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THROUGHFALL MEASUREMENTS OF NITROGEN AND SULPHUR COMPOUNDS

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The wet- and throughfall deposition of nitrogen and sulphur compounds to a spruce forest edge in Sweden was studied using preserved as well as unpreserved collectors. During the warmer part of the year inorganic nitrogen was lost in unpreserved throughfall collectors, if they were not shielded from light. Several days of light exposure was needed to transform most of the ammonium, most likely to an organic form. The rate was enhanced by the addition of glucose. High throughfall deposition of organic nitrogen has been found using preserved collectors. The origin of this organic nitrogen in throughfall is not clear, but it seems likely that it comes from transformation of wet and dry deposited ammonium. Rough estimates of the dry deposition were made from air concentration measurements inside and outside the forest. The dry deposition of SO₂, HNO₃ and NH₃ was more significant than their particulate forms.

KEY WORDS : Troughfall, preservation, ammonium, nitrate, edge effects, spruce forest.

INTRODUCTION

Diffusion, impaction and sorption are important phenomena when air pollutants are dry deposited. The deposition therefore depends more on the properties of the receptor surface than what is the case for wet deposition (when gravitation is the dominating transport force). The dry deposition is therefore larger on rough surfaces, like forests, than on smooth surfaces. At a forest edge the advection of air can bring in so large amounts of air pollutants, that the dry deposition exceeds the wet deposition. Spruce acts as an efficient filter for air pollutants and is adapted to a low nitrogen level. In this project these two facts were the reason for investigating methods to estimate the dry deposition of nitrogen compounds to a spruce edge.

Throughfall is defined as precipitation that has passed through a tree canopy. The amount of a compound deposited as throughfall (and stem flow) is equal to the dry- (including occult-) and wet deposition plus needle ion leakage minus the uptake by the needles or other organisms living on them. There may also be conversions of some compounds into others on the needle surface, but if one considers elements instead of compounds, the interpretation given above is more correct. Provided that the interactions with the canopy are small in

comparison with the total deposition, throughfall measurements can be used to estimate the dry deposition of sulphur^{1,2}. If, on the other hand, the interaction processes are important, other techniques have to be used to estimate the dry deposition. In such a case a comparison between throughfall and dry deposition can be used to study the exchange between the atmosphere and the biosphere. This work is part of a subproject called BIOSphere ATmosphere EXchange (BIATEX) within Eurotrac. In this work the throughfall technique has been compared to rough estimates of the dry deposition from air concentration measurements. Throughfall measurements are inexpensive and simple to perform. Electricity is not needed in the forest. The throughfall technique has been used during many years and at many sites in Europe³.

At many places in Europe the atmospheric nitrogen deposition to conifers is higher than the critical load. The critical load for avoiding nutrient imbalance in a coniferous forest has been estimated to 70-85 mmole m⁻²yr⁻¹⁴. This deposition is even more enhanced at forest edges and other wind exposed sites even at places having a low average deposition^{5,6}. A high nitrogen input makes the trees grow faster, but leads to a poorer strength of the timber. It also favours species like algae, lichens and fungi on the spruce as well as other species in the forest that can stand more nitrogen. It can also displace the balance between different elements that are taken up (e.g. lead to magnesium deficiency). It has also been suggested to be partly responsible for the observed forest dieback in certain areas in Europe⁷.

EXPERIMENTAL

The sampling site is called Anten and is situated 10 km north west of Alingsås and approximately 60 km from the Swedish west Coast (58° 00'N, 12° 26'E) having an altitude of 100 m. The forest stand which is healthy, consists of 50 year old Norway spruce (*Picea abies* (L.) Karst) trees 18-20 m tall. The experiments were carried out in a corner of the forest. One edge is facing south and the other east. Bulk collectors were placed in four rows 0, 10, 30 and 60 m from the southern edge i.e. the main wind direction. Each row consisted of ten collectors with a distance of about 10 m. 5 bulk collectors for precipitation were placed 10 m outside the forest. During the winter months (November - March) when the precipitation occasionally is in the form of snow, polyethylene buckets were used as collectors. During the other months the collectors consisted of a polyethylene funnel (Ø= 19 cm) containing a nylon net (mesh size 0.5 mm), that prevents litter fall from entering the sample, which was threaded to the lid of a 5 l polyethylene bottle. One series of collectors were dark (painted in black). For convenience disposable soft polyethylene bags were inserted and connected to the bottle by folding it over the threading. Polyethylene bags were also used in the buckets. To every second sampler 0.5 g iodine was added as a preservative before the sampling to avoid growth of microorganisms. During April - October a second set of samplers consisted of non painted (semi transparent) bottles were used. Precipitation and throughfall were collected monthly. An aliquot proportional to the total throughfall volume was taken from all samples from the same row and series, mixed in a bottle and sent to the laboratory. If bird droppings were observed in a funnel, this sample was discarded. All funnels were cleaned using a brush and de-ionized water in connection with the collecting of the samples.

Preserved and unpreserved synthetic throughfall solution were stored in closed semi transparent bottles during the warmest months to see if any of the analyzed ions interfered with the materials used. This was not the case.

Preservation of samples

Since the sampling time is so long (one month) and because it had earlier been observed that the ammonium deposition in throughfall is lower than in precipitation during the summer, it was decided to investigate the stability of the samples. Normally precipitation samples are not preserved. No information as to whether it is necessary to preserve throughfall samples could be found in the literature. A preservative was chosen with a low vapour pressure, in order to avoid high losses, and being as a harmless compound as possible to man and nature. The preservative must of course not interfere with the analysis. Iodine was chosen since it met the two criteria mentioned and also because it is known to react rapidly. It is well known that iodine and ammonia can form the highly explosive compound $\text{NI}_3 \cdot \text{NH}_3$, but this is not the case during these circumstances. In Australia thymol (5-Methyl-2(1-methylethyl)phenol) has earlier been used to preserve water samples (Greg Ayers pers. comm.). This compound was used in some experiments.

Sampling techniques for air-borne compounds

The concentrations of the most important air-borne compounds for the dry deposition of sulphur and fixed nitrogen were measured 10 m outside the forest edge and 40 m inside (from the southern as well as the eastern edge). Wind speed and wind direction were also measured at the two points. A rough estimate of the dry deposition should be made by a mass balance approach in which wind and concentration data is combined with assumptions on how the concentration decreased with the distance from the top of the first row of trees via the top of the last row of trees to the ground under the measuring point in the forest. There was unfortunately a problem with the data logger connected to the wind monitoring device when the air concentrations were measured. SO_2 and HNO_3 were measured with 75 cm long cylindrical denuders, coated with sodium carbonate⁸. Particulate SO_4^{2-} and NO_3^- were measured on a sodium carbonate impregnated filter behind the denuders. NH_3 and particulate NH_4^+ were measured analogously with 50 cm long denuders and filter that were coated and impregnated with oxalic acid⁹. We have participated with the two denuders in two large European intercomparison campaigns^{10, 11}. The denuders were mounted in two aluminum boxes. Each box contained sixteen denuders with filters behind and a 60W bulb, to avoid condensation of water and deposition of fog droplets. Each box was mounted on two parallel lift masts so that the lower part of the denuders (the inlets) were 3 m above the ground. The outlet of the filters were connected to four automatic sample changers via thirty two 40 m long polypropylene tubings. The flow was kept constant by mounting glass capillaries between the pumps and the manifolds in the sample changer. The air flows were measured intermittently during 7.5 min every 30 min behind each of the four pumps by an acoustic flow meter connected to a personal computer. A high accuracy in the volume

measurement was then obtained. Sampling was made during October on a 24 hour basis starting at 06.00 GMT. NO_2 was not measured at the two points, because more units could not be connected to the flow meter. It was assumed that the dry deposition of NO_2 should be so low that a measurement without a very high precision would be meaningless¹². The denuders and filters were leached separately in four ml de-ionized water and analyzed using the same technique as for the throughfall.

Analysis

Cl^- , NO_3^- and SO_4^{2-} were analyzed using ion chromatography (Dionex AS4A column with a Dionex AMMS-1 membrane suppressor). Iodine did not interfere with the analysis, but a late peak (I) was observed after the chromatogram. Our laboratory runs a large number of samples routinely using an auto sampler. Instead of analyzing the preserved samples separately, a sample containing pure water was placed behind each preserved sample. This dummy was enough to get the high and tailing iodide peak out before the injection of the next sample. Thymol which was used as a preservative in some experiments gave a broad peak near the chloride peak and made the evaluation more difficult. A negative peak before the nitrate peak was also observed. NH_4^+ was analyzed using flow injection analysis¹³. Reduced organic nitrogen compounds were analyzed using a variant of the Kjeldahl technique¹⁴. The sample was then digested together with sulphuric acid, potassium- and copper sulphate, before analysis of its ammonium concentration. The Kjeldahl-N represents the ammonium plus the organic nitrogen compounds that can be transformed to ammonium in the digestion process. Neither of the preservatives interfered with this technique.

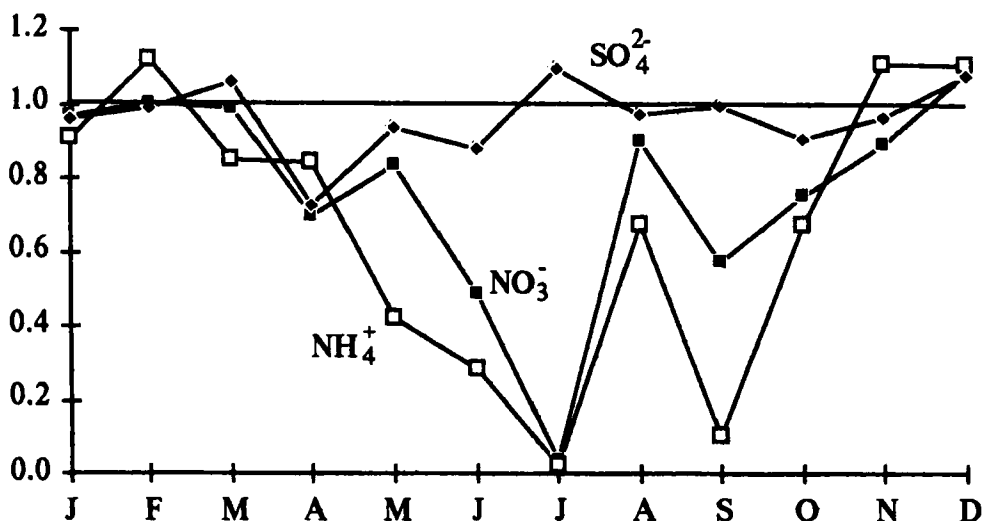


Figure 1 Average ratio of throughfall deposition in unpreserved and preserved solutions during 1990.

RESULTS

When the results from dark and semi transparent bottles with and without iodine were compared, it was found that the ammonium and nitrate amounts were often lower in the bottles that were semi transparent and unpreserved than in the others. Such a decrease was never observed for sulphate or chloride. The deposition in the semi transparent bottles that did not contain iodine divided by the deposition in the dark and preserved bottles (the arithmetic averages of all distances) are plotted in Figure 1. There is a high variation in this

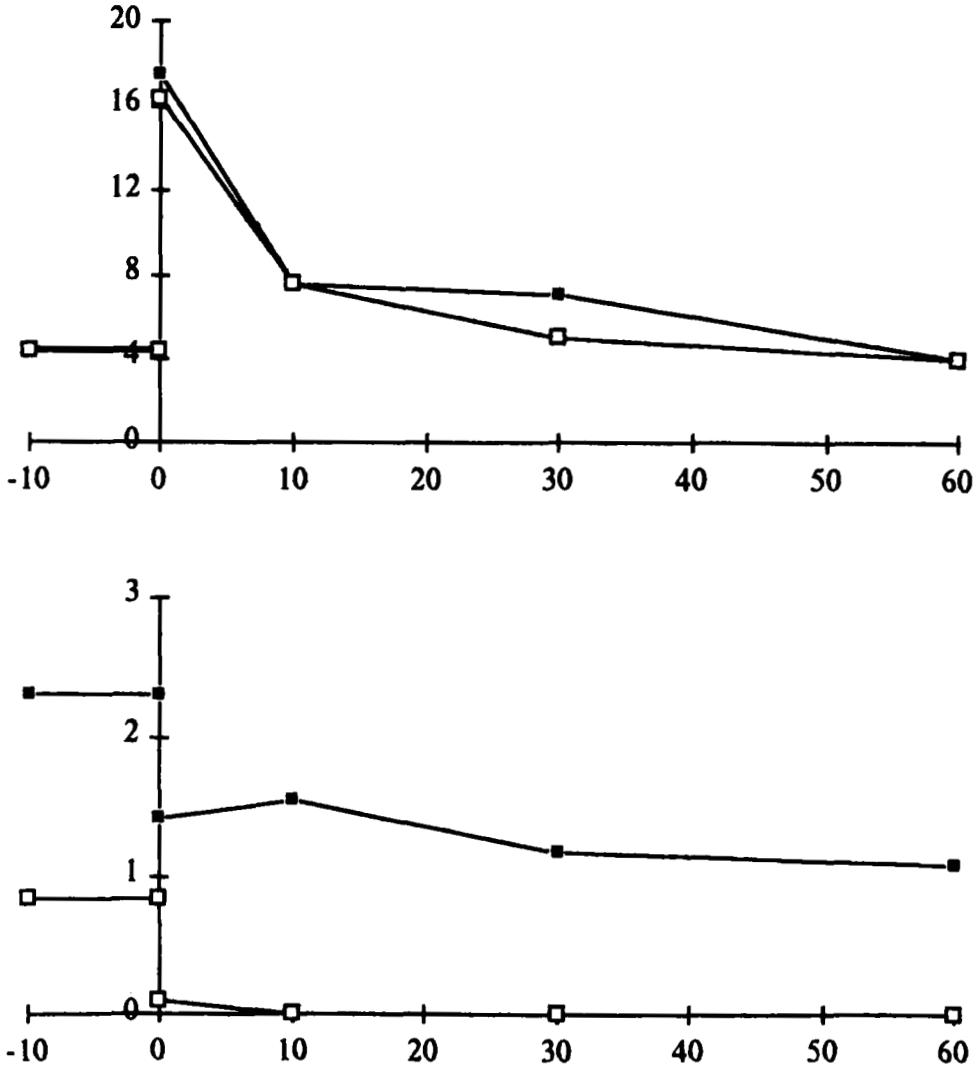


Figure 2 Wet and throughfall deposition of ammonium as a function of the distance from the forest edge. The open squares represent unpreserved and the filled preserved bottles. The upper curve represents January and the lower July 1990.

Table 1 Throughfall deposition of NH_4^+ (mmole m^{-2}) during May - October 1990 measured using different collectors.

<i>Distance</i>	<i>-10</i>	<i>0</i>	<i>10</i>	<i>30</i>	<i>60</i>
<i>Dark:</i>					
unpreserved	18	16	16	13	9
preserved	20	20	14	8	9
<i>Semi transparent:</i>					
unpreserved	8	3	10	5	4
preserved	18	12	14	14	11

ratio, but a clear decrease for both ammonium and nitrate during the brighter and warmer part of the year can be seen. This loss of nitrogen was extreme in July when neither ammonium nor nitrate were found in the unpreserved bottles. The standard deviation when the average of five samples are compared to the average of another set of five samplers in the same row is approximately $\pm 15\%$. The curve for chloride resembles that for sulphate. i.e. the ratio fluctuates around one without any seasonal trend. In Figure 2 two examples are shown (January and July) how the throughfall deposition of ammonium varies with distance from the edge. As can be seen the TD of ammonium is smaller than the wet deposition at all distances during July, even when preserved collectors are used. This loss of ammonium can either have been caused by uptake or by transformation to other nitrogen forms. The transformation ability is very high in throughfall during July (see Figure 1). In January the throughfall deposition of ammonium is equal or larger than the wet deposition and the differences between preserved and unpreserved samples are small, and within experimental errors.

The throughfall deposition of ammonium and nitrate during May to October in different type of collectors and at different distances from the edge are shown in Table 1 and Table 2 respectively. The loss of ions are more significant for ammonium than for nitrate. The ammonium loss is substantial at the edge and not unimportant in the open field. The results further show that unpreserved bottles can be used if they are kept dark (which is a normal sampling precaution). Before preservative was used, a dark sequential throughfall collector showed extremely small ammonium content in the first millimetres of throughfall. There were unusually high amounts of pollen during that occasion. Therefore and because some light can always reach the sample through the funnel it seems safer to use dark preserved bottles to study the throughfall deposition and transparent bottles to study the nitrogen conversion ability.

Table 2 Throughfall deposition of NO_3^- (mmole m^{-2}) during May - October 1990 measured using different collectors.

<i>Distance</i>	<i>-10</i>	<i>0</i>	<i>10</i>	<i>30</i>	<i>60</i>
<i>Dark:</i>					
unpreserved	18	41	23	13	10
preserved	17	46	20	10	12
<i>Semi transparent:</i>					
unpreserved	14	25	21	7	6
preserved	16	31	19	12	13

The importance of using a net in the funnel was investigated using semi transparent unpreserved bottles with and without a net, during two months (July and August). Higher ammonium concentrations were found when no net was used. There was no difference in the sulphate amounts, but a small increase in the nitrate amounts when a net was not used. The nets provide a good environment for algae and other species. It is exposed to both light and humidity. They often became green. It therefore seems likely that the net enhances the conversion of ammonium in light and unpreserved collectors.

In another experiment 1 g D(+) glucose, which normally is present in throughfall¹⁵ was added to semi transparent bottles. Unfortunately most ammonium had already disappeared, in the unpreserved bottles without glucose, during this month (September, see Figure 1). When glucose was added both ammonium and nitrate disappeared completely.

Several experiments were carried out in order to find to what compound ammonium and nitrate were transformed. The whole throughfall sample was therefore analysed in a few experiments by placing 100 ml Pyrex test tubes (Kjeldahl tubes), with a small funnel (\varnothing 5 cm) and net attached to the tube, at the forest edge.

After sampling the tubes were sealed using special butyl rubber stoppers and incubated for several days. The N_2O content of the air above the throughfall sample was analysed on several occasions¹⁶. Acetylene was added to some samples to inhibit the N_2 formation¹⁷. No increase in N_2O concentration was found in the samples, indicating that the loss by denitrification is less than about $0.01 \text{ mmole m}^{-2}$ per day. The whole sample, except for a small portion that was needed for the analysis of the other ions, was then used for Kjeldahl analysis. The results from three events are presented in Table 3. When the standard deviation is given behind the figures it means that two or three parallel samples have been taken. Surprisingly no ammonium was lost in the Kjeldahl tubes in June 1990 as it was in the semi transparent bottles. Since it was not known how fast the transformation occurred, the next two samples were exposed to daylight approximately two weeks after they had been capped.

Table 3 Analysis results from throughfall collected in Pyrex tubes at the forest edge during three occasions. Two different preservatives were used, namely iodine (I₂) and thymol (Th.). On one occasion D(+) glucose (gl.) was added as well. (mmole m^{-2})

Date and treatment	mm	NH_4^+	NO_3^-	SO_4^{2-}	Cl	org-N
<i>90-06-21</i>						
Unpr.	16±9	1.3±0.7	2.4±0.8	0.8±0.3	3.7±0.5	11.4±2.3
I ₂	12±8	1.6±0.3	2.8±0.5	0.8±0.1	4.0±0.2	10.8±3.3
<i>91-05-06</i>						
Unpr.	26.4±0.2	0.8±0.2	3.1±0.6	0.8±0.1	3.0±0.5	3.6±0.2
I ₂	23±5	1.3±0.2	2.9±0.0	0.7±0.1	2.6±0.2	2.8±0.0
Th.	23±5	1.3±0.1	3.1±0.0	0.8±0.1	2.9±0.5	3.3±0.1
<i>91-06-04</i>						
Unpr.	17.6±0.4	0.2±0.2	1.5±0.3	0.6±0.08	10.6±1.6	5.2±0.3
I ₂	14.9±1.3	0.5±0.1	1.5±0.4	0.6±0.08	8.6±1.2	3.6±0.6
Th.	14.9±1.2	0.4±0.03	1.4±0.1	0.5±0.05	8.6±1.1	3.7±0.2
gl.	15.2	0.0	0.0	0.6	11.6	7.8
gl. + I ₂	11.8	0.4	1.4	0.6	8.1	2.6
gl. + Th.	10.7	0.4	1.4	0.5	6.6	3.1

Ammonium was transformed on both these occasions (Table 3). In June 1991 glucose was added to one sample and both ammonium and nitrate disappeared completely. At the last event (91-06-04) ammonium analysis were also carried out in the three unpreserved tubes on three occasions after sampling (2 hours, 2 days and 13 days). The average throughfall deposition of NH_4^+ on the three occasions were 0.58 (close to the amount in the preserved samples) 0.48 and 0.15 mmole m^{-2} respectively. There was, however, almost no loss at all in one of the three samples. A high variability in the ammonium transformation rate had already been observed in June 1989, when all the semi transparent throughfall samples were analyzed. The rel. S.D. between preserved samples was then about 20% and between unpreserved about 70%.

Glucose was added to one unpreserved sample before exposure. Ammonium was completely lost in this sample. The NH_4^+ amounts found there were 0.47, 0.20 and 0.00 mmole m^{-2} respectively at the three different times after the sampling. Nitrate could not be detected in this sample and the amount of organic nitrogen was higher than in the other samples. The organic nitrogen deposition was very high when throughfall was sampled using this technique. It is therefore difficult to conclude whether the lost ammonium was transformed to organic forms quantitatively. The throughfall deposition of organic nitrogen is, however, always higher in the unpreserved tubes. It therefore seems likely that ammonium is transformed to organic compounds in throughfall samples exposed to light.

The concentration of Kjeldahl nitrogen (ammonium plus organic nitrogen) was also analysed in both preserved and unpreserved samples during 8 months, using the ordinary throughfall collectors. The average depositions are given in Table 4. Results from the individual months show that the throughfall deposition of organic nitrogen is always higher than the wet deposition of organic nitrogen at all distances from the forest edge. There is no evidence that all the lost ammonium is transformed into organic nitrogen quantitatively in this test, because the Kjeldahl nitrogen is smaller in the unpreserved collectors. Micro organisms containing organic nitrogen may stick to the walls, especially in unpreserved samples, and will therefore not be analyzed when a portion is taken out.

A survey of a number of sites in Sweden, Denmark, North Germany and the Netherlands has shown that the amounts of the green alga (*Pleurooccus vulgaris*) on needles increases with the nitrogen deposition and that the algal growth starts earlier when the nitrogen deposition is high¹⁸. The province where Anten is situated has the largest amounts of algae

Table 4 Average throughfall deposition of ammonium, organic nitrogen (org.-N) and their total (Kj-N) during eight months (June '89, March, July-Sept, Nov 1990, Jan-Feb '91) in mmole m^{-2} .

Distance:	-10	0	10	30	60
NH_4^+ unpr.	2.05	2.68	1.97	1.17	1.07
NH_4^+ pres.	2.79	3.57	2.62	1.89	1.79
org-N unpr.	0.61	3.56	2.16	2.24	1.84
org-N pres.	0.79	4.68	2.76	2.82	2.54
Kj-N unpr.	2.66	6.24	4.13	3.41	2.91
Kj-N pres.	3.58	8.25	5.38	4.71	4.33

Table 5 Wet and throughfall deposition during 1990 ($\text{mmole m}^{-2}\text{yr}^{-1}$) measured using dark and preserved collectors at different distances from the edge.

Distance:	WD		—TD—			NTD
	-10	0	10	30	60	
mm	1099	862	793	790	890	-278
SO_4^{2-}	41	130	67	78	61	35
Cl^-	95	768	241	247	194	181
NO_3^-	43	162	73	55	41	22
NH_4^+	45	87	46	31	28	-6
org.N	8	90	42	52	37	40

in Sweden. Lichens are more sensitive to pollution. The amounts of the bladder lichens (*Hypogymnia physodes*) which is a less sensitive group, was in Sweden lowest on the west coast. A survey has, however, not yet been made at Anten. Only a few studies of microbes in air or precipitation can be found in the literature. Herlihy *et al.*¹⁹ found that the total number of bacterial cells in precipitation was higher from April to September than during the rest of the year. It has also been found that the number of microorganisms in aerosol particles is smaller during the winter months than during the rest of the year^{20,21}.

The total wet and throughfall depositions of water and ions during 1990 as a function of distance from the forest edge are given in Table 5. The results were obtained using dark collectors containing iodine. As can be seen there is a pronounced edge effect for all ions i.e. higher depositions near the edge. The average throughfall deposition (TD) to the whole investigated part of the forest (0 to 60 m) was estimated by drawing straight lines between the measuring points and integrating the area under it and dividing it with the total distance (60 m). The net throughfall deposition (NTD) i.e. the throughfall deposition (TD) minus the wet deposition (WD), should be equal to the dry deposition (DD) if there is no interaction with the vegetation. The stem flow deposition was never measured, but is believed to be small in a spruce stand in comparison to the throughfall deposition. The sulphate deposition has not been corrected for the contribution from sea spray. The NTD of ammonium is almost always negative at 30 and 60 m distance from the edge during all months of the year. It is, however, more negative during the brighter part of the year with a minimum in the summer. At the edge and 10 m inside the forest the NTD of ammonium is positive during winter and spring and only negative during summer and autumn at 10 m. The average NTD of ammonium as a function of the month is shown in Figure 3. The average NTD of nitrate resembles that of ammonium, but the curve is displaced toward higher values (Figure 4). The disappearance of ammonium has been observed earlier^{22,23}, as well as the edge effect⁵. The air concentrations are given in Table 6 and will be discussed in the next section.

Comparison between the observed NTD and the estimated DD

As mentioned earlier the mass balance technique to estimate the dry deposition of nitrogen compounds was not successful in this study, because air measurements could only be performed at one point in the forest and the wind measurements failed in most cases. The

Table 6 Measured concentrations in air (nmole m^{-3}) during October 1990 and measured and estimated concentrations (at Rðrvik) during the whole of 1990. The dry depositions ($\text{mmole m}^{-2}\text{yr}^{-1}$) during 1990 are calculated from assumptions given in the text.

Compound	---Concentration---			Deposition 1990
	field	forest	1990	
SO ₂	34.5	28.9	57	29
part.SO ₄ ²⁻	33.6	32.2	49	6
HNO ₃	8.96	3.90	15	25
part.NO ₃ ⁻	25.0	21.9	26	10
NH ₃	7.62	3.51	22	36
part.NH ₄ ⁺	66.4	66.5	55	7

measurements (see Table 6), however, can be used to estimate a "relative" deposition velocity for the different air-borne precursors. It was assumed that the concentration difference for all the species was caused by deposition and not by gas-particle interactions. The relative deposition velocity was calculated from the concentration outside the forest minus the concentration in the forest and then divided by the concentration outside the forest. It was highest for HNO₃ and NH₃ (57% and 54% respectively), somewhat lower for SO₂ (16%) and lowest for the particulate forms. This implies that the edge effect in throughfall deposition of sulphate is only to a minor extent caused by a lower concentration inside the forest and to a major extent by a more efficient mass transfer at the edge. Although there are some controversies about the interactions of sulphur species with canopies, many studies have shown that this interaction is negligible for conifers and that the net throughfall deposition thus represents the dry deposition, ^{1, 2, 24}. The NTD of sulphate was therefore used here to calculate the relationship between the air concentration decrease in the forest and the dry deposition.

The absolute deposition velocity was then estimated from a comparison between the yearly average SO₂ and particulate SO₄²⁻ concentration, the relative deposition velocity and the NTD of sulphate at Anten according to eq. 1.

$$[\text{SO}_2]_{1990} \cdot \frac{[\text{SO}_2]_s - [\text{SO}_2]_f}{[\text{SO}_2]_s} \cdot K + [\text{SO}_4^{2-}]_{1990} \cdot \frac{[\text{SO}_4^{2-}]_s - [\text{SO}_4^{2-}]_f}{[\text{SO}_4^{2-}]_s} \cdot K = \text{NTD}_{1990} \quad (1)$$

Index *s* denotes the surroundings (outside the forest) and *f* inside the forest. The deposition of nitrate and ammonia was calculated using the same constant *K* obtained in eq. 1 (0.09 m s^{-1}) and analogous formulas. This way of estimating the deposition requires that all the compounds have a similar deposition pattern. This is not an unreasonable assumption, because they are all mainly deposited to the needles and NH₄⁺, NO₃⁻ and SO₄²⁻ show quite a similar NTD pattern during the winter. It further requires that their deposition velocities have a similar seasonal variation, which is not entirely proper, because HNO₃ can be deposited without uptake through stomata. October is, however, not an extreme month with respect to temperature and sun intensity. The value of *K* is mainly determined by the SO₂ concentration gradient, which is intermediate between the most reactive gases and the particles. Both these circumstances make the dry deposition estimates less erroneous. If the

uptake through stomata and the deposition to other surfaces than stomata varies considerable with the month, the estimated seasonal trend of the deposition (Figures 3-5) will be wrong. This will generally lead to an overestimation in the winter and an underestimation in the summer.

Measurements of air-borne nitrogen compounds at Anten were only performed in October, but results are available from an EMEP station 75 km south west of Anten (Rörvik). The sum of the gaseous and particulate NH_4^+ and NO_3^- concentrations was measured on a daily basis during the whole of 1990 using single impregnated filters²⁵. The gaseous fraction of the nitrates were estimated to 36% of the total concentration using data from an earlier investigation²⁶. Simultaneous measurements of NH_3 and particulate NH_4^+ concentration have only been made occasionally in Sweden²⁷. The NH_3 concentration has been measured on a daily basis during two years at Ekeröd and during one year at Rörvik. At both stations the ammonia concentration followed the temperature and showed a minimum in winter ($\approx 2 \text{ nmole m}^{-3}$) and a maximum in summer ($\approx 50 \text{ nmole m}^{-3}$). These results have been used to estimate the monthly ammonia concentrations at Anten. SO_2 and particulate SO_4^{2-} concentrations were also taken from Rörvik.

The average deposition velocities to the forest edge (0 - 60 m) using this approximation is for HNO_3 , NH_3 and SO_2 : 5.1, 4.9 and 1.5 cm s^{-1} respectively, for particulate SO_4^{2-} 0.4 cm s^{-1} (the same magnitude as the experimental error) and for particulate NO_3^- 1.1 cm/s . The NH_4^+ concentration inside the forest was slightly higher than on the outside. The same deposition velocity for particulate NH_4^+ as for particulate SO_4^{2-} was therefore used. All the estimated and measured average concentrations are given in Table 6.

NO_2 can also be deposited to conifers. Johansson¹² found that the dry deposition rate per projected needle area of NO_2 to Scots Pine is 1-2 mm s^{-1} during the day and 0.05 - 0.2 mm s^{-1} during the night, at NO_2 concentrations larger than 400 nmole m^{-3} and zero below this concentration. The NO_2 concentration at Rörvik was 160 nmole m^{-3} . Granat and Hällgren²⁸ have exposed a Scots Pine forest to NO_2 , but found no increased TD of nitrate. It is therefore believed that the dry deposition of NO_2 was negligible for the throughfall composition at Anten.

When the net throughfall deposition (Table 5) is compared to the estimated dry deposition (Table 6), quite reasonable values are obtained for NO_3^- , considering that the dry depositions estimated in this way are very rough (22 of estimated 35 $\text{mmole m}^{-2}\text{yr}^{-1}$ were found). It is, however, obvious that the throughfall technique cannot be used to estimate low depositions of ammonium (-6 of 43 $\text{mmole m}^{-2}\text{yr}^{-1}$ have been found). If, however, the organic nitrogen that was found mainly originates from dry deposited NH_4^+ , a better agreement is obtained (34 of 43 $\text{mmole m}^{-2}\text{yr}^{-1}$).

DISCUSSION

The throughfall measurements have shown that ammonium and nitrate ions are partly lost in the canopy during the brighter and warmer part of the year and that the ability to transform

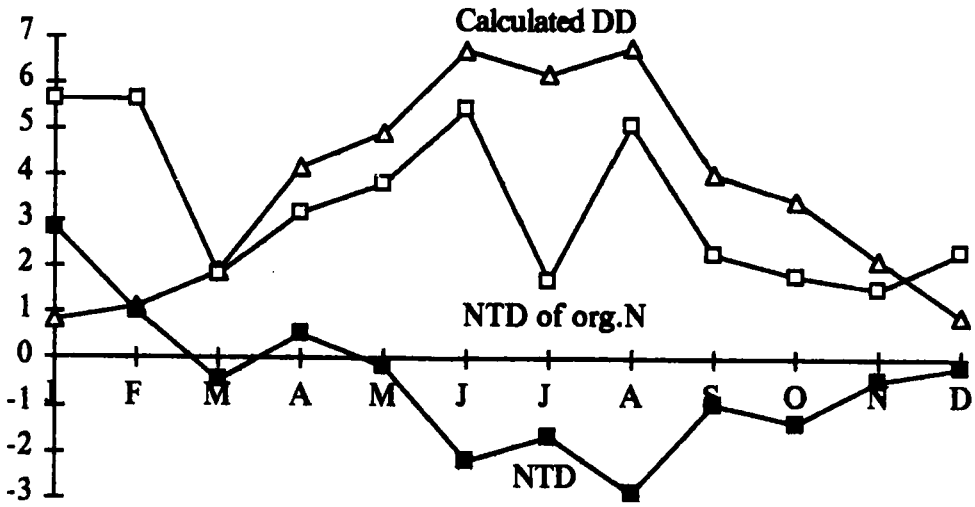


Figure 3 Monthly average net throughfall deposition of NH_4^+ and organic nitrogen together with estimated (see text) total dry deposition of NH_3 and particulate NH_4^+ (mmole m^{-2}) during 1990.

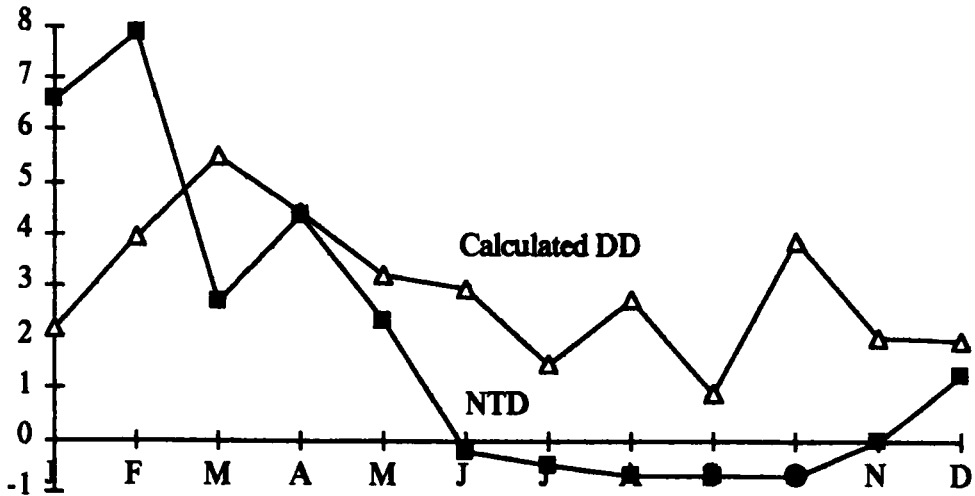


Figure 4 Monthly average net throughfall deposition of NO_3^- together with estimated (see text) total dry deposition of HNO_3 and particulate NO_3^- (mmole m^{-2}) during 1990.

these ions remain after the rain has left the canopy. Throughfall measurements of NH_4^+ and NO_3^- can consequently not be used to estimate the dry deposition of the precursors for ammonium and nitrate when the ability to transform the nitrogen species is high compared to the deposition.

If one assumes that the dry deposition of nitrogen compounds have the same distribution with distance as the observed NTD of SO_4^{2-} , then the difference between the observed NTD and the calculated DD is positive at the edge, ≈ 0 at 10 m and negative at 30 and 60 m for both NH_4^+ and NO_3^- during 1990. This can either be interpreted that the dry deposition of the nitrogen compounds have a steeper slope with distance than SO_4^{2-} (which is reasonable considering the observed relative deposition velocities), or that the uptake of nitrogen compounds is higher inside the forest. The precipitation and throughfall deposition as a function of distance gives some information on the origin of the compound. A compound originating from the atmosphere shows a much higher deposition at the edge compared to further in, in the forest. A compound that mainly is recirculated within the forest has a much higher deposition in the forest than outside it (in precipitation). Na^+ and SO_4^{2-} have typical patterns for atmospheric origin while K^+ and Mn are good examples of internal circulation. The sum of NH_4^+ and organic deposition shows a pattern that is typical for atmospheric origin.

The seasonal variation of the NTD and the estimated dry deposition are given for all three species in Figures 3-5. As can be seen from the Figures most species have a maximum NTD in the winter and a minimum in the summer. The very high NTD in the winter may be caused by the very high precipitation amounts at that time. The estimated DD of NH_4^+ show an opposite pattern and resembles the NTD of organic nitrogen.

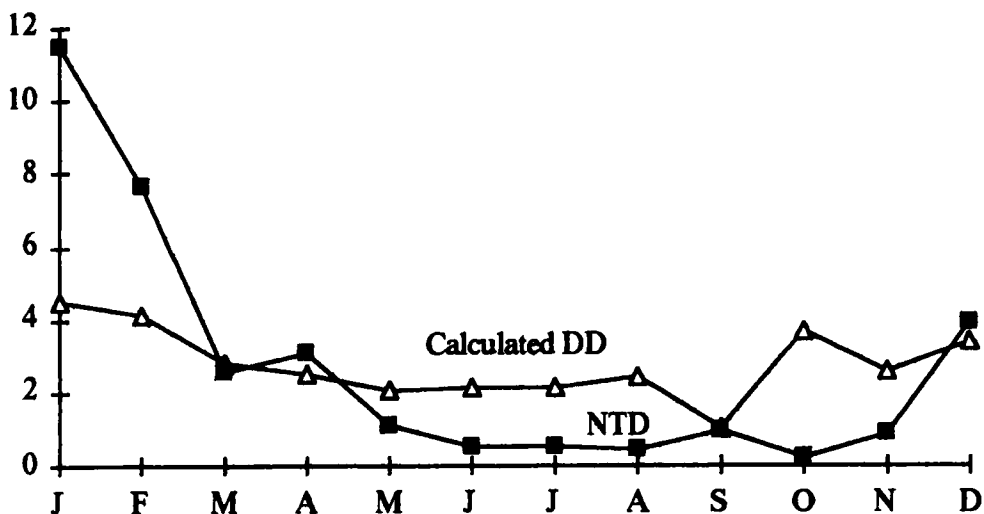


Figure 5 Monthly average net throughfall deposition of SO_4^{2-} together with estimated (see text) total dry deposition of SO_2 and particulate SO_4^{2-} (mmole m⁻²) during 1990.

Since the annual variations in the estimated depositions are for all species so very different from the observed net throughfall deposition, it seems likely that throughfall measurements cannot be used to estimate the dry deposition during shorter periods. It can further not be used to estimate the total deposition of ammonium at this site. During the summer when more NH_4^+ has disappeared in throughfall than corresponding to the dry deposition, the throughfall deposition of organic nitrogen species is very high, roughly corresponding to the missing ammonium. The linkage between these two fluxes will be the subject of future investigations. In another study in Sweden the TD of ammonium to a forest, situated near a chicken farm, was 3 - 4 times higher than the WD, in the summer (Ferm unpublished). The observed negative NTD of NH_4^+ at Anten is most likely only representative for forests having a small dry deposition.

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