

# Atmospheric deposition of base cations, nitrogen and sulphur in coniferous forests in Sweden — a test of a new surrogate surface

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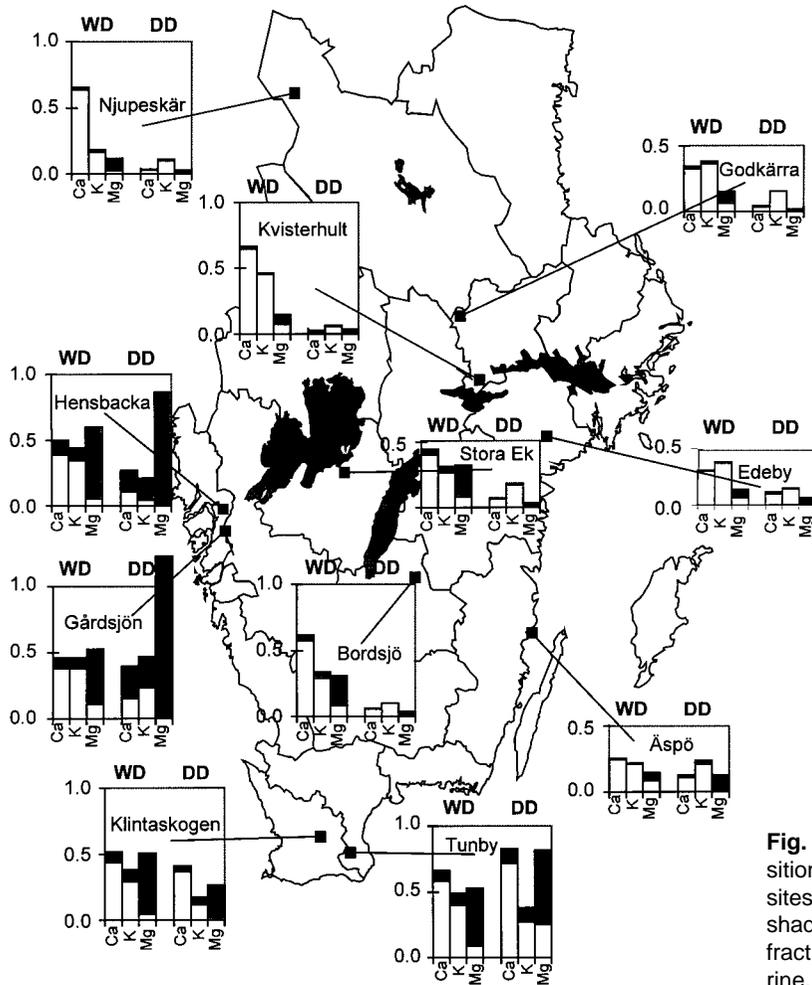
Ferm, M., Westling, O. & Hultberg, H. 2000. Atmospheric deposition of base cations, nitrogen and sulphur in coniferous forests in Sweden — a test of a new surrogate surface. *Boreal Env. Res.* 5: 197–207. ISSN 1239-6095

Dry deposition of base cations, nitrate, as well as particulate ammonium, and sulphate in coniferous forests was measured using a surrogate surface in combination with net throughfall measurements at 11 sites in southern Sweden. The measurement technique involved monitoring gaseous pollutants with diffusive samplers and assuming common dry deposition rates on forest and the surrogate surface. The dry deposition of base cations was important as compared to the wet deposition at all coastal (windy) sites. Correlations of the internal fluxes of potassium and calcium were identified with regard to the deposition of reduced nitrogen compounds and sulphur dioxide respectively. In addition, the results outline the significance of dry deposition compared to wet deposition and trends relating to the net throughfall of nitrogen compounds. The net throughfall of nitrogen compounds was often negative, but approached the estimated dry deposition with increasing load.

## Introduction

Sweden is forested to ca. 70%, and most of its forest soils have a very low weathering rate. The critical load for acidification is therefore low and the forest has adapted to a low input of inorganic nitrogen compounds. Consequently, the high atmospheric input of acidifying and eutrophying compounds experienced today results in negative effects on the forest ecosystems such as changes

in biodiversity and a loss of base cations from the soil. In the latter case, hydrogen and aluminium ions replace calcium, magnesium and potassium (base cations) on cation exchange sites of soil particles. The atmospheric deposition of these base cations is thus an important contribution to forest soils with low weathering rates. The dry deposition is large to forests due to their rough surface and because the needles of the conifers are efficient in trapping large particles.



**Fig. 1.** Average wet and dry deposition of Ca<sup>2+</sup>, K<sup>+</sup> and Mg<sup>2+</sup> at the 11 sites used (mmol m<sup>-2</sup> month<sup>-1</sup>). The shaded areas represent the marine fraction and the white the non-marine.

Dry deposition can be estimated with different techniques using modelling, short-term leaching of collected needles, inert surrogate surfaces, ratios between net throughfall in the forest and a forest edge, isotopic ratios in tree bole, precipitation and throughfall and micro-meteorological studies (eddy correlation and gradient technique). In order to estimate the dry deposition in large regions over longer periods using actual measurements it is necessary to have simple, reliable and cost-efficient techniques. The throughfall technique is simple to use, but can only be applied to compounds that do not interact with the canopy, in cases where the canopy exchange cannot be estimated.

It is well known that base cations are extruded from the tree needles and are leached by the throughfall. This ion leakage or internal circula-

tion can be large in comparison with the dry deposition. It is also well known that nitrate and ammonium are lost in throughfall especially during the growing season. By combining the throughfall technique with deposition measurements to an inert surface that resembles the needles, deposition estimates can be made for atmospheric particulate compounds. This approach was considered the most suitable technique for this study. A special way of calculating the deposition using ion to sodium ratios has previously been utilised (Ferm and Hultberg 1995, Hultberg and Ferm 1995, Dambrine *et al.* 1998). Ulrich (1983) used the ion to sodium ratio in precipitation to calculate the dry deposition. The ion to sodium ratio in precipitation can, however, be very different from that on the surrogate surface (Hultberg and Ferm 1995, Ferm and Hultberg 1999).

Another advantage in addition to low cost and simplicity of the surrogate surface is that no electricity is needed. The techniques can therefore be applied to remote forest sites.

Nitrogen compounds are present in both gaseous (ammonia, nitric acid, nitrogen oxides) and particulate forms (ammonium and nitrate). Nitric acid has a high sticking coefficient for all kinds of surfaces and will therefore partly be deposited on the surrogate surface. In order to estimate the ammonia deposition, atmospheric concentrations were measured with a passive (diffusive) sampler that does not need electricity (Ferm and Rodhe 1997). This technique was also applied to sulphur dioxide and nitrogen dioxide.

## Materials and methods

Eleven stations were selected to represent different environments such as coast, mountain area and agriculture (Fig. 1). All forest stands consist of spruce except for the pine stand at Äspö. Stand characteristics are given in Table 1. The measurements started in October 1997 and ended in September 1998, except for Hensbacka where they started in November 1997 and ended in October 1998.

Throughfall (TF) was collected during winter in open buckets lined with polyethylene bags. During summer polyethylene funnels threaded into the lid of polyethylene bottles were used. To avoid conversions of ammonium to organic nitrogen by algae (Ferm 1993), the polyethylene

bottles were wrapped with aluminium foil. Plastic bags were also used inside these bottles. Approximately 10 throughfall collectors, in a cross-shaped pattern, were placed in a homogeneous part of the forest (30 × 30 m), at all sites. This approach had previously given good agreement as compared with using a higher number of collectors (unpublished results). For spruce stands stemflow can be assumed as negligible (Moldan *et al.* 1998).

Wet deposition (WD) was collected using similar collectors as throughfall (bulk samplers). One or two collectors were placed in a clearing or in a suitable location outside the forest.

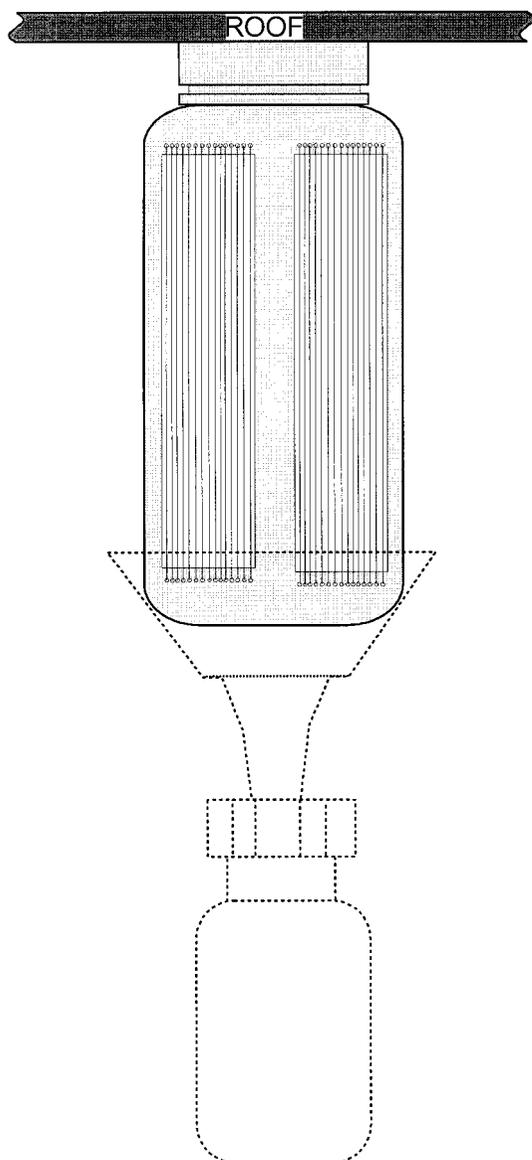
The surrogate surface consisted of ca. 13-m long Teflon thread (diameter 0.4 mm) mounted across three rectangles (7.5 × 13.5 cm) cut in a 1 l polyethylene bottle, *see* Fig. 2. The lid of the polyethylene bottle was screwed under a roof (1.2 × 1.5 m) that protected the surrogate surface from precipitation. At the base, a wide hole was made so that a funnel could be attached using nylon screws. The pipe of the funnel was threaded into a 200 ml sample bottle. After exposure the thread was sprayed with a fine mist of de-ionised water (ca. 100 ml) and the leachate sample collected in the 200-ml bottle. The dry deposition of an ion X ( $DD_x$ ) was estimated with Eq. 1.

$$DD_x = \frac{[X]_{ss}}{[Na^+]_{ss}} NTF Na^+ \quad (1)$$

where  $[X]_{ss}$  and  $[Na^+]_{ss}$  denote the concentration of species X and  $Na^+$  in the leachate from the surro-

**Table 1.** Stand characteristics and location of sites. The site index H100 is the expected tree height at 100 years of age. Äspö consists of pine trees and the other stands consist of spruce.

Site	Age years	Tree height m	Stems/ha	Site index H100	Latitude °N	Longitude °E	Altitude m
Äspö	70	11	300	15	57.41	16.66	10
Njupesjär	130	12	300	14	61.38	12.43	720
Godkärra	92	22	644	26	59.56	15.46	175
Kvisterhult	75	24	516	28	59.21	15.56	40
Edeby	67	21	568	28	58.57	16.59	50
Stora Ek	56	21	724	30	58.37	13.46	88
Hensbacka	77	23	439	26	58.26	11.44	120
Gårdsjön	90	13	653	16	58.07	12.02	120
Bordsjö	45	15	1600	28	57.50	14.59	285
Klontaskogen	39	18	1179	34	55.37	13.26	105
Tunby	44	19	1104	32	55.36	14.06	125



**Fig. 2.** The surrogate surface used. It consists of Teflon strings attached to a frame made from a polyethylene bottle.

gate surface, respectively. NTF denotes the net throughfall i.e. throughfall (TF) minus wet deposition (WD). The NTF of sodium represents the DD of sodium since no internal circulation of sodium takes place.

Originally the technique was only intended to be used to estimate the base cation deposition. In this case, it was assumed that sea spray and particles containing base cations were deposited with similar rates, because they had similar size. This

was verified by dry deposition measurements of non-marine calcium, which were in close agreement with model calculations (Ferm and Hultberg 1995). The technique was subsequently applied for determining accumulation mode particles (i.e. small particles of size 0.1–1  $\mu\text{m}$ ).

It is not necessarily true that the ratio of deposition of an ion, X, to the sodium ion, is the same on the surrogate surface as on the trees. This is especially so where the X ion predominates in smaller particles while the sodium ion is usually associated with larger particles. In this case, wind speed and geometry become influential factors. The importance of the locality (different wind speeds) of the surrogate surface has previously been examined (Ferm and Hultberg 1999). It was found that at a more wind exposed site, the deposition to the surrogate surface was higher. The calculated dry deposition for both coarse and accumulation mode particles to the forest was in this case, however, rather independent of the influence of the wind exposure on the surrogate surface. The similar ratio between the deposition of fine and large particles to the surrogate surface and to the forest was explained by model calculations if the deposition due to impaction was the dominant deposition process. It was therefore believed that most of the deposition occurred during occasions with high wind speed.

The internal circulation or ion leakage (IC) and uptake (UP) are correlated according to Eq. 2.

$$\text{TF} = \text{WD} + \text{DD} + \text{IC} - \text{UP} \quad (2)$$

Throughfall, precipitation and the leachate from the surrogate surface were analysed for  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$  and  $\text{Mn}^{2+}$  concentrations using ion chromatography.  $\text{H}^+$  was determined with a glass electrode and  $\text{NH}_4^+$  with the flow injection analysis. The Kjeldahl nitrogen ( $\text{NH}_4^+$  + organic nitrogen) concentration was analysed with the Technicon Industrial Method (1982). Air concentrations of  $\text{SO}_2$ ,  $\text{NH}_3$  and  $\text{NO}_2$  were measured with diffusive (passive) samplers (Ferm and Rodhe 1997) synchronously with throughfall and precipitation (monthly basis). The accuracy of the techniques was previously investigated by comparison with an active sampling for both  $\text{SO}_2$  and  $\text{NO}_2$  (Ferm and Svanberg 1998) and  $\text{NH}_3$  (Kirchner *et al.* 1999). The diffusive samplers were placed under a rain shield near the sur-

rogate surface. Exposure time of the diffusive samplers coincide with throughfall, precipitation and surrogate surface sample changes.

The dry deposition of base cations and nitrates were calculated from Eq. 1 and the internal circulation of base cations from Eq. 2 (where UP = 0). The dry deposition of SO<sub>2</sub> was obtained from the difference in two calculations; (i) determining the dry deposition SO<sub>2</sub> and particulate sulphate with Eq. 2 (where IC and UP are zero), and (ii) determining the dry deposition of particulate sulphate from Eq. 1.

It is very difficult to estimate the dry deposition of NH<sub>3</sub> from the atmospheric NH<sub>3</sub> concentration. Published numbers on the deposition velocity for NH<sub>3</sub> are usually obtained with the gradient technique. Van Oss *et al.* (1998) observed that the NH<sub>3</sub> gradient above the forest sometimes decreased with height during the day, indicating an apparent emission of NH<sub>3</sub>. Evaporating NH<sub>4</sub>NO<sub>3</sub> particles caused this reverse gradient. Duyzer *et al.* (1994) estimated the dry deposition velocity of NH<sub>3</sub> on a Douglas fir forest in the Netherlands to 19–30 mm s<sup>-1</sup>. In an earlier investigation at Gårdsjön, a deposition velocity of twice the average deposition velocity for SO<sub>2</sub> was used (Ferm and Hultberg 1999). The same approach was used in this study where the measured NH<sub>3</sub> concentrations were multiplied with a deposition velocity of 16 mm s<sup>-1</sup>. It was assumed that HNO<sub>3</sub> was deposited so effectively on the Teflon strings that the dry deposition value for nitrate represents both HNO<sub>3</sub> and particulate nitrate. Since background concentra-

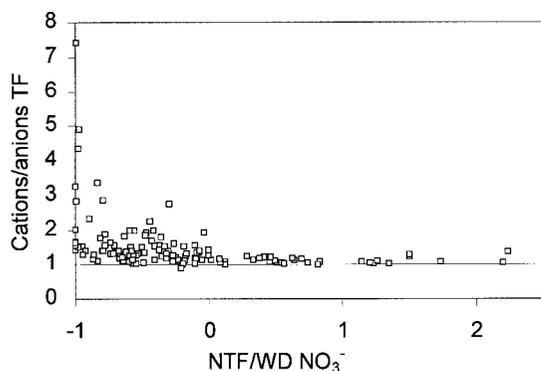
tions of NO, NO<sub>2</sub>, HNO<sub>2</sub> and peroxyacetyl nitrate are very low, their contribution to the measured dry deposition was neglected. For NO<sub>2</sub>, Granat and Hällgren (1992) used a deposition velocity of 1.3 mm s<sup>-1</sup> for a coniferous forest and, found that lower nitrate fluxes in throughfall occurred when the trees were exposed to NO<sub>2</sub> indicating an increased nitrogen conversion. Consequently, in the present study the NO<sub>2</sub> fluxes are anticipated to be very small and therefore assumed as negligible.

## Results

The measured wet depositions of ions and precipitation amount at the sites are shown in Table 2. Since the concentrations at Klintaskogen were significantly higher than at nearby stations abnormally high dry deposition in the bulk collector was suspected. Thus concentration data from a nearby station (Arup) were therefore used for Klintaskogen. Similarly, Hensbacka also had unusually higher concentrations than nearby stations. An average from three surrounding stations was therefore used for Hensbacka. The wet and calculated dry depositions of calcium, potassium and magnesium are shown on the map of stations in Fig. 1. The depositions have been divided into marine and non-marine fractions based on the sodium deposition and the composition in the sea. As can be seen from the figure, the dry deposition is very important for the total deposition at the coastal sites where the wind speeds are generally higher.

**Table 2.** Precipitation amount (*P*, mm month<sup>-1</sup>) and wet (bulk) deposition (mmol m<sup>-2</sup> month<sup>-1</sup>) of different ions and organic-N. Index nm denotes non-marine.

	<i>P</i>	H <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	Org.-N	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup> ,nm	Na <sup>+</sup>	Mg <sup>2+</sup> ,nm	Ca <sup>2+</sup> ,nm	K <sup>+</sup> ,nm	Mn <sup>2+</sup>
Njupeskar	86	1.7	1.2	0.9	1.4	1.0	0.8	0.03	0.6	0.2	0.01
Godkärra	72	2.0	1.5	0.7	1.9	0.9	0.8	0.06	0.3	0.4	0.02
Kvisterhult	66	1.0	1.3	0.3	1.5	0.8	0.6	0.07	0.6	0.5	0.02
Edeby	58	0.9	1.3	0.9	1.4	0.8	0.7	0.06	0.3	0.4	0.01
Stora Ek	79	1.3	1.7	0.7	1.9	1.0	2.1	0.08	0.4	0.3	0.04
Hensbacka	107	3.2	3.4	0.6	3.5	1.6	4.9	0.05	0.4	0.3	0.04
Gårdsjön	97	2.0	3.2	0.7	3.1	1.4	3.7	0.11	0.4	0.4	0.03
Bordsjö	89	1.8	2.6	0.9	2.8	1.4	2.0	0.08	0.6	0.3	0.02
Äspö	46	1.8	1.6		1.3	0.8	0.6	0.08	0.2	0.2	0.01
Klintaskogen	90	2.7	4.4	1.2	3.9	1.7	4.1	0.05	0.4	0.3	0.04
Tunby	81	2.3	5.0	0.7	4.5	2.1	3.8	0.09	0.6	0.4	0.03



**Fig. 3.** Cation to anion ratio in throughfall ( $\text{m eq. m}^{-2} \text{ month}^{-1}$ ) as a function of net throughfall to wet deposition ratio of nitrate.

### Internal circulation of base cations

The internal circulation was calculated from the net throughfall minus the calculated dry deposition according to Eqs. 2 and 1 respectively. Calcium, magnesium, potassium and manganese are internally circulated (leaking from the canopy). The leakage of potassium is, however, much higher than for the other ions (Table 3). As cations leak from the canopy, a corresponding amount of anions must follow. The hydrogen concentration of the throughfall was much lower than in precipitation, and in some cases the throughfall was alkaline indicating weak acids such as  $\text{HCO}_3^-$ . The alkalinity was analysed when pH was above 5.4.

The throughfall of cations was on average 23% higher than the measured throughfall of anions

based on charge. The excess of measured cations was linked to the transformation of nitrate to organic nitrogen. Fig. 3 illustrates the relative excess of cations as a function of the dry to wet deposition ratio of nitrate. When the net throughfall of nitrate is positive the cation:anion ratio is on average 1.09 (Fig. 3). When it is negative the cation excess becomes 37% on average. Very high excess is found when no nitrate is found in the throughfall. This implies that there must also be anions to stronger acids present, which were not measured.

The excess of cations in precipitation was on the average 9% for all samples and the same tendency as in throughfall was observed. When NTF:WD of nitrate was negative the cation:anion excess in the corresponding bulk collector was 11%. When NTF:WD of nitrate was positive only 6% excess of cations in bulk precipitation was found.

The NTF:WD ratio was much higher for manganese and potassium than for magnesium and calcium. The ratio between the concentration in precipitation and throughfall for potassium and manganese was on average 0.06 using the one with the smallest ratio at each occasion. Extra control analysis ruled out any contamination of throughfall in the bulk samples.

It was observed earlier at Gårdsjön that the internal circulation flux of calcium follows the dry deposition flux of sulphur dioxide (Hultberg and Ferm 1995). This was also verified at all stations in this study. Using the data in Table 3 (IC

**Table 3.** Internal circulation (IC), and calculated dry deposition (DD) of base cations and manganese and net throughfall (NTF) of sodium ( $\text{mmol m}^{-2} \text{ month}^{-1}$ ). Index nm denotes non-marine.

	$\text{Ca}^{2+}$ IC	$\text{Ca}^{2+}$ ,nm DD	$\text{Na}^+$ NTF	$\text{Mg}^{2+}$ IC	$\text{Mg}^{2+}$ ,nm DD	$\text{K}^+$ IC	$\text{K}^+$ ,nm DD	$\text{Mn}^{2+}$ DD	$\text{Mn}^{2+}$ IC
Njupesjär	-0.2	0.0	0.2	0.1	0.0	1.2	0.10	-0.003	0.08
Godkärra	0.3	0.0	0.2	0.2	0.0	3.3	0.15	0.001	0.21
Kvisterhult	-0.1	0.0	0.3	0.2	0.0	2.2	0.06	0.001	0.14
Edeby	0.3	0.1	0.6	0.3	0.0	3.4	0.13	0.002	0.15
Stora Ek	0.0	0.1	0.3	0.2	0.0	2.7	0.17	0.002	0.10
Hensbacka	0.7	0.1	7.6	0.3	-0.1	4.5	0.04	0.001	0.07
Gårdsjön	0.5	0.2	10.8	0.5	-0.4	3.2	0.24	0.004	0.01
Bordsjö	-0.2	0.1	0.3	0.1	0.0	3.3	0.10	0.001	0.19
Äspö	0.3	0.1	1.0	0.3	0.0	1.5	0.21	0.004	0.02
Klontaskogen	0.6	0.4	2.3	0.3	0.0	4.1	0.12	0.002	0.43
Tunby	0.2	0.7	5.0	0.0	0.3	4.6	0.28	0.005	0.38

of  $\text{Ca}^{2+}$ ) and Table 4 (DD of  $\text{SO}_2$ ), the two fluxes for six stations were calculated. In general, a good correlation was obtained both regarding time and actual amounts (Fig. 4).

The wet and estimated dry depositions of ammonium, sulphate and nitrate are shown in Fig. 5. The estimated dry depositions are as for the base cations more pronounced at the coastal sites (Fig. 5).

The ion leakage (IC) of potassium correlated very well with the total  $\text{NH}_x$  deposition (Fig. 6) although the reason for this correlation is not fully understood. One hypothesis is that both parameters decrease (for different reasons) with increasing latitude. The correlations during individual months were, however, poorer but the correlation improved with integration time. A possible explanation can be that the leaching of potassium is a slow process requiring large amounts of precipitation; thus the ion leakage therefore increases with precipitation amount. Potassium leaching was previously commented on in the literature. Lovett *et al.* (1989) noticed that the top of the canopy depleted the throughfall of  $\text{NH}_4^+$  and enriched it in  $\text{K}^+$ . Roelofs *et al.* (1985) found that base cations (especially potassium) were released when needles were leached in ammonium sulphate.

## Air concentrations

The average concentrations of the measured gaseous pollutants are shown in Table 5. The dry depo-

sition velocity for  $\text{SO}_2$  (Table 5) was calculated by dividing the calculated dry deposition of  $\text{SO}_2$  with the average  $\text{SO}_2$  concentration at that site.

## Nitrogen deposition

The concentration of organic nitrogen was calculated from Kjeldahl-N minus  $\text{NH}_4^+$  concentration. Since the Kjeldahl-N concentration in some cases was smaller than the  $\text{NH}_4^+$  concentration some doubt can be cast on the sampling and/or analysis of these species. In an earlier study (Ferm and Hultberg 1998), higher Kjeldahl-N concentrations were obtained if the throughfall collectors were pre-treated with iodine which appeared to keep the collector free from material sticking to the walls. In retrospect, this iodine pre-treatment ought to have been included in the present study.

The measured net throughfall of  $\text{NH}_4^+$  was negative at all sites except Tunby, where the estimated dry deposition of  $\text{NH}_4^+$  was highest (Table 4). Even the net throughfall of Kjeldahl-N (*see* NTF  $\text{NH}_4^+$  + NTF org.-N in Table 4) was often negative indicating that deposited reduced nitrogen species do not appear in throughfall. Even NTF of  $\text{NO}_3^-$  was negative in most cases. Fig. 7 shows the net throughfall of all nitrogen species ( $\text{NH}_4^+$  + org.-N +  $\text{NO}_3^-$ ) as a function of estimated dry deposition of nitrogen ( $\text{NH}_3$ , particulate  $\text{NH}_4^+$ ,  $\text{HNO}_3$  and particulate  $\text{NO}_3^-$ ). The estimated dry deposition is only similar to the net throughfall at the site with the highest deposition (Tunby situated in an

**Table 4.** Throughfall amount (TF, mm), net throughfall (NTF) and calculated dry deposition (DD) of hydrogen ions, nitrogen and sulphur species ( $\text{mmol m}^{-2} \text{month}^{-1}$ ). Index nm denotes non-marine.

	TF mm	H <sup>+</sup> NTF	NH <sub>4</sub> <sup>+</sup> NTF	Org.-N NTF	NH <sub>x</sub> DD	NO <sub>3</sub> <sup>-</sup> NTF	NO <sub>3</sub> <sup>-</sup> DD	SO <sub>4</sub> <sup>-2</sup> ,nm DD	SO <sub>2</sub> DD
Njupesjär	37	-0.4	-1.0	0.3	0.0	-1.1	-0.1	0.0	-0.4
Godkärra	46	-0.8	-0.8	0.9	1.7	-1.5	0.1	0.1	0.2
Kvisterhult	38	-0.3	-0.7	0.8	0.4	-0.6	0.1	0.0	0.0
Edeby	40	-0.5	0.0	1.0	0.5	-0.4	0.5	0.2	0.4
Stora Ek	49	-1.5	-0.8	0.7	0.9	-0.6	0.3	0.1	-0.2
Hensbacka	68	-2.2	-1.3	1.6	1.4	-0.2	1.2	0.1	0.3
Gårdsjön	65	-0.3	-1.3	1.5	1.9	0.2	2.5	0.4	0.2
Bordsjö	52	-1.5	-2.2	0.6	1.8	-2.4	0.5	0.2	-0.5
Äspö	42	-0.3	-0.2	1.3	1.3	-0.1	0.8	0.2	0.1
Klintaskogen	38	-1.2	-0.3	0.9	3.2	1.0	1.6	0.4	0.8
Tunby	43	-1.4	2.2	2.7	5.0	1.9	3.1	1.0	1.1

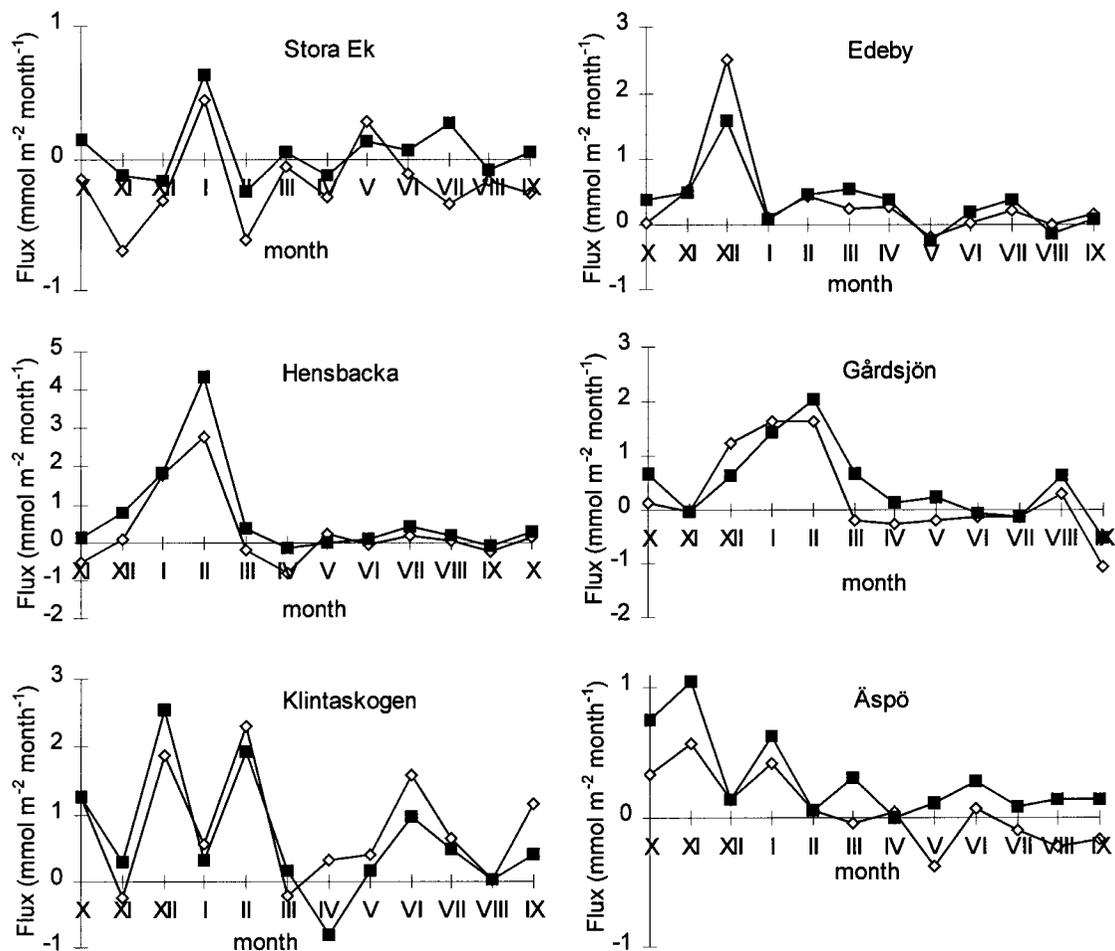


Fig. 4. Internal circulation of  $\text{Ca}^{2+}$  (filled squares) and dry deposition of  $\text{SO}_2$  as a function of month.

Table 5. Average concentrations in air ( $\mu\text{g m}^{-3}$ ) and deposition velocity ( $V_d$ ) of  $\text{SO}_2$  ( $\text{mm s}^{-1}$ ).

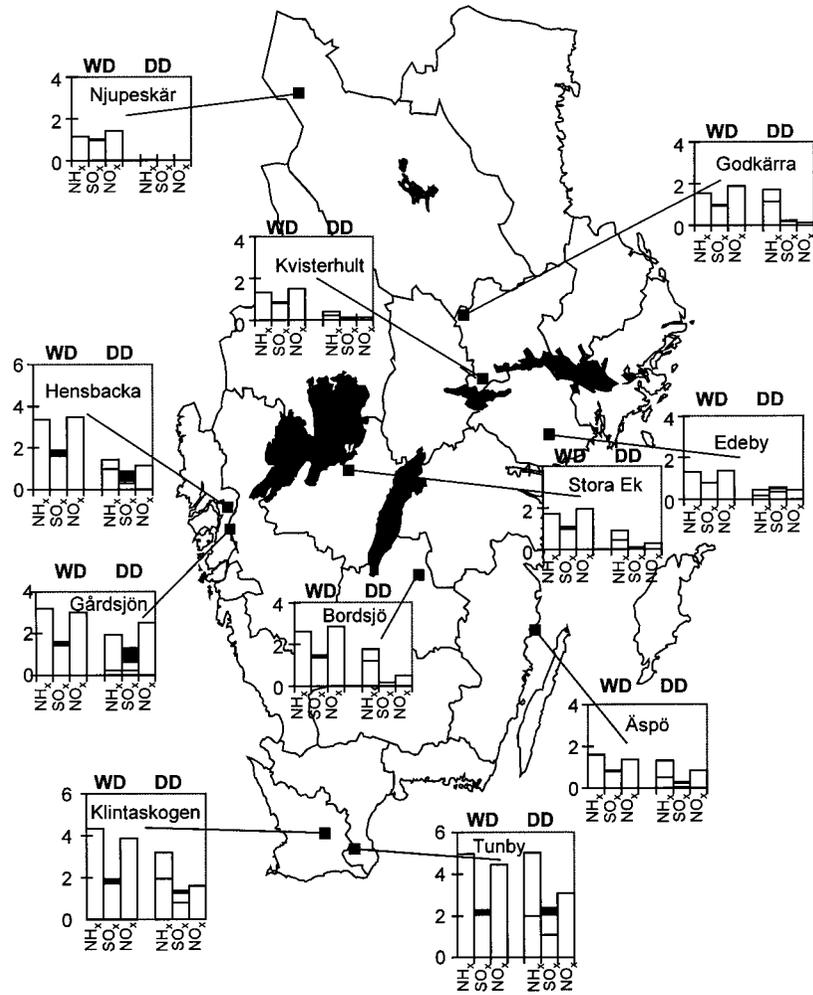
	$\text{SO}_2$	$\text{NH}_3$	$\text{NO}_2$	$V_d$
Njupesjär	0.2	0.0	0.9	
Godkärra	0.4	0.7	2.4	9
Kvisterhult	0.5	0.1	3.0	2
Edeby	0.7	0.1	2.6	13
Stora Ek	0.5	0.2	3.4	
Hensbacka	0.7	0.4	3.0	10
Gårdsjön	0.8	0.1	4.0	7
Bordsjö	0.7	0.5	2.5	
Äspö	0.8	0.2	2.7	2
Klintaskogen	1.9	0.8	7.6	10
Tunby	1.6	0.8	6.0	17

agricultural area). The missing nitrogen can probably partly be explained by litterfall containing nitrogen originating from dry deposition.

## Discussion

The calculated depositions were negative during certain months. Several explanations can account for this:

- (i) if the wet deposition occur as snow, it will not be collected in the throughfall collectors synchronously with the precipitation,
- (ii) the intercept ( $\text{WD} - \text{TF}$  of water) can be sub-

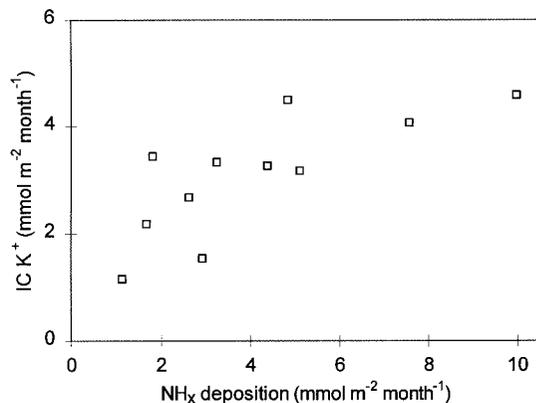


**Fig. 5.** Regional deposition pattern for  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  ( $\text{mmol m}^{-2} \text{ month}^{-1}$ ). The lower fraction of the dry deposition represents gaseous  $\text{NH}_3$  and  $\text{SO}_2$  and the fraction on top of that particulate  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$ . The shaded areas represent the marine fraction of the sulphur deposition.

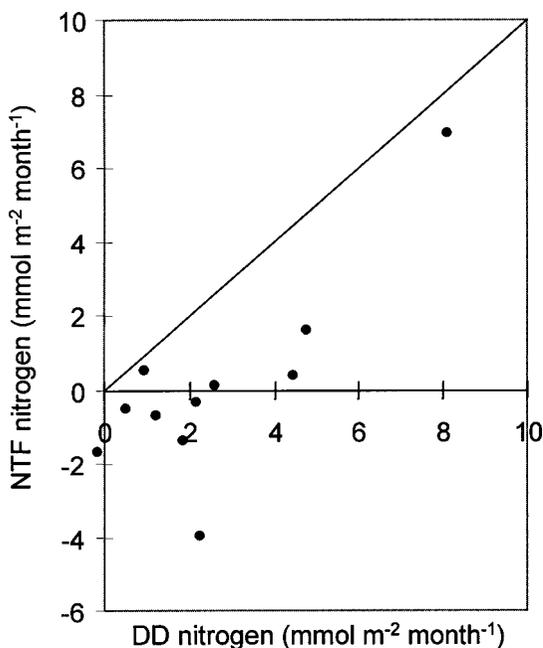
stantial compared to throughfall if there were many precipitation events with small amounts,

- (iii) the bulk collectors can be contaminated by throughfall,
- (iv) dry deposition can occur in bulk collectors (no correction was made for this), and
- (v) precipitation measurement errors caused by the collector affecting the wind above it and thereby the trajectory for the rain droplets or snow flakes.

The last two error sources are presently being investigated. Unfortunately wet-only collectors were not an option in this study since the stations



**Fig. 6.** Internal circulation of potassium as a function of WD + calculated DD of  $\text{NH}_x$ .



**Fig. 7.** Net throughfall of nitrogen ( $\text{NH}_4^+$ , organic-N and  $\text{NO}_3^-$ ) as a function of calculated dry deposition of  $\text{NH}_3$ ,  $\text{HNO}_3$  and particulate  $\text{NH}_4^+$  and  $\text{NO}_3^-$  at the 11 forest sites.

lacked electricity.

The wet and dry depositions will be affected if dry deposition occurs in the bulk collectors. The calculated wet plus dry deposition will, however, only be affected to a minor degree in this case. Van Leeuwen *et al.* 1995 made an overview of the correction factors for the contribution of dry deposition onto bulk collectors in different areas in Europe. For  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , the correction factor ranges from 13%–17%, and for  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$  from 24%–32%. They divided the correction term for NaCl into continental areas (14%) and coastal areas (32%).

The anomalously low deposition velocities for  $\text{SO}_2$  at Kvisterhult, Stora Ek and Bordsjö were probably a result of difficulties in obtaining correct deposition amounts of water. The accuracy in the estimated dry deposition of  $\text{SO}_2$  was reduced since it was calculated as the difference between two numbers (NTF of sulphur and DD of particulate sulphate). The deposition of particulate sulphate in forests is nowadays often larger than the  $\text{SO}_2$  deposition, *see e.g.* Gårdsjön in Fig. 5. The  $\text{SO}_2$  concentrations in air at Gårdsjön have

decreased substantially during the last 15 years while the particulate sulphate concentrations have only decreased marginally (Ferm and Hultberg 1998). The average deposition velocity for  $\text{SO}_2$  at the stations listed in Table 5 was  $8 \text{ mm s}^{-1}$ . This value is close to the value estimated by Hultberg and Grennfelt (1992) for Gårdsjön ( $7\text{--}8 \text{ mm s}^{-1}$ ), but lower than the deposition velocity measured and modelled by Erisman (1994) for a forest in the Netherlands ( $17 \text{ mm s}^{-1}$ ).

The rough estimate that the dry deposition velocity for gaseous  $\text{NH}_3$  is  $16 \text{ mm s}^{-1}$  is rather important for the estimated  $\text{NH}_x$  deposition. The estimated dry deposition of  $\text{NH}_3$  was on average 50% of the total dry deposition of  $\text{NH}_x$  and 20% of the total  $\text{NH}_x$  deposition. The high correlation between calculated and observed dry depositions of nitrate which was earlier observed in the dryer NITREX area at Gårdsjön (Ferm and Hultberg 1999) was not observed at the stations in this study, not even at Gårdsjön since another more humid micro-catchment was used (untreated control area). The best correlations were observed at the sites with the highest net throughfalls of nitrate (Klintaskogen and Tunby). Dry deposition of nitrogen compounds is probably more difficult to estimate in the Nordic countries than in central Europe because the uptake, or conversion of inorganic nitrogen to organic nitrogen species, is large as compared with the small dry deposition.

## Conclusions

The use of a surrogate surface was demonstrated for estimating dry deposition to forested areas on a national scale. The methodology is cost effective (low manpower requirement) and can be operated at locations lacking electricity. At present, error sources are largely related to the uncertainties in determining wet deposition which has promoted further development work aimed at improving the WD sampler.

The equivalence between  $\text{Ca}^{2+}$  leaching and  $\text{SO}_2$  deposition fluxes on a monthly basis observed at the Gårdsjön site in a previous study was confirmed for all the sites used in this investigation. In addition a correlation between internal circulation of  $\text{K}^+$  and deposition of  $\text{NH}_x$ , on a time basis of several months was identified. Further correla-

tions of the data set strongly linked the uptake or transformation of nitrate to the poor ion balance sometimes observed in throughfall. The net throughfall of nitrogen measured was always less than the estimated dry deposition of nitrogen and often negative. In general, the measured dry depositions were more significant at coastal sites than at inland sites.

*Acknowledgements:* Financial support has been gratefully received from: Air Quality Protection associations, Regional Forest and Environmental Authorities, Swedish Environmental Protection Agency, IVL Swedish Environmental Research Institute and Åspö Environmental Research Foundation.

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Received 4 November 1999, accepted 20 December 1999