Decreased deposition of sulphate and the responses in soilwater at Estonian integrated monitoring sites 1995–2004

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Abstract

This paper presents the results of trend analyses of a ten-year study of deposition (throughfall+stemflow) and soilwater in two pine stands and a spruce stand (ICP IM areas). The reported decreasing trends of deposited sulphate and cations at the easterly located Saarejärve integrated monitoring area are in good agreement with the decline of SO_2 and fly ash emissions in Estonia. At Vilsandi pine stand, which has the westernmost location and is under a marine influence, the decrease of sulphur deposition was comparable with that of the eastern Saarejärve pine stand. However, total base cation load in Vilsandi pine stand remained unchanged resulting in a decrease of throughfall acidity. At Saarejärv coniferous stands deposition of base cations decreased more than that of acid anions causing an increase in K leaching from canopies. A good accordance between sulphate decline in deposition and topsoil water was accompanied by base cation decline in soilwater under organic horizon at both IM areas. In podzolized soil at Saarejärve the decline of SO_4 and base cations resulted in increased levels of total soluble Al.
Keywords: deposition, throughfall, stemflow, pine and spruce stand, soilwater, sulphate, cations, aluminium, trend analyses.

1 Introduction

Predominant sources of SO_2 and particle emission in Estonia are four large oil-shale-based thermal power plants and chemical industries in the Northeastern region. Oil shale mining and combustion accounted for about 81% of total

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harmful emissions up till 2005. Estonian oil shale as a fuel is characterized by high ash share (45-50%) and moderate sulphur content (1.4-1.8%). A peculiarity of Estonian oil shale is its chlorine content (0.75%) combined with organic matter. Oil-shale-centred energetics and economy have led to specific deposition patterns. The high amount of alkaline dust emitted contributed to a considerable neutralization of acid pollutants already in the atmosphere, and even resulted in alkalinization and damage of sensitive ombrotrophic raised bogs [1]. A rapid decrease in emissions took place in 1990s due to reshaping of local economy after restoration of independent statehood in 1991. During the study period (1995-2004), the quantities of emitted SO_2 and fly ash decreased by 40% and 65%, respectively, mostly due to a decline in annually combusted oil shale amounts (from about 24 megatons in 1994 to 13 megatons in 2004) i.e. due to a decrease in production of electric energy in the power plants.

The decrease of emissions led to a decline in concentrations of both anions (SO_4 and Cl) and cations (Ca, Mg, Na and K) in bulk precipitation at all Estonian monitoring stations during 1994-2001 [2].

The first long-term national intensive ecosystem monitoring programme in Estonia: International Co-operative Programme on Integrated Monitoring (ICP IM) under LTRAP Convention was initiated by the Nordic Council of Ministers in 1994 [3]. In the framework of ICP IM, an intensive monitoring site at Lake Saare forested catchment area in eastern Estonia and a biomonitoring site in the westernmost Island Vilsandi were established. The IM monitoring sites represent areas of boreal coniferous forest receiving background loads of air pollution and deposition. Although the two sites are not regionally representative, they provide an opportunity to monitor changes in air pollution and its impacts on the environment of coniferous stands at the western border of Estonia (Vilsandi), where higher concentrations of SO_2 are measured from southern and south-western air mass transport direction [4], and in eastern Estonia (Lake Saare area), which is more affected by local sources of air pollution from the region of oil shale industry in North-Eastern Estonia.

The current paper presents results of a ten-year study of throughfall, stemflow and soilwater in two pine stands and one spruce stand under the conditions of declining SO_2 and base cation emissions.

2 Material and methods

2.1 Site characteristics

The study was carried out in the forested subcatchment area (109 ha) of Lake Saare in eastern Estonia (58º39′ N, 26º45′ E), hereafter referred to as Saarejärve, and in Vilsandi, Estonia's westernmost island (58º34′ N, 21º50′ E). At Saarejärve water and litter samples were collected from two permanent plots of the Scots pine (120 years old) and the Norway spruce (90 years old) stands. The permanent plots are situated on nearly flat surfaces, in areas representative of dominant forest site types in the catchment area. The *Rhodococcum* type Scots pine stand is located at an elevation. The *Vaccinium* type Norway spruce stand is situated lower than the pine stand, near the bottom of a slope. At both stands the parent material is glaciofluvial sand, on which moderately eluviated Haplic Podzols have developed.

The permanent plot in Vilsandi is a 100-year-old Scots pine stand (*Fragaria* type) on Calcari-Gleyic Leptosol.

Mean annual precipitation during the study period (1995-2004) was 630 mm at Saarejärve and 535 mm in Vilsandi.

Table 1: Stand characteristics of sample plots.

Permanent plot	Vilsandi pine stand	Saarejärve pine stand	Saarejärve spruce stand
Site type	*Fragario-Pinetum*	*Rhodococco-vitis-idaeo-Pinetum*	*Vaccinio-myrtilli-Piceetum*
Soil type	*Calcari-Gleyic Leptosol*	*Haplic Podzol*	*Haplic Podzol*
Age of dominant trees	100	120	90
Number of trees in ha^{-1}	440	551	672
Mean diameter (m)	0.29	0.37	0.26
Mean height (m)	16.9	28.7	22.5
Annual average throughfall amount (mm)	282	513	430
Annual average soilwater amount from depth of 10 cm (mm)	101	57	113
Annual average soilwater amount from depth of 40 cm (mm)	98	25	74

2.2 Sampling and chemical analyses

Bulk deposition was collected using two NILU-type collectors [5] at both monitoring areas. Throughfall deposition was collected by polyethylene funnel-type bulk collectors (20 cm in diameter, at a height of about 150 cm) in snow free time, and by buckets during winter. Spiral silicone collectors fitted to three trees per plot were used for collecting stemflow. Water volumes were measured on the field by graduated cylinder. Sampling frequencies were once a fortnight in summer and once a month in winter. Sampling areas and stand characteristics are given in table 1.

Soil water was sampled with zero-tension plate lysimeters of 0.1 m^2 [6]. At Saarejärve pine and spruce stands the lysimeters were inserted into depths of 5 to 10 cm under organic horizon and about 40 cm under eluvial horizon with 6 replications per depth. At Vilsandi the lysimeters were installed under humus horizon (into depth of 5 to 10) and illuvial horizon ($BC_{(g)}$ into depth of about 35 cm). At both sites percolation water was collected approximately at 1-month intervals during the snow-free period along with deposition samples.

Water samples from Vilsandi and Saarejärve were analyzed in the Estonian Environmental Research Centre in Tallinn and in the Environmental Studies

Laboratory in Tartu, respectively. Both laboratories have continuous quality control programmes, and they participate regularly in international intercalibration exercises.

Major anions (Cl^-, NO_3^-, SO_4^{2-}) in precipitation and soilwater were analysed by ion chromatography. Base cations were determined using atomic absorption spectroscopy or ion chromatography depending on laboratory, pH was measured potentiometrically.

The nonparametric Mann-Kendall test was used to estimate significance ($p<0.05$) of the trends in annual values. The slope of a linear trend was estimated with the nonparametric Sen's method [7].

3 Results

3.1 Decline of sulphur deposition

During 1995-2004 a significant decline was observed in concentration and deposition of sulphate in bulk precipitation and in pine and spruce stands' throughfall and stemflow at the integrated monitoring sites in Estonia (Table 2). Mean annual concentration of SO_4-S in bulk precipitation decreased from 2.2 mg l^{-1} to 0.37 mg l^{-1} at Saarejärve and from 1.4 to 0.51 mg l^{-1} at Vilsandi. Sulphur load dropped from 9.1 to 3.2 kg ha^{-1} yr^{-1} at Saarejärve. At Vilsandi the highest load was 5.1 kg ha^{-1} yr^{-1} in 1995 and the lowest 2.4 kg ha^{-1} yr^{-1} in 2002.

The prevailing anion in throughfall of the pine and spruce stand at Saarejärve was SO_4^{2-}, which formed 58% and 66% of summed anions, respectively. Sea salt correction shows that marine fraction of sulphur is less than 8% in bulk- and throughfall precipitation at Saarejärve. At the remote island Vilsandi, however, the prevailing anion in throughfall was Cl^{-1} (53%), sulphate formed only 29% of summed anions. Marine fraction of sulphate was on average 10% in bulk deposition and 25% in throughfall flux.

The throughfall flux of S decreased significantly from 8.2 and 18.8 kg ha^{-1}, in 1995 to 4.2 and 4.8 kg ha^{-1} in 2004 in Saarejärve pine and spruce stands, respectively. At Vilsandi pine stand the decrease in sulphur deposition was about the same as in Saarejärve pine stand (50%) (Fig. 1). The concentration of the other two main anions (NO_3 and Cl) also seems to have decreased along with the decline of sulphate at Vilsandi pine stand (Fig. 1). Comparison of TF from the two monitoring sites shows that NO_3-N deposition is higher at Vilsandi (2.3 kg ha^{-1}) than Saarejärve (1.0-1.4 kg ha^{-1}) pine stand. The decrease of nitrate deposition on Fig.1 could be explained by variation between the selected monitoring years. Furthermore, throughfall NO_3 content is more influenced by internal cycling in canopy [8] than the SO_4 content.

Actual annual S input flux into the soil comes from S of throughfall, stemflow and litterfall. Stemflow water was usually negligible in volume forming 2-5% of throughfall in the spruce and pine stand at Saarejärve and less than 1% in the pine stand at Vilsandi. However, due to the high concentration of SO_4-S, significant transport of S took place by stemflow, at least at Saarejärve, in the first years of the monitoring period. Sulphur input by litterfall formed on average one third of total S input (TF+SF+LF) in the studied stands.

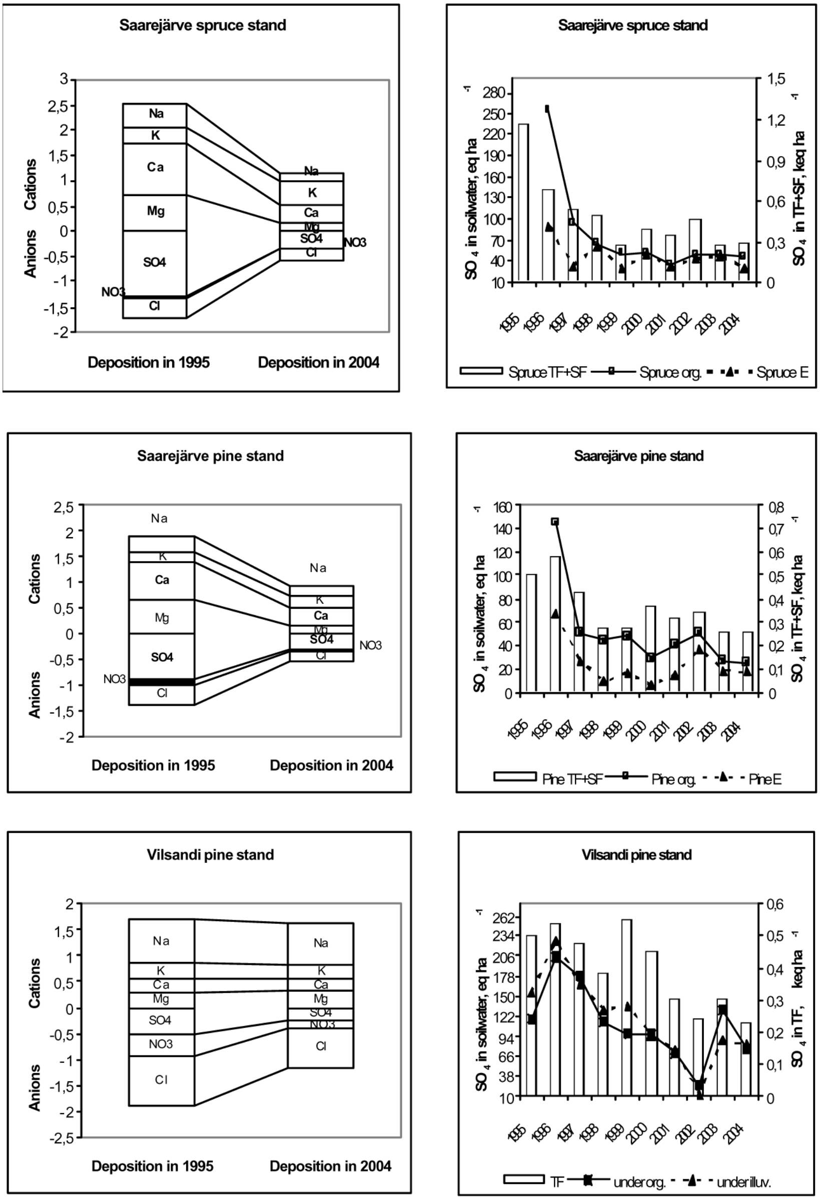

Figure 1: Decline of throughfall+stemflow deposition (keq ha^{-1} y^{-1}), comparison of first and last monitoring years in spruce stand and pine stand at Saarejärve and Vilsandi on the left side. Sulphate decline in deposition (throughfall+stemflow) and in soilwater under organic (org.) and eluvial (E) horizons of spruce and pine stands at Saarejärve and under organic and illuvial (illuv.) horizons in Vilsandi pine stand on the right side.

During the study period the actual S input decreased about 2 times in the pine stands and 4 times in the spruce stand. It should also be pointed out that, judging by annual litterfall amounts (needles only); the crown needle surface of spruce canopy is about three times bigger than that of pine canopy. The sulphur content in litter will be a more important part in the S-circle due to decreased atmospheric loads of S.

3.2 Decline of base cation deposition

The decreasing trend of SO_4^{2-} concentration in throughfall+stemflow is in good accordance with decreasing trends of the concentrations of most important base cations, Ca and Mg at Saarejärve coniferous stands. The share of Ca^{2+} and Mg^{2+} was on average 45% and 15% of summed cations, respectively. Decreasing flux of summed base cations (Ca+Mg+K+Na) during the study period was statistically significant at Saarejärve (Table 2).

Table 2: Trends in data series ("-"decreasing and "+" increasing) of annual mean concentration in throughfall (TF+SF) and soil water (SW) from 1995-2004. Estimated by Mann-Kendall nonparametric test (significance levels ***p< 0.001; **p<0.01; *p<0.05).

Stand	Saarejärve spruce stand			Saarejärve pine stand			Vilsandi pine stand		
	TF+ SF	SW 10 cm	SW 40 cm	TF+ SF	SW 10 cm	SW 40 cm	TF+ SF	SW 17 cm	SW 35 cm
SO_4	-***	-***	-***	-*	-	-*	-*	-*	-*
Ca	-**	-*	+	-*	-	-			
Mg	-**	-*	-***	-*	-	-*		-*	
K	+	-*	-**	+	-	-		-*	
Sum of cations	-**	-**	-*	-*	-	-*		-*	
Sum of anions	-**	-	-*	-*	-	-*			
Al_{Tot}		+	+**		+*	+			
Al^{3+}		-	-*		+*	+***			
H^+	-	+*	+	*+	+	-*	-*	+*	

There was a clear change in proportion of various cations in throughfall. Proportions of Ca^{2+} and Mg^{2+} in summed cations decreased by 0.1% and 0.4% per year, accordingly, in pine throughfall, while the proportion of K increased by 1.6% per year ($p<0.05$) obviously due to leaching (K did not increase in open area precipitation). In the spruce stand the decrease of the share of Ca^{2+} and Mg^{2+} in summed cations was 1.2% and 0.38% per year, accordingly, and the increase of K^+ due to leaching was 2.8% per year ($p<0.05$).

Due to its location the dominant cation in Vilsandi TF is Na (40% of summed cations on average), the remaining 60% is Ca+Mg+K in almost equal parts. There was no significant decreasing trend of base cation concentration or deposition at the Vilsandi pine stand.

At Vilsandi deposition of base cations neutralised the acidic deposition in bulk precipitation to a larger extent than in throughfall, while H+ flux also decreased in the throughfall of the pine stand. At the same time bulk precipitation was more acidic than total deposition in the pine and spruce stands at Saarejärve. The annual mean pH decreased in the bulk deposition (from 4.8 to 4.7) as well as in the throughfall (from about 5.4 to 5.2) during the study period, and the increase of H+ flux in the pine stand was significant (Table 2).

3.3 Responses of soil solution chemistry to decline of deposition

There were statistically significant declines in sulphate concentration, sum of cations and pH (from 5.5 to 4.9) in soilwater under organic horizon at Vilsandi. At Saarejärve statistically significant declining trends in sulphate concentration, sum of cations and sum of strong anions (SO_4+Cl+NO_3) were estimated in soilwater under both horizons of the spruce stand, and under eluvial horizon of the pine stand. Concentrations of SO_4 and of most cations also decreased below the organic horizon of the pine stand but the trends were not significant (Table 2). SO_4 concentrations were about 10% higher in soilwater under the eluvial horizon than under the organic horizon at Saarejärve. Likewise, a statistically significant decreasing timetrend of sulphate amount in soil water output from organic horizon was observed in the spruce and pine stands at Saarejärve. The output of sulphate flux from organic horizon decreased from 0.25 to 0.05 keq ha^{-1} y^{-1} (about 5 times) in the spruce stand and from 0.14 to 0.025 keq ha^{-1} y^{-1} (6 times) in the pine stand at Saarejärve area. The decline of sulphate output fluxes from deeper horizons was not statistically significant, although leaching from eluvial horizon in the spruce stand decreased from 90 to 30 eq ha^{-1} y^{-1} and in the pine stand from 67 to 18 eq ha^{-1} y^{-1}. At the remote island Vilsandi sulphate output fluxes decreased from 0.12 to 0.08 keq ha^{-1} y^{-1} (1.5 times) under organic horizon and from 0.16 to 0.08 keq ha^{-1} y^{-1} (about 2 times) under illuvial horizon. SO_4 content under deeper (B) horizon was remarkable higher in Vilsandi pine stand than at Saarejärve (Fig.1 on the right).

The decline in soilwater sulphate was to a great extent matched by a decrease in most cations in organic horizons of the spruce and pine stands, and to a lesser extent also in the eluvial horizon of both stands at Saarejärve. In the soilwater of carbonate-rich soil at Vilsandi the cation content decreased in good accordance with SO_4 decline under organic horizon but was not influenced by a decline of sulphate in illuvial horizon.

Total soluble Al contents increased in the soil water from both depths of both stands at Saarejärve (Table 1), although the trends were statistically significant only below organic horizon in the spruce stand and below eluvial horizon in the pine stand.

4 Discussion

Decrease in sulphur deposition is often accompanied by decline of base cations. At Vilsandi pine stand the total deposition of summed base cations did not significantly decrease while the cation flux under humus horizon decreased significantly during the monitoring period. Thereby, it could be suggested that a substantial share of cations got deposited not along with sulphate ions at Vilsandi. On the other hand SO_4 from deposition plays important role as an accompanying anion for cations, which readily moves down with percolation water through organic horizon.

Throughfall composition forming processes (dry deposition, interception, leaching) in canopy changed in both stands at Saarejärve during the study period. Deposition of anions via throughfall and stemflow decreased by about 1 keq ha^{-1} in the spruce stand and 0.8 keq ha^{-1} in the pine stand. At the same time deposition of cations at Saarejärve decreased by 1.5 and 1 keq ha^{-1} in the spruce and pine stands, respectively. Since the input of dust-associated base cations decreased more than the acid anion input, acidity of throughfall should increase, and cause increased leaching of K from canopies.

Good accordance between sulphate decline in deposition and topsoil water is partly due to the use of zero-tension lysimeters. Percolation water obtained by zero-tension lysimeters is the soil water fraction that is primarily involved in soil formation processes, e.g. transport of ions down the soil profile, from one horizon to another *prior* to e.g. buffering processes [9].

The decline of sulphate fluxes in deposition and under organic horizon of soil water at Saarejärve area resulted in a decrease of SO_4 retention in organic horizon. The retention of sulphate via adsorption processes decreased from about 0.44 to 0.24 keq ha^{-1} in the spruce and pine stands suggesting a decrease in consumption of protons (potential increase of H^+) by about 0.2 keq ha^{-1} in the spruce and pine stands' organic horizon. The decline in the retention of sulphate in eluvial horizon occurred to a lesser extent, and resulted in the potential increase of H^+ by about 0.15 and 0.07 eq ha^{-1} in the spruce and pine stand, respectively. Via proton consumption the sulphate retention had a decisive role in proton budgets in organic layers of the spruce and pine stands at Saarejärve in the first five years of the monitoring period [10]. The decline in SO_4 retention in Vilsandi organic horizon was 0.16 keq ha^{-1}, which is about the same as in Saarejärve. Higher output of SO_4 from illuvial horizon than from organic horizon indicates suitable conditions for adsorption/desorption processes. The increase of H^+ in percolation water of both horizons in the spruce stand and under the organic horizon of the pine stands could be due to changes in SO_4 retention, as well as due to the decline of summed cations in soilwater, which reflects intensive accumulation of base cations into biomass or/and a shortage of exchangeable cations in soil. Although desorption of SO_4 anion appeared to be much slower than adsorption [11], the previously adsorbed sulphate would have got released and thus delayed the decrease of SO_4 concentration in deeper horizons.

Only additional H^+ can increase both total Al and soluble free Al^{3+} concentration in soil water. The pH of solutions in the studied soil water was normally well below 5 at Saarejärve and, in fact, the pH of throughfall was commonly higher than that of the soil solution receiving it. The increase of total soluble Al in podzolized soil indicates an ongoing process of podzolization due to dissociated organic acids derived from mineralisation of conifer litter, and is probably attributable to decreased retention of sulphate in soil horizons.

5 Conclusions

The decreasing trends of deposited sulphate and cations at Saarejärve integrated monitoring area are in good agreement with the decline of SO_2 and fly ash emissions in Estonia, as well as with SO_4 time series from local precipitation monitoring stations during the study period. At Vilsandi pine stand, which has the westernmost location and is under marine influence, the decrease of sulphur deposition was comparable with that of the eastern Saarejärve pine stand, but the total base cation load in Vilsandi pine stand remained unchanged over the entire monitoring period resulting in a decrease of throughfall acidity. Deposition of base cations at Saarejärve coniferous stands decreased more than that of acid anions causing an increase in K leaching from canopies.

A good accordance between sulphate decline in deposition and in topsoil water was accompanied by base cation decline in soilwater under organic horizon at both IM areas. In podzolized soil at Saarejärve the decline of SO_4 and base cations resulted in increased levels of total soluble Al.

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