



Jane FREY* and Anneli PALO**

DEPOSITION OF MAIN IONS ON OPEN LAND AND IN CROWN THROUGHFALL OF SPRUCE AND PINE STANDS

Abstract. The concentrations of eight ions (Na^+ , K^+ , NH_4^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , NO_3^-) and pH in canopy throughfall water and in bulk precipitation on open landscape have been studied in a pine stand at Pikasilla and in a spruce stand at Voore, Estonia.

It was found that the mean concentration of ions in throughfall was 1.3—5.5 times higher than in open land precipitation, except NO_3^- and NH_4^+ concentrations in the pine stand at Pikasilla. On both sample plots the pH of throughfall was normal or slightly increased. So, precipitation did not cause direct acidification in the studied stands, though the deposited sulphur amounts were high in both sites.

The nitrogen load in the spruce stand was 2.4—3.9 times higher than for open land; however, for the pine stand the corresponding value was slightly lower.

Key words: air pollution, throughfall, deposition, pH, sulphur, nitrogen.

Introduction

The forest damage, widespread in the Northern Hemisphere, has been studied in Estonia since 1986. For monitoring the vitality and state of health of conifers ten permanent sample plots were established in coniferous forests in collaboration with the Ministry of Environment and the Laboratory of Ecosystems of Tartu University. In order to obtain the background levels of main polluting anions (SO_4^{2-} , Cl^- , NO_3^-) and acidity, precipitation samples of open land near permanent sample plots were collected (Frey et al., 1987; Frey et al., 1988a, 1988b). Having established the main anion fallout loads of open land, we continued our programme and extended it to include the determination of anions, cations, and acidity in throughfall of canopy on two sample plots (a spruce stand at Voore and a pine stand at Pikasilla).

As the branches and leaves of trees act as pollution filters with an extended surface, the bulk concentration of water reaching the ground, i.e. throughfall, depends on several factors, e.g. the position of the coppice or trees on the relief (Berljand, 1982; Iwens et al., 1988), the density of the stand and its species composition (Miller, 1985; Smith, 1981), and, naturally, weather conditions and season.

On the other hand, in the case of acid precipitation K^+ , Ca^{2+} , and Mg^{2+} -ions are leached from the young leaves of deciduous trees. Coniferous trees show an insignificant leaching of these components due to well-developed cuticular and wax layers covering the surface and stomata of needles (Smith, 1981).

* Ecology Station, Tartu University, Ülikooli St. 18, EE-2400 Tartu, Estonia.

** Ministry of Environment, Toompuiestee St. 18, EE-0110 Tallinn, Estonia.

In Estonia ion concentration changes in canopy throughfall water have been studied under individual trees (Martin et al., 1985). It was concluded that a rise in the proton level is connected with the out-washing of acid deposits. However, a decrease in the H⁺-ion concentration may occur due to neutralization processes on leaves. The final result depends also on the balance between these processes (Yoshida and Ichikumi, 1989).

It is unclear, however, how these processes are connected with forest damage. In order to compare ion amounts in throughfall of spruce and pine stands and bulk precipitation on open landscape outside the forest, we carried out sampling at Voore in 1989 (Frey and Palo, 1991) and at Pikasilla in 1990.

The forests of both areas are evidently damaged, so defoliation of canopy and drying of trees have been observed earlier. The damage of fine roots is extensive, and the Ca/Al molar ratio, indicating soil acidification, is very low (Löhmus and Lasn, 1991).

Voore is situated 40 kilometres north of Tartu in the area affected by the pollution from the North-East industrial region (Paalme et al., 1990). An attempt has been made to connect damage effects in the Pikasilla site at the southern tip of Lake Võrtsjärv mostly with long-range pollution (Etverk, 1988).

Material and Methods

The Voore permanent sample area is situated on the NE slope of a drumlin surrounded by agricultural land with cattle-farms only a few kilometres apart. The Pikasilla permanent sample area is located within a forest area on a rolling landscape, agricultural land lying about 3 kilometres away (Table 1).

Table 1

Characteristic	Stand	
	Voore	Pikasilla
Forest	9Sp1B	7P3Sp
Mean height, m	20	11
Age, years	50	63
Basal area, m ²	33.0	26.8
Site quality class	I	II
Soil type	brown lessive	podzolic

Samples were collected at Voore from June to November 1989, and from May to October 1990; at Pikasilla from May to October 1990. Both areas were supplied with 11 permanently open sampling vessels consisting of plastic bottles placed at a height of 1.5 m above the ground and covered with a 15-cm-diameter funnel. To avoid contamination from trash, the funnels were provided with a thin nylon net. The duration of the sampling period depended on the amount of precipitation; as a rule, however, samples were collected immediately after prolonged rains to avoid the concentration of ions as a result of evaporation. The samples were stored in cold and dark.

To determine the pH of water, a pH-meter pH-673M was used. The device was previously calibrated with standard buffer solutions. The pH value was determined immediately as the mean result of two to three consecutive measurements.

The concentrations of eight ions (Na^+ , K^+ , NH_4^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , NO_3^-) were determined at the Chemistry Laboratory of the Tartu Public Health Service using ion chromatography. The eluents, eluting velocities, and separation columns used are listed in Table 2.

Table 2

Eluents and separation columns used in ion chromatography		
Ions	Eluent	Separation column
Anions (Cl^- , SO_4^{2-} , NO_3^-)	2.5 mM Na_2CO_3	HIKS-1 150×30 mm; Anieks N 55×4 mm;
Monovalent cations (Na^+ , K^+ , NH_4^+)	3 mM HNO_3	Katieks K 150×3 mm
Divalent cations (Ca^{2+} , Mg^{2+})	10 mM tartaric acid and 2 mM ethylendiamine	Biotronik BT IV KA 100×3 mm

Results and Discussion

The pollution levels were evaluated using the scale elaborated in Austria (Smidt, 1986).

(1) Acidity of precipitation:

normal: pH=5.11–6.10,

acid:

basic:

strongly:	pH < 4.11	pH > 7.10
significantly:	pH = 4.11–4.60	pH = 6.51–7.10
weakly:	pH = 4.61–5.10	pH = 6.11–6.50

(2) Ion contents of precipitation, $\text{mg}\cdot\text{l}^{-1}$:

(SO_4^{2-} , Cl^- , NO_3^- , NH_4^+ , K^+ , Mg^{2+} ions)

low	< 2.5
normal	2.6–5.0
high	5.1–10.0
very high	> 10.1

It was found that maximal ion concentrations (c) of open land bulk precipitation (Table 3) often varied from high to very high: $c > 5.1 \text{ mg}\cdot\text{l}^{-1}$ (Cl^- , SO_4^{2-} , NH_4^+ , K^+ , Mg^{2+}). The contents of Na^+ and Ca^{2+} were somewhat lower: $c < 5.0 \text{ mg}\cdot\text{l}^{-1}$. In the Voore area rains of acid reaction were sometimes observed ($\text{pH}_{\text{min}} = 3.8$).

The mean concentrations of Cl^- , NO_3^- , NH_4^+ , Na^+ , K^+ , Ca^{2+} , and Mg^{2+} during the sampling periods (Table 4) at Voore were below $5.0 \text{ mg}\cdot\text{l}^{-1}$, only SO_4^{2-} contents were higher (8.2 – $9.6 \text{ mg}\cdot\text{l}^{-1}$). The samples collected at Pikasilla showed Cl^- , NO_3^- , NH_4^+ , Na^+ , K^+ , and Ca^{2+} concentrations below $5.0 \text{ mg}\cdot\text{l}^{-1}$; NH_4^+ and Mg^{2+} concentrations were a little

higher ($5.9 \text{ mg}\cdot\text{l}^{-1}$ and $5.6 \text{ mg}\cdot\text{l}^{-1}$, respectively). The mean pH of precipitation at Voore was normal (5.18–6.12); at Pikasilla even a slight rise was detected (6.45).

Precipitation water reaching beneath the canopy is enriched with substances deposited in it during dry periods (dry deposition). The composition of canopy throughfall reflects indirectly the amount of air pollution with the structure of the stand (density, composition of species, leaf area, and exposition) being also significant.

At Voore the mean concentration of ions in throughfall was 1.3–5.5 times higher than in open land precipitation (Table 4). In throughfall pH usually increased as well, being 0.15–1.09 units higher than in simultaneous samples from open land. At Pikasilla NO_3^- and NH_4^+ concentrations in throughfall decreased slightly (1.3 and 1.1 times, respectively) while pH dropped by 0.37 units. On both sample plots the pH of throughfall was normal or slightly increased (6.08–6.37).

Table 3

Maximum ion concentrations ($\text{mg}\cdot\text{l}^{-1}$) of open land bulk precipitation

Ions	Sample plot and years		
	Voore		Pikasilla
	1989	1990	1990
Cl^-	2.5	14.4	4.0
SO_4^{2-}	23.3	41.7	6.4
NO_3^-	8.7	14.4	9.8
Na^+	3.5	2.9	3.9
NH_4^+	5.4	7.1	19.5
K^+	12.3	10.4	6.0
Ca^{2+}		5.0	5.0
Mg^{2+}		6.7	8.9
pH	3.79	4.45	5.82

Table 4

Mean ion concentrations ($\text{mg}\cdot\text{l}^{-1}$) of throughfall and open land

Ion	Sample plot and years					
	Voore				Pikasilla	
	1989		1990		1990	
	Forest	Open land	Forest	Open land	Forest	Open land
Cl^-	2.9 ± 0.3	1.3 ± 0.3	5.8 ± 0.8	4.5 ± 1.6	3.8 ± 0.4	2.4 ± 0.5
SO_4^{2-}	22.7 ± 2.2	8.2 ± 2.0	16.7 ± 2.8	9.6 ± 3.8	8.4 ± 1.0	3.4 ± 0.9
NO_3^-	2.2 ± 0.3	1.2 ± 0.2	7.2 ± 2.3	2.8 ± 1.5	1.9 ± 0.4	2.4 ± 1.9
Na^+	6.0 ± 1.2	1.1 ± 0.3	2.9 ± 0.5	1.6 ± 0.3	5.3 ± 1.2	2.5 ± 0.4
NH_4^+	11.4 ± 1.2	2.5 ± 0.9	6.7 ± 0.6	5.1 ± 1.4	5.4 ± 0.5	5.9 ± 2.8
K^+	13.5 ± 1.5	4.5 ± 1.2	7.0 ± 0.5	4.3 ± 1.1	5.0 ± 0.4	3.2 ± 0.7
Ca^{2+}	30.7 ± 4.8		5.6 ± 0.6	3.6 ± 1.5	4.9 ± 0.4	2.9 ± 0.5
Mg^{2+}	13.9 ± 2.9		7.2 ± 0.7	4.0 ± 0.8	7.2 ± 0.4	5.6 ± 1.0
pH	6.37 ± 0.08	6.12 ± 0.3	6.27 ± 0.07	5.18 ± 0.24	6.08 ± 0.09	6.45 ± 0.37

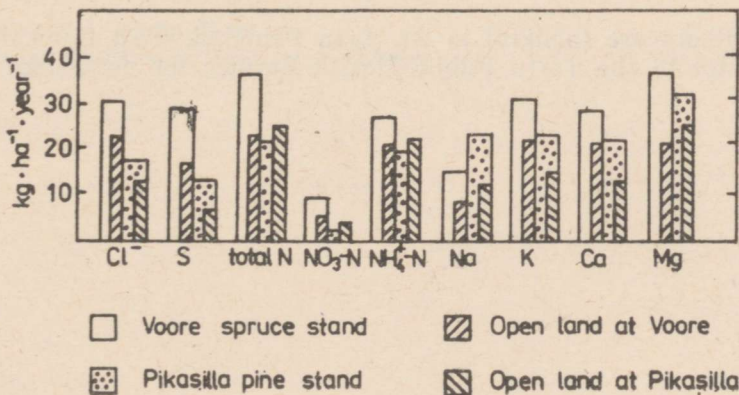
To establish the balance between anions and cations the mean concentrations of ions are expressed in micro-equivalents per litre. Here a comparison of two extreme cases is presented as an example of potential acidification for November 11, 1989, with pH 3.79, and for May 13, 1990, when an extremely high anion concentration was registered in Voore samples (Table 5). It turns out that on an average the concentration of cations exceeded that of anions. Consequently, the neutralizing potential of the canopy was not yet exhausted. On the other hand, the unbalanced values refer to a possible systematic error in the determination of anion or cation contents, i.e. several ions significant for the balance have been neglected. This suggestion is supported by the existence of several unidentified peaks appearing at times on chromatograms: CO_3^{2-} , F^- , PO_4^{3-} , and some organic acids should be considered. In the case of divalent cations, systematic errors can occur as the method used is relatively new.

Table 5

Cation and anion balance (microequivalents per litre)

Ion	Sample plot and sampling time									
	Voore								Pikasilla	
	1989		1990		11. 11. 89		13. 05. 90		1990	
	Forest	Open	Forest	Open	Forest	Open	Forest	Open	Forest	Open
H ⁺	20	30	30	340	236	941	0.4	0.3	40	20
Anions	243	93	324	192	40	25	320	24	142	80
Cations	1608	729	801	513	113	58	130	88	684	508

Anion concentrations in the samples were mostly in a good correlation. The correlation coefficient is always significant, $r=0.61-0.94$ in seven cases out of nine. SO_4^{2-} and Ca^{2+} concentrations are always in a good correlation ($r=0.68-0.81$), while Ca^{2+} and Mg^{2+} concentrations correlate only slightly ($r=0.58-0.63$). The correlativity of anions may be due to their common origin. The correlation between Ca^{2+} and SO_4^{2-} refers to Ca^{2+} being the main neutralizer of SO_4^{2-} .



Depositions of throughfall and open land at Voore and Pikasilla, $\text{kg} \cdot \text{ha}^{-1}$.

The total amounts of deposition were high (Figure). The open area sulphur load at Voore was $11 \text{ kg}\cdot\text{ha}^{-1}$ in 1989, and $17 \text{ kg}\cdot\text{ha}^{-1}$ in 1990; at Pikasilla the mean value of $5 \text{ kg}\cdot\text{ha}^{-1}$ was obtained for 1990. The deposition load in the Voore forest was 1.7–2.8 times higher, and in the Pikasilla forest 2.5 times higher than on open landscape.

The nitrogen consumption capacity of a temperate forest stand is $10\text{--}20 \text{ kg}\cdot\text{ha}^{-1}\cdot\text{year}^{-1}$, in the case of especially sensitive ecosystems only $5\text{--}10 \text{ kg}\cdot\text{ha}^{-1}\cdot\text{year}^{-1}$ (Nilgård, 1990). The nitrogen amount precipitating on open landscape at Voore during the year was $9 \text{ kg}\cdot\text{ha}^{-1}$ in 1989, and even $23 \text{ kg}\cdot\text{ha}^{-1}$ in 1990. The Pikasilla site also received a heavy load, $24 \text{ kg}\cdot\text{ha}^{-1}$. The nitrogen load reaching the Voore forest was 2.4–3.9 times higher than the amount for open land; for the Pikasilla forest the corresponding value was slightly lower.

According to literature leaves and branches (epiphytic green algae and lichens) can assimilate nitrogen immediately from precipitation, especially in the case of nitrogen deficit in soil (Helmisaari and Mälkönen, 1989). Such a phenomenon is to be expected in the conditions of Pikasilla site, populated by Scotch pine on sandy soil, which forms a boreal pine forest dominated by red whortleberry (*Vaccinium vitis-idaea*). The opposite situation occurs at Voore where the atmospheric nitrogen supply from deposition is up to $35 \text{ kg}\cdot\text{ha}^{-1}$, but brown lessive soils on drumlins provide already a good nitrogen supply. The forest stand has a multi-layered nemoral coniferous-hardwood composition dominated by Norway spruce in canopy and having a rather rich in species herb layer. Here the nitrogen load may introduce considerable changes in the growth of trees, their susceptibility to diseases, frost and drought stress.

Conclusions

1. Precipitation does not cause direct acidification in the stands studied.
2. The stands deposit large amounts of sulphur.
3. Estimated total nitrogen input to the nemoral spruce stand at Voore is rather big; additional amounts deposited from the air may act as the main factor causing changes that lead to the deterioration of the forest state.

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REFERENCES

- Berljand, M.* 1982. *Moderne Probleme der atmosphärischen Diffusion und der Verschmutzung der Atmosphäre.* Springer, Berlin.
- Etverk, I.* 1988. Mets muutuvus keskkonnas. — *Eesti Loodus*, 6, 354—360.
- Frey, J., Frey, T., Rästa, E.* 1988a. Tähtsamate saasteainete koormus 1987. a. sademetes. In: Kaasaegse ökoloogia probleemid. Vabariikliku 4. ökoloogiakonverentsi teesid. Tartu, 20—22.
- Frey, J., Frey, T., Rästa, E., Pentšuk, J.* 1988b. Vihmavete saastatusest 1986—1987. aastal ja selle võimalikust mõjust metsadele. — *Keskkonnakaitse*, 1, 3—10.
- Frey, J., Palo, A.* 1991. Tööstusaaste sadenemisest Voore kuusikus ja metsakahjustused. In: Kaasaegse ökoloogia probleemid. Eesti 5. ökoloogiakonverentsi teesid. Tartu, 29—32.
- Frey, T., Pentšuk, J., Rästa, E., Sallo, A., Frey, J.* 1987. Esialgseid andmeid sademete ioonilisest koostisest Eestis. — *Keskkonnakaitse*, 3, 1—8.
- Helmisaari, H.-S., Mälkönen, H.* 1989. Acidity and nutrient content of throughfall and soil leachate in three *Pinus sylvestris* stands. — *Scand. J. Forest Res.*, 4, 1, 13—28.
- Iwens, W. P. M. F., Draaijers, G. P. J., Bos, M. M., Bleuten, W.* 1988. Dutch Forests as Air Pollutant Sinks in Agricultural Areas. Department of Physical Geography, State University of Utrecht, 1—43.
- Lõhmus, K., Lasn, R.* 1991. Alumiiniumi toksilisusest Eesti kuusikutes. In: Kaasaegse ökoloogia probleemid. Eesti 5. ökoloogiakonverentsi teesid. Tartu, 98—100.
- Martin, J., Utsvatov, V., Geletjuk, N., Virolainen, V.* 1985. Sademete keemiline koostis ja selle muutumine puutaimede mõjul Eesti NSV rannikualadel. In: Kaasaegse ökoloogia probleemid. Vabariikliku 3. ökoloogiakonverentsi teesid. Tartu, 85—87.
- Miller, H. G.* 1985. Acid flux and the influence of vegetation. In: Symposium on the Effects of Air Pollution on Forest and Water Ecosystems. Helsinki, April 23—24, 37—46.
- Nilgård, B.* 1990. Nitrogen pollutants seriously stressing Europe's forests. — *Acid Enviro*, 9, 22—24.
- Paalme, L., Voll, M., Urbas, E., Palvadre, R., Johannes, I., Kirso, U.* 1990. Põlevkivirajooni mõjust Peipsi järvele atmosfääri kaudu. — *Eesti TA Toim. Keemia*, 39, 1, 18—27.
- Smidt, St.* 1986. Bulkmessungen in Waldgebieten Österreichs. — *FBVA Berichte*, 13, 1—28.
- Smith, W. H.* 1981. *Air Pollution and Forests. Interaction between Air Contaminants and Forest Ecosystems.* New York.
- Yoshida, S., Ichikumi, M.* 1989. Role of forest canopies in the collection and neutralization of airborne acid substances. — *The Science of the Total Environment*, 84, 35—43.

Presented by J. Martin, D. Sc.,
Member of the Estonian Academy of Sciences

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