9 (0.4)	1,260 (39)	73.2 (28)
9	2000–2010	20	46.3 (9)	0.7 (0.1)	11 (2)	100 (9)	81 (9)	0.5 (0.1)	1,490 (297)	6.7 (1.8)
10	2000–2005	17	46.2 (9)	1.8 (0.3)	32 (5)	83 (11)	100 (12)	2.4 (0.4)	1,320 (153)	24.4 (11)
11	2000–2010	26	93.1 (34)	2.6 (0.8)	49 (15)	98 (29)	150 (32)	3.6 (0.5)	1,440 (160)	29.8 (9.5)
12	2000–2011	10	33.6 (13)	2.1 (0.7)	23 (4)	86 (23)	86 (17)	1.6 (0.2)	1,370 (200)	15.6 (3.1)
13	2000–2010	10	0.3 (0.1)	0.3 (0.03)	4 (0.6)	21 (3)	16 (2)	0.2 (0.02)	1,060 (162)	0.4 (0.3)
14	2000–2011	15	6.1 (1)	1.0 (0.1)	37 (3)	42 (7)	41 (3)	1.0 (0.1)	1,290 (162)	7.3 (2.0)
15	2000–2010	13	0.6 (0.2)	0.5 (0.1)	14 (2)	14 (1)	18 (1)	0.4 (0.04)	760 (75)	3.9 (1.1)
16	2000–2006, 2008	16	2.2 (0.9)	1.4 (0.6)	14 (2)	19 (6)	37 (5)	0.8 (0.1)	1,550 (237)	3.1 (1.2)
17	2000–2010	10	0.6 (0.5)	0.6 (0.1)	19 (3)	32 (16)	41 (2)	0.8 (0.2)	2,690 (199)	0.7 (0.5)
18	2000, 2002, 2004, 2005, 2007	18	6.9 (1.2)	1.0 (0.1)	25 (1)	84 (13)	54 (3)	1.3 (0.2)	2,240 (326)	4.8 (1.2)
19	2000–2010	10	1.1 (0.8)	0.6 (0.1)	28 (3)	10 (2)	32 (2)	0.4 (0.1)	1,840 (160)	0.8 (0.3)
20	2000–2010	12	10.6 (2)	1.6 (0.3)	68 (17)	47 (7)	62 (5)	0.9 (0.1)	2,180 (362)	11.0 (3)
21	2000–2010	22	0.7 (0.2)	0.2 (0.04)	6 (2)	6 (1)	19 (4)	0.2 (0.02)	930 (126)	nd
22	2000–2009	18	1.1 (0.4)	0.6 (0.1)	31 (4)	16 (5)	41 (2)	0.8 (0.1)	2,550 (264)	0.6 (0.3)
23	2000–2009	10	0.7 (0.4)	0.8 (0.1)	23 (2)	23 (8)	36 (3)	0.7 (0.1)	2,200 (275)	0.9 (0.3)
24	2000–2010	10	0.5 (0.2)	0.7 (0.2)	43 (12)	6 (2)	27 (3)	0.3 (0.1)	1,980 (206)	1.2 (0.9)
25	2000–2010	10	1.2 (0.9)	0.4 (0.1)	25 (3)	10 (4)	42 (2)	0.6 (0.1)	2,990 (248)	0.5 (0.2)
26	2000–2011	17	10.7 (2.3)	0.9 (0.1)	46 (4)	27 (7)	51 (2)	1.2 (0.1)	1,420 (172)	8.6 (3.0)
27	2000–2010	10	0.5 (0.2)	0.6 (0.1)	33 (7)	5 (2)	29 (3)	0.3 (0.1)	1,960 (164)	1.1 (0.4)

Standard deviation is in parenthesis.  
nd = not determined.





**Figure 3.** Mean (+SD) annual atmospheric SO<sub>4</sub> and NO<sub>3</sub> (**A**), and Fe and Mn deposition (**B**) and the molar ratio of SO<sub>4</sub>, NO<sub>3</sub>, Fe, and Mn of the total TEA deposition (**C**) in southern, central, and northern Finland during the years 2000–2011.

molar share of TEAs was similar in all the three sites, NO<sub>3</sub> and SO<sub>4</sub> being the dominant TEAs (Figure 3C). In runoff, the variation in the average annual concentrations of NO<sub>3</sub> (range 0.3–130 μmol l<sup>-1</sup>), Mn (0.2–4.7 μmol l<sup>-1</sup>), Fe (2–122 μmol l<sup>-1</sup>), and SO<sub>4</sub> (5–189 μmol l<sup>-1</sup>), among the catchments was large (Table 2). The concentration of NO<sub>3</sub> increased with Field% (NO<sub>3</sub> = 3.1 Field% + 5.5,  $r^2 = 0.89$ ), with only two “non-agricultural” catchments (1 Yli-Knuuttila and 9 Teeressuonoja) having a high NO<sub>3</sub> concentration. The concentration of Fe also correlated positively with Field%, although less than NO<sub>3</sub> (Fe = 1.7 Field% + 22,  $r^2 = 0.57$ ). In agricultural catchments, Fe and Mn concentrations correlated positively with TSS ( $r = 0.93$ ,  $P < 0.01$ ), indicating that Fe and Mn were mainly in a particulate form. The concentrations of SO<sub>4</sub> increased with Field% and decreased with Peat%. The concentrations of SO<sub>4</sub> correlated best with total N ( $r = 0.89$ ,  $P < 0.01$ ) and NO<sub>3</sub> ( $r = 0.87$ ,  $P < 0.01$ ) out of the determined water quality variables. Catchment 18 (Kesselinpuro) had a high SO<sub>4</sub> concentration despite a negligible Field%, which is probably related to the presence of black schists in the bedrock of this catchment.

The variation in the TEA export among the catchments (Figure 4) was highest for NO<sub>3</sub> (range 50–40700 mol km<sup>-2</sup> a<sup>-1</sup>, the maximum export was 814 times higher than the minimum export) followed by Fe (850–44,300 mol km<sup>-2</sup> a<sup>-1</sup>, max/min = 52×), Mn (50–1470 mol km<sup>-2</sup> a<sup>-1</sup>, max/

min = 29×), and SO<sub>4</sub> (1790–42260 mol km<sup>-2</sup> a<sup>-1</sup>, max/min = 24×). The relative distribution of the concentrations and exports of TEAs were rather similar (Figure 5). NO<sub>3</sub>, Mn, and SO<sub>4</sub> exports were highest in the agricultural catchments (Figure 4). Fe exports were higher in agricultural and peatland-dominated catchments than in forest-dominated catchments. The exports of Mn, Fe, and SO<sub>4</sub> exceeded their inputs from atmospheric deposition (Figures 3, 4). In contrast, NO<sub>3</sub> exports from forest- and peatland-dominated catchments were smaller than inputs from the deposition. The molar distribution of TEAs in runoff differed greatly from that in atmospheric deposition; SO<sub>4</sub> and Fe were the dominant TEAs in runoff, the proportion of Mn being only 0.5–4% (Figure 5). The proportion of NO<sub>3</sub> was highly variable among catchments (1–46%). Atmospheric deposition was a poor predictor for Fe ( $r^2 = 0.002$ ,  $P = 0.316$ ) and SO<sub>4</sub> ( $r^2 = 0.001$ ,  $P = 0.321$ ) export and explained only 24% and 27% of the variation in NO<sub>3</sub> and Mn exports, respectively ( $P < 0.01$ ).

### Effect of Land Cover on TEA Export

According to PCA, land cover explained 76% of the variation in TEA export ( $F = 13.0$ ,  $P = 0.002$ ). The first two axes represented 68 and 7% of the total variation. The PCA ordination indicated that the export of TEAs increased with Field% (Figure 6A). The export of SO<sub>4</sub> was also positively correlated with Built-up%. The increase in Forest% decreased

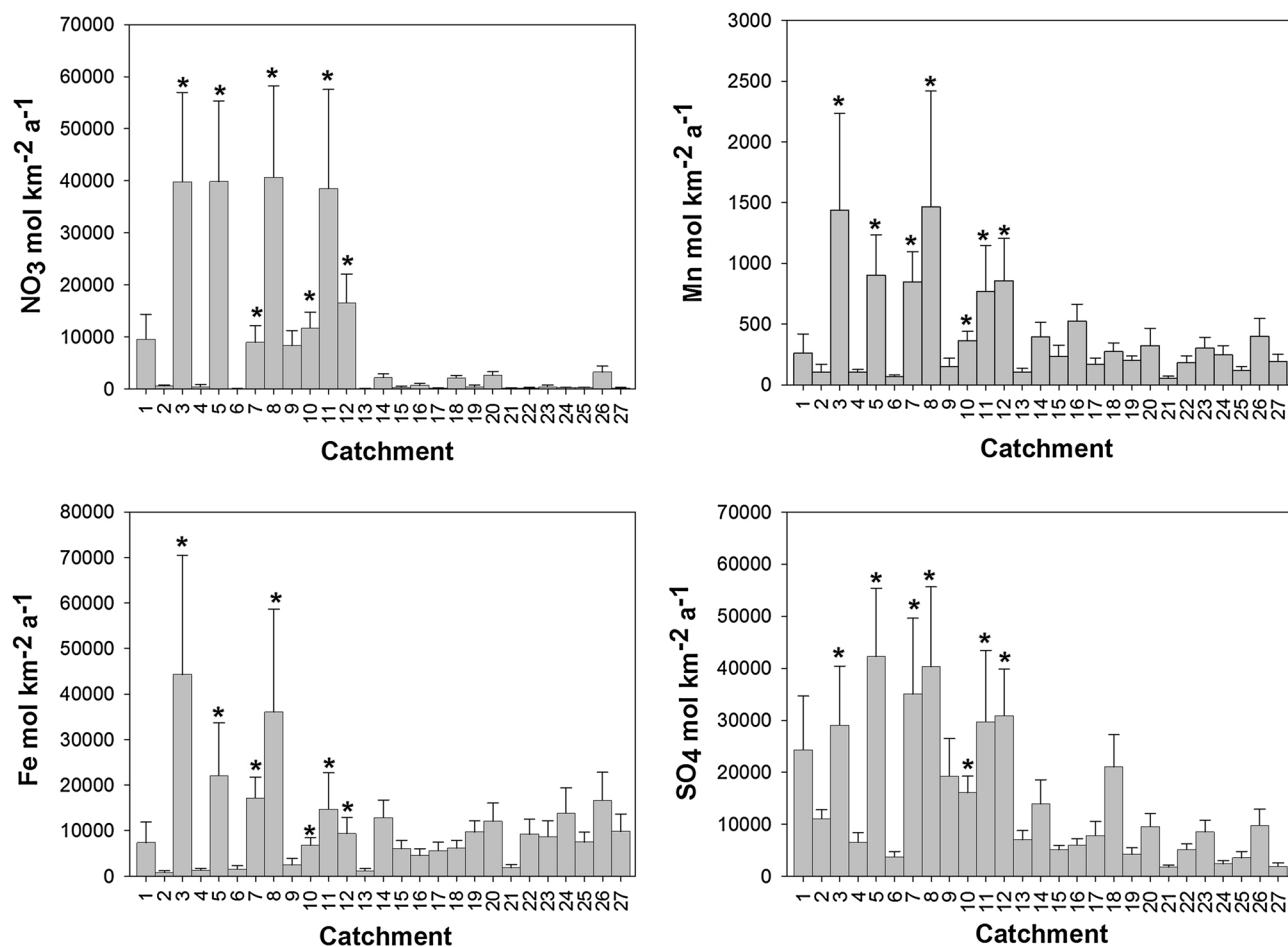


Figure 4. Mean (+SD) annual TEA export from the catchments during the years 2000–2011. The catchments in which the proportion of fields exceeds 10% are marked with \*.

the export of Fe, and an increase in Peat% decreased the export of SO<sub>4</sub> (Figure 6A).

Land cover explained 76% of the variation in TEA proportions ( $F = 13.3$ ,  $P = 0.002$ ). The PCA ordination indicated that the proportion of NO<sub>3</sub> flux increases with an increasing Field% and Built-up% (Figure 6B). Peat% increased the proportions of Mn and Fe and resulted in a low proportion of SO<sub>4</sub>. The proportion of SO<sub>4</sub> increased with Forest%.

Multiple regression analysis showed that out of the land-use classes, Field% and Peat% best described the TEA export. Together, they explained as much as 93, 80, 75, and 67% of the NO<sub>3</sub>, Mn, Fe, and SO<sub>4</sub> export, respectively, when all the catchments were included in the analysis (Figure 7). The coefficients of SO<sub>4</sub> and NO<sub>3</sub> for Peat% were negative. The model validation gave similar results. The models for the 14 catchments predicted 93, 86, 76, and 76% of the NO<sub>3</sub>, Mn, Fe, and SO<sub>4</sub> exports for the 13 validation catchments, respectively. The

exports estimated from the regression models show that the increase in Field% enhances the export of all TEAs (Figure 8A), but that the proportion of SO<sub>4</sub> in the TEA export decreases (Figure 8C). On the other hand, an increase in Peat% decreases for NO<sub>3</sub> and SO<sub>4</sub> exports (Figure 8B), Fe being the major TEA from peaty catchments (Figure 8D).

## DISCUSSION

### Deposition and TEA Export

Our study showed that the export and molar ratios of TEAs in northern European boreal catchments are predominantly a function of land cover and catchment processes, rather than atmospheric deposition (Figure 7). This is also the case for the export of NO<sub>3</sub>, although in boreal forest- and peatland-dominated catchments, atmospheric deposition is the major N source, larger than N fertilization (Kortelainen and others 1997) and

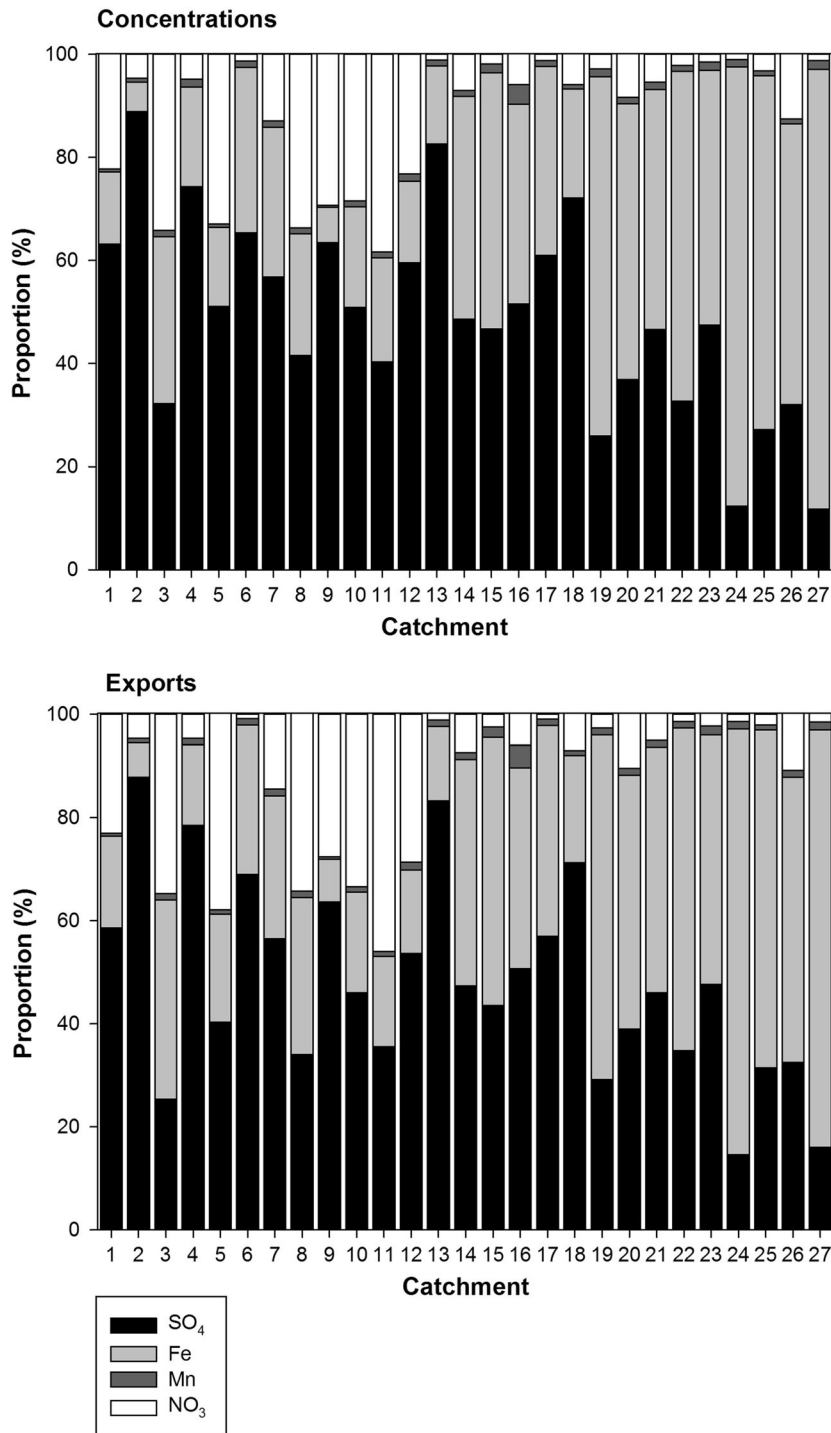


Figure 5. Proportion of SO<sub>4</sub>, NO<sub>3</sub>, Fe, and Mn as a percentage of the TEA concentrations and exports.

N-fixation (DeLuca and others 2002). The deposition of NO<sub>3</sub> and SO<sub>4</sub> in Finland (5,300–11,200 mol km<sup>-2</sup> a<sup>-1</sup> NO<sub>3</sub>, 3,100–5,600 mol km<sup>-2</sup> a<sup>-1</sup> SO<sub>4</sub>) is small, compared to central and southern Europe (43,000–135,000 mol km<sup>-2</sup> a<sup>-1</sup> NO<sub>3</sub>, 25,000–87,000 mol km<sup>-2</sup> a<sup>-1</sup> SO<sub>4</sub>) (Lorenz and others 2008). In areas of higher deposition,

NO<sub>3</sub> and SO<sub>4</sub> exports are presumably more closely linked to atmospheric deposition (Dise and Wright 1995; Gundersen and others 2006; Evans and others 2008). Despite the fact that Finland is a long country and the deposition decreases from south to north, the molar ratio of TEAs in the deposition was similar in both southern and northern Finland.

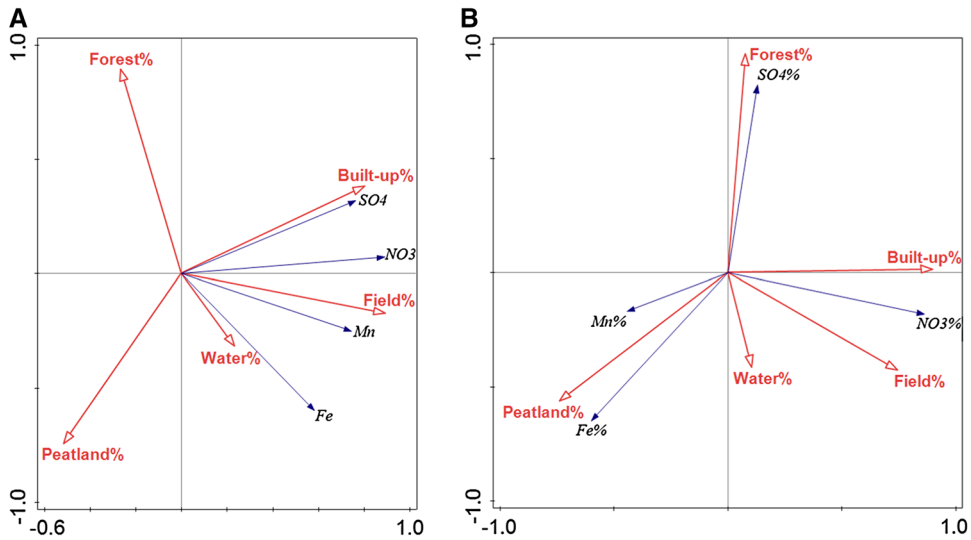


Figure 6. Principal component analysis ordination diagrams showing the main patterns of the variation of TEA exports (A) and molar ratios (B) in relation to the land use.

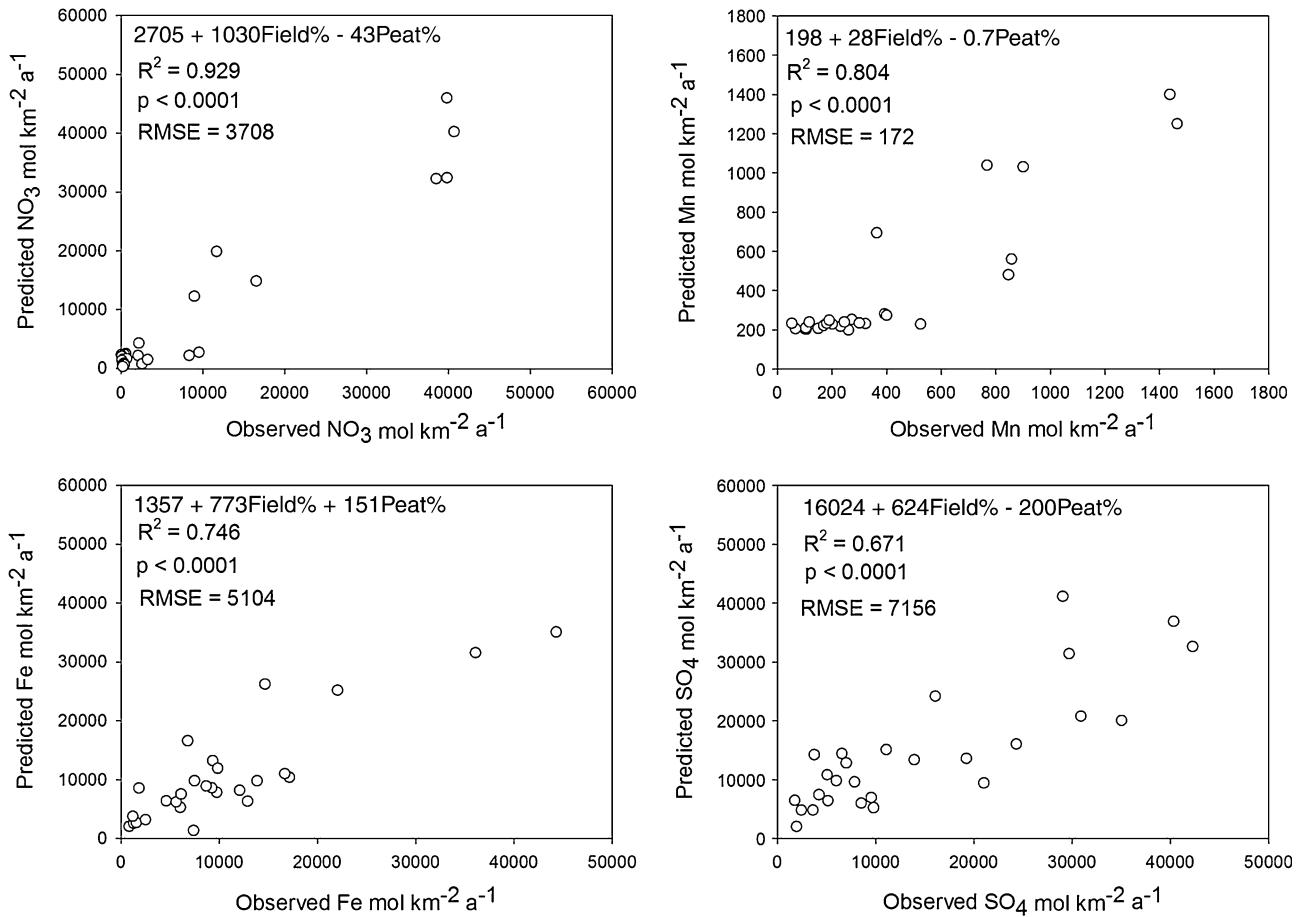


Figure 7. Regression models for estimating TEA export and the observed and predicted NO<sub>3</sub>, Mn, Fe, and SO<sub>4</sub> exports.

### Agricultural Land and TEA Export

Fields produced the highest TEA export (Figure 4), the high molar share of NO<sub>3</sub> giving field runoff an identifiable signature (Figures 5, 6B). Several factors affect the large TEA export from fields. Agri-

cultural lands are fertilized and tend to locate on clayey soils that are sensitive to erosion. The soils have high concentrations of Mn and Fe (Sippola 1974) and are well drained by ditches and subsurface-drains. The surface is also tilled and often lacks

vegetation during high run-off periods in the spring and autumn. Soil erosion was presumably the major source of Mn and Fe, as suggested by their close correlation with TSS, whereas NO<sub>3</sub> and SO<sub>4</sub> probably mainly originated from fertilizers, organic matter degradation, and atmospheric deposition (Vuorenmaa and others 2002; Mattsson and others 2007; Ekholm and Lehtoranta 2012). Annually about 650,000–850,000 mol N km<sup>-2</sup> and 47,000–62,000 mol S km<sup>-2</sup> are added with fertilizers to agricultural fields in Finland (Salo and others 2007; Yli-Halla and others 2011). Both NO<sub>3</sub> and SO<sub>4</sub> concentrations have also been shown to correlate positively with Field% in previous studies (for example, Korkman 1973; Ekholm and others 2000; Strayer and others 2003; Williams and others 2005; Mattsson and others 2005, 2007).

### Forests and TEA Export

Forests exported TEAs much less than fields (Figure 4). Boreal forests are N-limited and the losses of NO<sub>3</sub> are negligible (Tamm 1991; MacDonald and others 2002), if extensive forestry operations have not been carried out (Palviainen and others 2014). In podzolic forest soils, Mn and Fe are enriched and retained in the B-horizon as oxides and hydroxides (Lundström and others 2000). SO<sub>4</sub>, in turn, is adsorbed onto the surfaces of aluminum and iron oxides and hydroxides in mineral soils (Gustavsson and Jacks 1993; Piirainen and others 2002). TEA concentrations and exports in forest-dominated catchments were of the same order of magnitude as previously reported for boreal forested catchments (Nilsson 1985; Tarvainen and others 1997; Kortelainen and Saukkonen 1998; Mattsson and others 2003; Finér and others 2004; Kortelainen and others 2006; Björkvald and others 2008). Forests leached proportionally more SO<sub>4</sub> than peatlands. Coniferous trees are efficient at intercepting SO<sub>4</sub> dry deposition and, therefore, throughfall in the forest contains more SO<sub>4</sub> than bulk deposition (Piirainen and others 2004). The export of Mn, Fe, and SO<sub>4</sub> in runoff exceeded the atmospheric input which is in line with other mass balance studies from forested catchments (Navrátil and others 2007; Watmough and others 2005, 2007; Björkvald and others 2009).

### Peatlands and TEA Export

The water-logged peatlands produced low exports of NO<sub>3</sub> and SO<sub>4</sub>, but high exports of Fe. Retention of NO<sub>3</sub> is usually high in northern peatlands and

NO<sub>3</sub> concentrations in peatland waters are low (Gorham and others 1984; Lepistö and others 2001). Nitrogen mineralization and nitrification rates are lower in peatlands than in mineral forest soils (Devito and others 1999), and a high water table promotes anaerobic conditions in peatlands, which can result in increased denitrification and consequently low NO<sub>3</sub> export (Martikainen and others 1993; Regina and others 1996). The increase in Peat% decreased the export of SO<sub>4</sub>. Unlike well-aerated forest soils, anaerobic peat layers may immobilize S in the form of organic C bonded S, Fe monosulfide (FeS), and pyrite (FeS<sub>2</sub>) by means of dissimilatory bacterial SO<sub>4</sub> reduction (Mörth and others 1999; Eimers and others 2004; Novák and others 2005). Significant negative correlation between Peat% and NO<sub>3</sub> and SO<sub>4</sub> concentrations have also been observed in other boreal headwater and river basins (Kortelainen and Saukkonen 1995; Eimers and others 2004; Finér and others 2004; Mattsson and others 2005, 2007; Kortelainen and others 2006; Björkvald and others 2009; Pester and others 2012). Fields produced the highest export of Fe, but it is evident that peat environments are also a major source of terrestrial Fe in surface waters, as highlighted by previous studies (Heikkinen 1994; Kortelainen and Saukkonen 1998; Dillon and Molot 1997; Kortelainen and others 2006). Fe export from peatland-dominated catchments correlated with TOC export ( $r = 0.599$ ,  $P = 0.007$ ). The biogeochemical cycles of TOC and Fe are strongly interlinked (for example, Shapiro 1966; Knorr 2013) and a major part of Fe is exported as organic Fe-rich colloids (Kortelainen and Saukkonen 1998; Björkvald and others 2008). Likewise, the mobilization of Mn is strongly controlled by dissolved organic matter (Tarvainen and others 1997; Graham and others 2002), which was reflected in our data as an increased proportion of Mn in the TEA export with increasing Peat%.

In addition to the above land-cover classes, other factors, such as bedrock, soil texture and fertility, weathering, the decomposition degree of peat, catchment slope, and land management practices, probably cause a variation in TEA export (Urban and others 1990; Ekholm and others 2000; Mattsson and others 2003; Finér and others 2004; Heranen 2009; Palviainen and others 2014). For example, a high NO<sub>3</sub> export from forested Catchments 1 (Yli-Knuutila) and 9 (Teeressuonoja) may be due to the abundance of fertile *Oxalis-Myrtillus* forest site types (Cajander 1949) in these catchments (Kortelainen and others 2006). Furthermore, geology and soil properties largely determine the land use. Generally, most fertile soils are converted

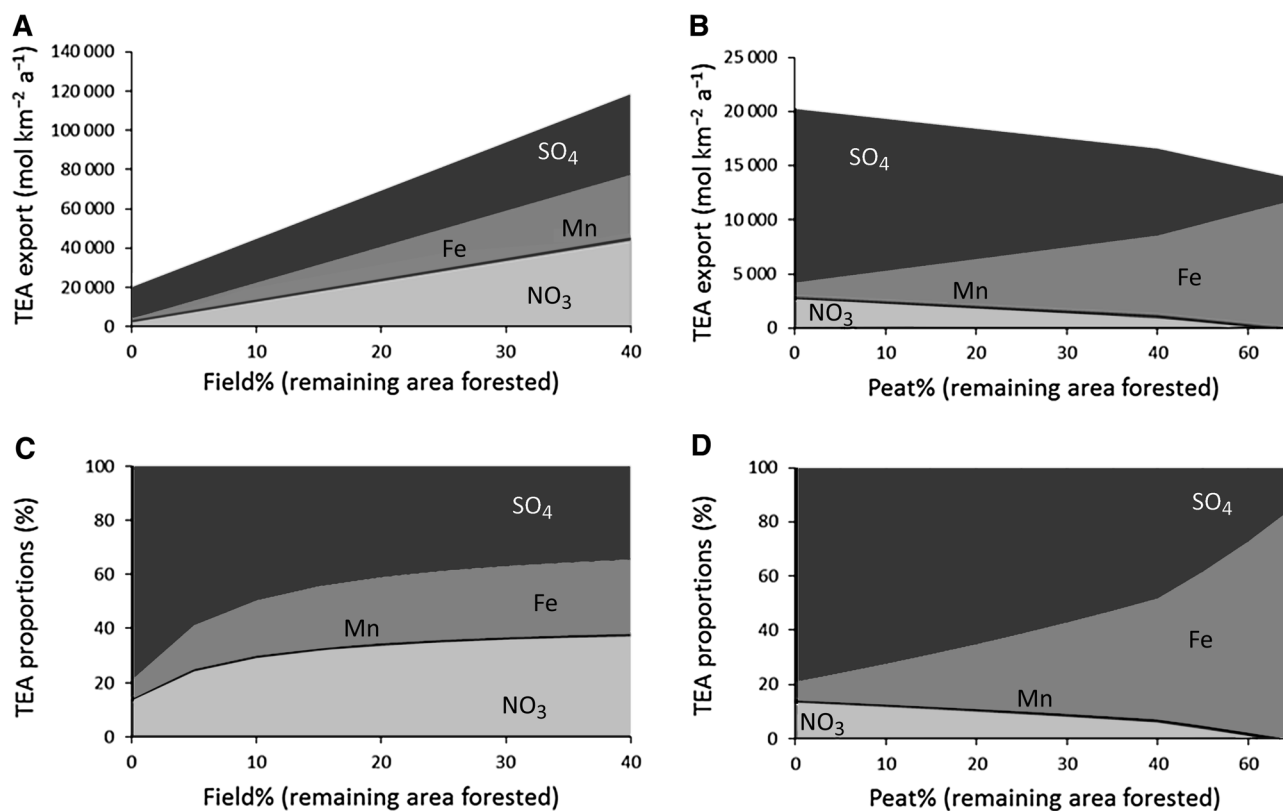


Figure 8. Proportions and exports of TEAs as estimated from regression models in Figure 7. Export of TEAs as a function of field percentage (A) and peat percentage (B); proportions of TEAs as a function of field percentage (C) and peat percentage (D).

to fields and, therefore, runoff chemistry is the combination of soil development and land use.

### Significance of TEAs

We have shown a great variability of the export of TEAs from different land-cover classes in the boreal zone, but the behavior and retention of TEAs and their significance may vary in the recipient system, depending on the morphology, retention time, and trophic status of the system (Rysgaard and others 2001; Thomsen and others 2004; Maerki and others 2009; Finlay and others 2013). The physical and chemical forms of NO<sub>3</sub>, Mn, Fe, and SO<sub>4</sub> determine whether these substances can actually be used as TEAs in anaerobic mineralization processes downstream. In our study, NO<sub>3</sub> and SO<sub>4</sub> are probably predominantly in a dissolved form, readily to be used as TEAs, whereas Mn and Fe were measured as total concentrations, which do not reveal their direct availability as TEAs in clay particles (Kostka and others 1999, 2002) or in organic complexes (Allard and others 2004; Gaffney and others 2008; Pédrot and others 2011). In agricultural and peat-

land catchments, Mn and Fe correlated with TSS and TOC, respectively, indicating that Mn and Fe were in a form that may settle on the bottom. In contrast, dissolved NO<sub>3</sub> and SO<sub>4</sub> are more likely to be transported through the system with less contact to anaerobic layers. Yet, the export of organic N and S may form a significant source for TEAs after mineralization and oxidation to NO<sub>3</sub> and SO<sub>4</sub>. TEAs also affect mineralization and material fluxes in the catchment, but their importance is pronounced in aquatic systems, where anaerobic mineralization plays an important role in sediments. Climate change scenarios predict increasing precipitation for northern Europe and an increasing frequency of heavy rainfalls over land areas (Denman and 2007), which can be supposed to result in an increased variation of redox conditions. Several recent studies suggest that climate change may lead to increased TEA export from temperate and boreal catchments, due to changes in precipitation, runoff regimes, and soil redox conditions (Heal 2001; Clark and others 2005; Kritzberg and Ekström 2012; Knorr 2013; Sarkkola and others 2013).

## CONCLUSIONS

Our study demonstrates that both concentrations and exports of TEAs are specific for each land-cover class (Figure 8). On the basis of our findings, changes in the export of TEAs may emerge through an increase in Field%, whereas afforestation may decrease TEA export, but increase the relative proportion of SO<sub>4</sub>. Clear-cutting, in turn, may enhance NO<sub>3</sub> fluxes (Palviainen and others 2014). Terrestrial ecosystems and their utilization create different premises for the anaerobic mineralization pathways. These pathways, in turn, may have fundamental effects on the system functions through the feedbacks on the retention ability of nutrients and harmful substances and the formation of greenhouse gas fluxes in the aquatic ecosystems. The acknowledgement of the concept of coupled biogeochemical cycles might enhance an understanding of not only the outcome of a diffuse load in a body of water, but also of the load generating factors in the catchments. This highlights the need for considering the influences of landscape characteristics on the export of TEAs—in addition to the load of organic C and nutrients—in predicting long-term changes in the biogeochemistry of terrestrial and aquatic systems.

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