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The CoTAG method compared
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Summary

Dry deposition velocity measurements for nitrogen and sulphur compounds have been carried out for 18 months at a semi-alpine site in Southern Norway (Storgama, 59° 01' N 8° 32' E, 600 masl), using the conditional time averaged gradient method. The results are compared with estimated wet deposition fluxes to assess the total pollutant input to the ecosystem, as well as with two sets of values estimated from a big-leaf dry deposition module, applying two different land use categories (short grass and forbs, tundra) with local micrometeorological parameters as input.

The velocity profiles are mainly governed by the meteorological conditions and annual mean values were 1.4, 11.8 and 4.0 mms^{-1} for NH_3 , HNO_3 and SO_2 , respectively, if all data were included and 10.8, 11.8 and 13.0 mms^{-1} , respectively, only considering positive values. The big-leaf module gives reasonable deposition velocities for this site throughout the year, but does not reproduce the large variability as shown in the measured data. No apparent seasonal variations were found from either measurements or module estimates, due to the very low productivity of the area, although a tendency for enhanced uptake in fall and minima in the summer months. Wet deposition flux was dominant, especially in the wetter months, counting for 81, 88 and 90 % of the total deposition for NH_4 , NO_3 and SO_4 , respectively, probably because of the fairly low pollutant concentrations in the air.

Summary in Norwegian

Her presenteres 18 måneder med målinger av tørravsetning av nitrogen- og svovelkomponenter fra en semi-alpin lokalitet i Sør-Norge (Storgama, 59° 01' N 8° 32' E, 600 moh). Metodikken er den såkalte conditional time averaged gradient method. Resultatene er sammenlignet med våtavsetningsmålinger og med modellerte resultater for to forskjellige overflater (short grass and forbs, tundra). I modellen er målte lokalmeteorologiske parametere brukt som inngangsdata.

Tørravsetningshastigheten er for det meste bestemt av meteorologiske forhold og årlige gjennomsnittverdier var respektivt 1.4, 11.8 and 4.0 mms-1 for NH₃, HNO₃ and SO₂ (alle data inkludert) og 10.8, 11.8 and 13.0 mms-1 når bare positive verdier ble regnet med. Den såkalte big leaf deposisjonsmodellen gir rimelige deposisjonshastigheter for denne lokaliteten gjennom året, men reporduserer ikke den store variabiliteten vi ser i dataene. Ingen åpenbare årlige sykluser ble observert eller modellert, men det er en viss tendens til høye hastigheter om høsten og minimum om sommeren. Dette er trolig fordi området har svært lav produktivitet. Våtavsetningen dominerer den totalte avsetningen og utgjør respektivt 81, 88 og 90% av den totale avsetningen for NH₄, NO₃ og SO₄. En viktig årsak til dette er trolig at luftkonsentrasjonene er veldig lave.

Analysis of dry deposition measurements in Storgama: The CoTAG method compared with wet deposition fluxes and modelled estimates

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1 Introduction

Although their role in atmosphere-biosphere exchange is well known, there is an obvious need for more knowledge about dry deposition velocities for reactive nitrogen (N) and sulphur (S) compounds to different ecosystems and land cover classes in Europe (Aneja et al., 2001; Erisman et al., 2001; Krupa, 2003; Tørseth, 2003; Erisman et al., 2005). Monitoring and modelling of air pollutant deposition is essential to generate reliable regional deposition maps and to develop and evaluate policies to abate the effects related to air pollution and to determine sinks of pollutants from the atmosphere (Erisman et al., 2005; Wichnik Kruit et al., 2007). Nitrogen compounds, ammonia and nitrate in particular, are recognized to be important in atmospheric chemistry, second particle formation and eutrophication of surface waters and ecosystems and their relative importance in acidification is increasing since sulphur concentrations in air and precipitation are decreasing. It has also been suggested that the deposition processes of the acidic pollutants interact and that reduced sulphur concentrations influence the surface affinity to N compounds (Sutton et al., 1993; Erisman and Wyers, 1993; Erisman et al., 2005).

Of the total deposition in Europe, dry deposition accounts for about 20%, with a range of 10 to 90 % in different regions (Erisman et al., 2001). Even within mainland Norway, dry deposition is estimated to vary from 10% in the precipitation rich southwest region (more than 3000 mm precipitation per year) to almost 80% in the sub-Arctic interior of Finnmark county (less than 500 mm precipitation per year) (Hole and Tørseth, 2002). While the concentration field and wet deposition of different atmospheric compounds are well monitored and modelled e.g. in the EMEP¹ programme, long term dry deposition data is only monitored at a handful advanced sites across Europe. National assessments and deposition mapping are very often based on deposition velocities reported in the peer review literature, and no reliable long term deposition data are available for a number of different land cover classes and regions (Erisman et al., 2005). New initiatives such as the COST 729 action (www.cost729.org) and the NitroEurope integrated project (www.nitroeuropa.eu) seek to better quantify the nitrogen balance and to get a more complete overview of atmosphere-biosphere fluxes in Europe.

Within the ACCENT² BiaFlux network (www.accent-network.org) process-oriented studies of nitrogen and sulphur air-surface exchange are a core activity. For this type of investigations measurements with high time resolutions are necessary, but the instrumentation required is expensive and labour intensive.

¹ Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe – www.emep.int.

² Atmospheric Composition Change the European Network of Excellence

Consequently the number of active field sites in Europe is limited. However, for many monitoring and long term modelling purposes (such as EMEP) monthly, seasonal or even annual deposition data are sufficient. Less expensive and simpler methods for deposition measurements will enhance the possibilities to obtain a denser network of flux measurement sites in Europe. Therefore, different low cost methods for flux monitoring have been developed and tested out in recent years (e.g. Hensen et al., 1999, Fowler et al., 2001). One of the most successful methods has been the Conditional Time Averaged Gradient method (CoTAG). Although not much reported in the literature yet, CoTAG measurements compare well with more sophisticated instrumentation, such as AMANDA (Wyers et al., 1993, Horváth et al., 2005), when data are averaged over one or two weeks (Erisman et al., 2001, Fowler et al., 2001, Hensen et al., 1999).

Here 18 months of dry deposition measurements for the main N and S atmospheric compounds from a semi-alpine moor in southeast Norway are presented. Compared to a similar analysis of the dry deposition velocities at the same site by Hole et al. (2007) the additional incorporation of wet deposition fluxes allows an improved picture of the total deposition and the relative importance of the two processes can be estimated. For three of the compounds (ammonia (NH₃), nitric acid (HNO₃) and sulphur dioxide (SO₂)), results are compared with output from an updated big-leaf deposition module (Zhang et al., 2003), using local meteorology as input. The main objective of the study is to summarize the monitoring activities and CoTAG measurements, in order to assess the prevalent deposition fluxes of the acidic compounds, and by comparing them with the modelled results, to evaluate the applicability of different parameterisations within the module for the investigated site and to discuss limits of measurements and model.

2 Site description

A five-year project called „Effect of climate and land use change on flux of N and C: air-land-freshwater-marine links“ has been established in Norway through an interdisciplinary cooperation between major environmental research institutes (www.umb.no/14988). From 2003 until 2007 modelling activities such as production of N deposition scenarios in Scandinavia under possible future climate regimes and modelling of the nitrogen ecosystem cascade air-freshwater-sea are carried out together with an extensive fieldwork programme and analysis of long term data series. The data presented here are from the period 16 June 2004 to 6 December 2005. The main field site is Storgama in Telemark county (59° 01' N 8° 32' E, 600 masl) (Figure 1), where micrometeorological and hydrological as well as soil and water chemistry measurements are carried out in parallel. Storgama is a very low-productive, semi-alpine ecosystem with patches of bare rock and some low Scots Pine trees. However the CoTAG system was established on a grass covered patch with a flat fetch of about 100 m in the sector studied (Figure 1). Soil depth to solid rock was only between 10 and 20 cm. Monthly average temperature ranged from -1.94 °C in February to 17.6°C in July and average annual rain sampled in the monitoring period was about 1160 mm. There is some agricultural activity in the village Treungen about 10 km down valley the west, but local pollutant sources are expected to be ignorable at this site.

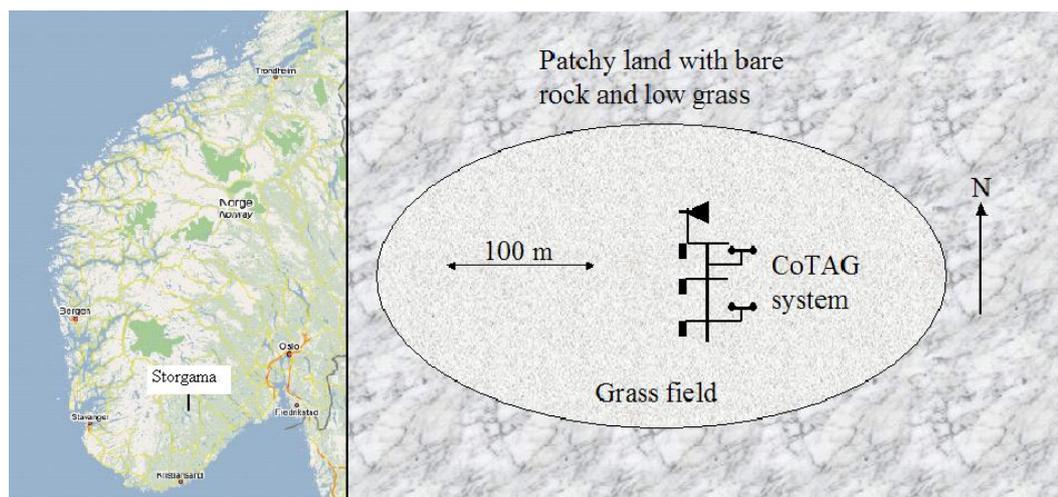


Figure 1: Map and sketch of the experimental site Storgama.

3 Instrumentation

The CoTAG system was set up in Storgama in mid June 2004. Traditionally these systems have been equipped with denuders for air chemistry sampling and battery-powered pumps with relatively low capacity. However, since 220 V main power was available here and values not far from the detection limit were expected, it was decided to use more powerful pumps with a capacity of approximately 5 litre air per minute and standard filter packs. The filters were analysed by the NILU/EMEP-CCC laboratory using ion chromatography and standard procedures for main atmospheric compounds (Uggerud et al., 2003). The filter packs were always stored and transported together with a blind filter pack to make sure that any contamination would be discovered. Blind values were subtracted from analysed values. Furthermore the system was equipped with the standard Campell 23R data logger and micrometeorological sensors. Compounds analysed for and presented here are SO₂-S, SO₄-S, HNO₃-N, NO₃-N, NH₃-N, NH₄-N, „sum NO₃-N“ (HNO₃-N and NO₃-N) and „sum NH₄-N“ (NH₃-N and NH₄-N). Cl, Na, K, Ca and Mg concentrations were also analysed but these results are not shown here. The sampling interval was set to 2 weeks to ensure that enough air volume was sampled and the measurements were disrupted from mid January to mid April 2005 due to deep snow. Air chemistry sampling heights were 0.45, 1.25 and 1.75 m.

Meteorological measurements were carried out at the same time at 0.5 and 1.5 m for the estimation of dynamic stability. Wind speed and temperature were detected at both heights and stored together with Richardson number, friction velocity, sensible heat flux and displacement height in 15 minutes intervals.

Precipitation in Storgama was collected in weekly intervals and the rain samples were analysed by the NILU/EMEP-CCC laboratory for concentrations of NO₃-N, SO₄-S, NH₄-N and Cl, Na, K, Ca, Mg. Again results for the metal ions are not presented here.

4 Method and data processing

4.1 CoTAG system

The vertical flux and the deposition velocity of the measured compounds have been calculated following the recommendations of Famulari et al. (2007), who developed the CoTAG method to overcome the limitations of the traditional averaged gradient methods when calculating fluxes from concentration gradients averaged over longer periods. The system determines the time average gradient, but only at periods when the constant flux layer approach is valid (Erisman et al., 2001). An intelligent data logger monitors atmospheric stability, and when the conditions are appropriate, the pumps collect the reactive trace gases at three different heights using annular denuders (Erisman et al., 2005). To avoid sampling during low wind speed stable conditions, the CoTAG system at Storgama was programmed to measure gradients only when the Richardson number Ri lied in the interval -0.05 to 0.05 . For the period studied, the overall CoTAG data capture was 38.3%, varying in monthly averages from 20 % to 60 % (Figure 2). Generally the sampling criteria seems to be better fulfilled in fall and winter months, giving a preliminary idea of the micrometeorological conditions at the measurement site.

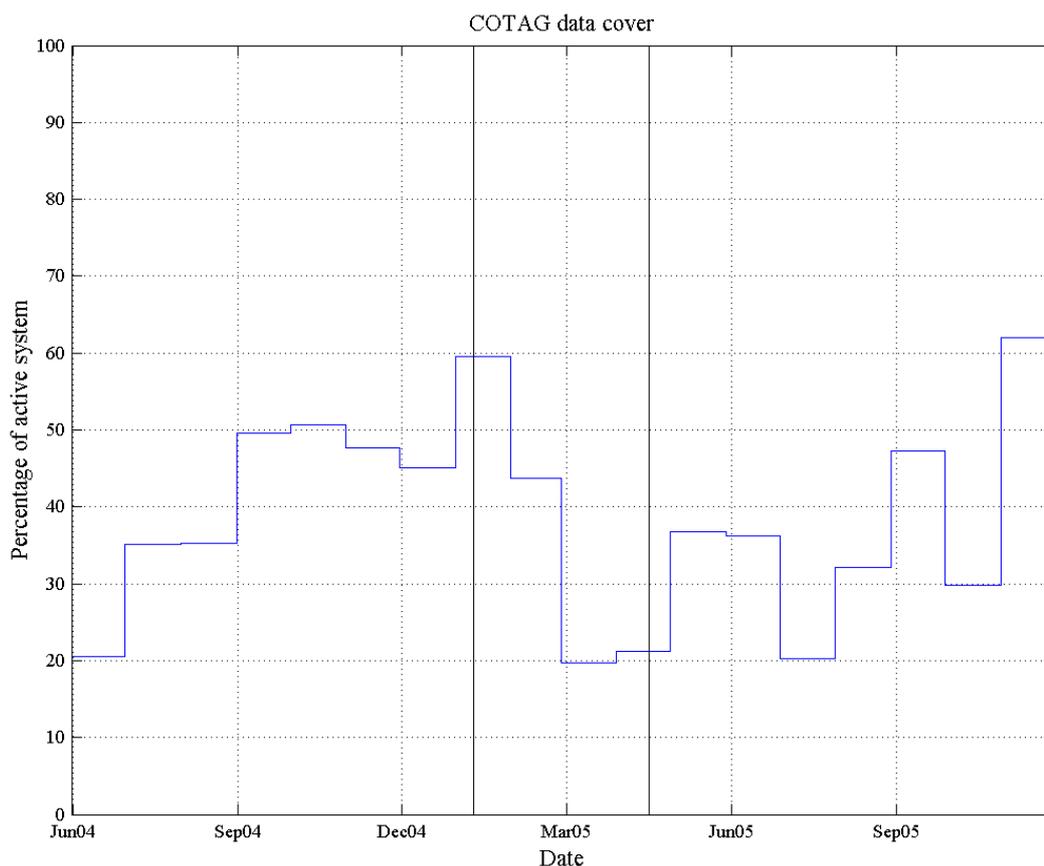


Figure 2: CoTAG data cover (monthly averages) for the time studied. The two lines marking the period without chemical sampling due to snow cover.

Using the equations of the original CoTAG system (Famulari et al., 2007) the vertical dry deposition fluxes F were calculated by

$$F = -\frac{k u_*}{\phi_h \phi_m} * \frac{\Delta c}{\Delta \ln(z-d)} \quad (1)$$

where k is the von Karman constant ($=0.41$), u_* is the friction velocity and ϕ_h and ϕ_m dimensionless stability coefficients for heat and momentum, respectively. The second term of the formula denotes the concentration gradient that was estimated using the least-square slope of the concentrations c , measured at three different heights z (0.45, 1.25 and 1.75m), corrected by the displacement height d . Depending on the wind direction, the value of d was set between 1 mm and 6 mm. The stability functions were determined by the following equations conditioned by the Richardson number Ri :

$$\phi_h = \frac{1}{\sqrt{1-16.2 Ri}} \quad \text{and} \quad \phi_m = \sqrt{\frac{1}{\sqrt{1-16.2 Ri}}} \quad \text{if } Ri < -0.02 \quad (2)$$

$$\phi_h = 1 \quad \text{and} \quad \phi_m = 1 \quad \text{if } -0.02 < Ri < 0.02 \quad (3)$$

$$\phi_h = \frac{1}{\sqrt{1-5 Ri}} \quad \text{and} \quad \phi_m = \frac{1}{\sqrt{1-5 Ri}} \quad \text{if } Ri > 0.02 \quad (4)$$

The first term in Esq. (1) was calculated from micrometeorological data for all

Sampling intervals where concentrations and gradients were smaller than the detection limit and the precision, respectively, for a certain compound (Aas, 2006) have not been included in the calculation of the deposition velocity V_d which was estimated at the uppermost measurement height $z=1.75$ m from its conventional definition:

$$V_d(z) = -\frac{F}{c(z)} \quad (5)$$

To assess the relative importance of the two deposition fluxes contributing to the total deposition at Storgama, the wet deposition flux was calculated for available substances using the relation

$$F = \frac{p_t c}{t} \quad (6)$$

where p_t is the precipitation measured during a certain period t and c the concentration of the compound in the collected rain sample. When calculating wet deposition according to this procedure, deposition by fog or dew is not included, since common rain samplers collect no precipitation from such events (Hole and Tørseth, 2002). The data to calculate the wet deposition have been corrected for negative concentrations as well as for values below detection limit (Aas, 2006) and were averaged from weekly to bi-weekly values for an improved comparison with the CoTAG measurements.

4.2 The dry deposition module

The deposition module used for the comparative modelling is based on the well-known resistance analogy to dry deposition, i.e. the dry deposition velocity V_d is defined to be the inverse of total resistance R_t (e.g. Wesely and Hicks, 2000). R_t consists of the sum of the aerodynamic resistance R_a , the quasi-laminar sub layer resistance R_b and the surface or canopy resistance R_c . R_a is only a function of micrometeorological conditions and the roughness characteristics of the underlying surface, and therefore independent of chemical species. R_b is a function of friction velocity and the molecular diffusivity of each chemical compound. The simple approach as used in Padro (1996) is adopted here to determine R_a and R_b , while the surface resistance R_c is calculated according to Zhang et al. (2003):

$$\frac{1}{R_t} = \frac{1}{R_a} + \frac{1}{R_b} + \frac{1}{R_c} \quad (7)$$

$$\frac{1}{R_c} = \frac{1}{R_{st}} + \frac{1}{R_{ns}} \quad (8)$$

where R_c is separated into two parallel paths, one is the stomatal resistance R_{st} with its associated mesophyll resistance R_m , and the other is the non-stomatal resistance R_{ns} . R_{ns} is further decomposed into resistance to soil uptake, which includes in-canopy aerodynamic resistance (R_{ac}) and the subsequent soil

resistance (R_g), as well as resistance to cuticle uptake (R_{cut}). W_{st} is the fraction of stomatal blocking under wet conditions and R_{st} is calculated using a sunlit/shade stomatal resistance sub-module. R_m is treated as dependent only on the chemical species, while R_{ac} and R_{cut} are parameterized as functions of friction velocity, relative humidity and leaf area index. R_g is given different values for different compounds and over different surfaces. Detailed descriptions of R_{st} and R_m can be found in Zhang et al. (2002), and of the rest of the terms in Zhang et al. (2003).

In order to compare the measurement results with the model output, the deposition module was run with local meteorology from the CoTAG system as input. The meteorological raw data have been corrected from noise and blind values using reasonable limits. In the records of the friction velocity and wind speed, values below 0 ms^{-1} and above 1 ms^{-1} , respectively 30 ms^{-1} , were removed and temperatures above $40 \text{ }^\circ\text{C}$ were treated as erroneous data as well as values below $-40 \text{ }^\circ\text{C}$. Taking into account the geographical position of the measurement site, sensible heat fluxes below -50 Wm^{-2} and above 500 Wm^{-2} were considered as noise. To serve as model input, the data series recorded in 15 minutes intervals had to be interpolated to hourly values. Since detailed precipitation data was not present, a typical precipitation of 0.1 mm per hour was used in the module for the whole period giving wet surface conditions. Incoming radiation was calculated according to latitude and season and a cloud cover of 0.5 was included as well as a snow cover in December until March.

The code by Zhang et al. (2003) was slightly modified to allow for direct input of hourly meteorological data.

Since CoTAG measurements are not suitable for detailed process studies, the deposition module output data have been averaged over the sampling intervals of the CoTAG system and are therefore presented as bi-weekly values.

5 Results

5.1 Deposition flux measurements at Storgama

To enable a comparison between the micrometeorological parameters and the calculated deposition velocities, Figure 3 shows values of friction velocity, sensible heat flux, temperature and wind speed averaged over the sampling intervals of the CoTAG system, comparing data points reported in periods when the pump was on with the entire dataset.

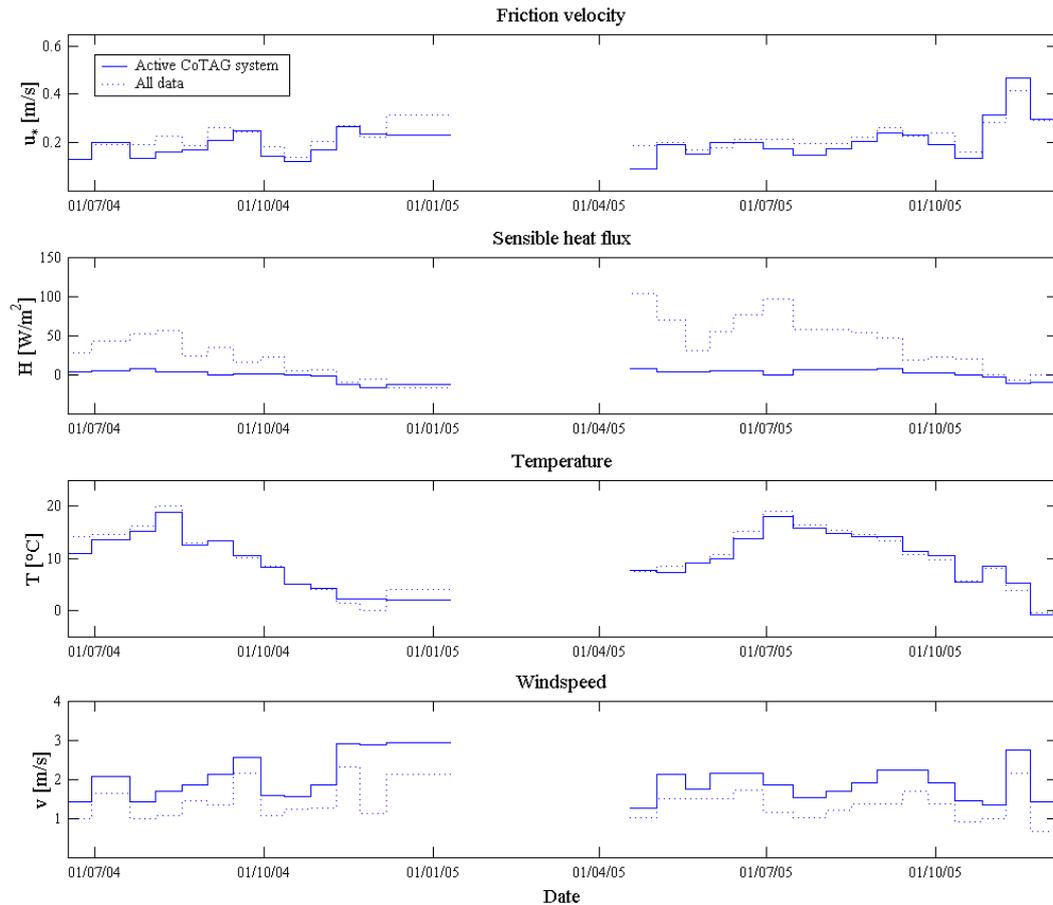


Figure 3: Friction velocity, sensible heat flux, air temperature and wind speed at Storgama averaged over the CoTAG sampling intervals.

The profile of the friction velocity shows no obvious pattern with values fluctuating around 0.2 ms^{-1} and a tendency for enhanced wind speeds in late fall. As expected the maxima and minima in wind speed during the monitoring period coincide with high and low values of the friction velocity. When comparing the pattern of the active system with the entire dataset, it can be seen that the CoTAG system was sampling in cases with high wind velocities and low sensible heat flux (close to neutral stability). The sensible heat flux as well as the air temperature demonstrate characteristic cycles with peaks during the warmer months and minima in winter. It is interesting to note that the average temperature was never below zero during the winter season 2004/2005. There were snowfall episodes starting in November, but no significant and lasting snow deposition occurred until mid January when the measurements were stopped until mid April. General weather records for Southern Norway picture that the winter this year was about $1.5 \text{ }^\circ\text{C}$ warmer than average (www.met.no). Similar enhanced averages are reported for fall and early winter 2005 and are also reported at Storgama (Figure 4).

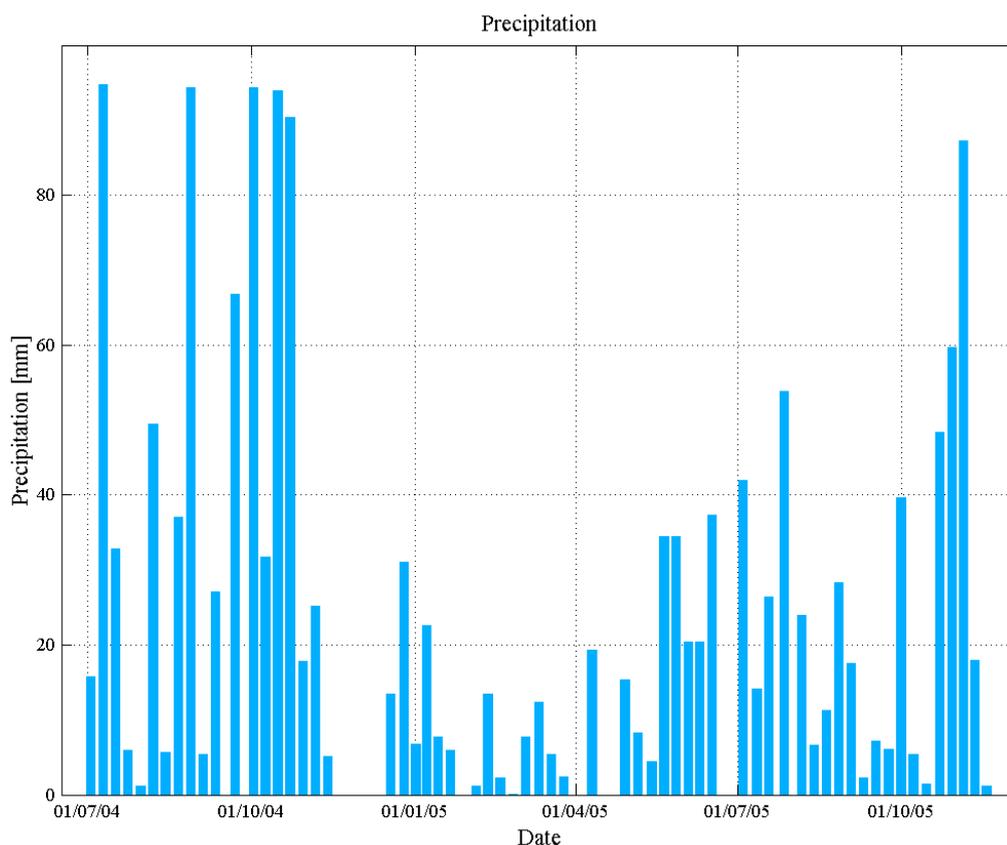


Figure 4: Precipitation sampled in weekly intervals at Storgama.

An overview of the weekly precipitation at Storgama is given in Figure 4. Beside three weeks without rain in April and June 2005, zero values represent periods when the measurements were interrupted and it is therefore reasonable to assume that the surface was wet most of the year. Total rainfall during the monitoring period was 1160 mm per year and thus around 22 mm per week and 0.13 mm per hour which is approximately the value used in the module parameterisation (see chapter 4.2.). However these mean values are most likely a slight underestimation, since in addition to the failure of the measurement system the collecting tank rent over three times between July and October 2004, noticeable as limited maximum values of around 95 mm in Figure 4. Generally the fall months in 2004 were much wetter than those in the following year where big rain events are less frequent and not reported until November. Several meteorological stations in the Southern part of Norway measured only 20 – 40 % of normal precipitation during fall 2005 (www.met.no).

Figure 5 shows all analysed concentrations for N and S compounds through the measurement period at the three different heights of the CoTAG sampling system. There is no clear seasonal pattern in the profiles, but most of the concentrations seem to be elevated in late summer and fall. As can be expected at a remote and unpolluted site like Storgama, concentrations are generally fairly low (below $0.6 \mu\text{g m}^{-3}$ for single substances), complicating deposition calculations. Regarding the nitrogen compounds, the contribution of ammonium (NH_4) and ammonia (NH_3) to the N burden in the air is higher than the one of nitric acid (HNO_3) and

nitrate (NO_3), respectively. Sulphate (SO_4) is the dominating sulphur compound in the air masses next to the soil at Storgama, whereas the sulphur dioxide (SO_2) concentrations remain small during the whole year.

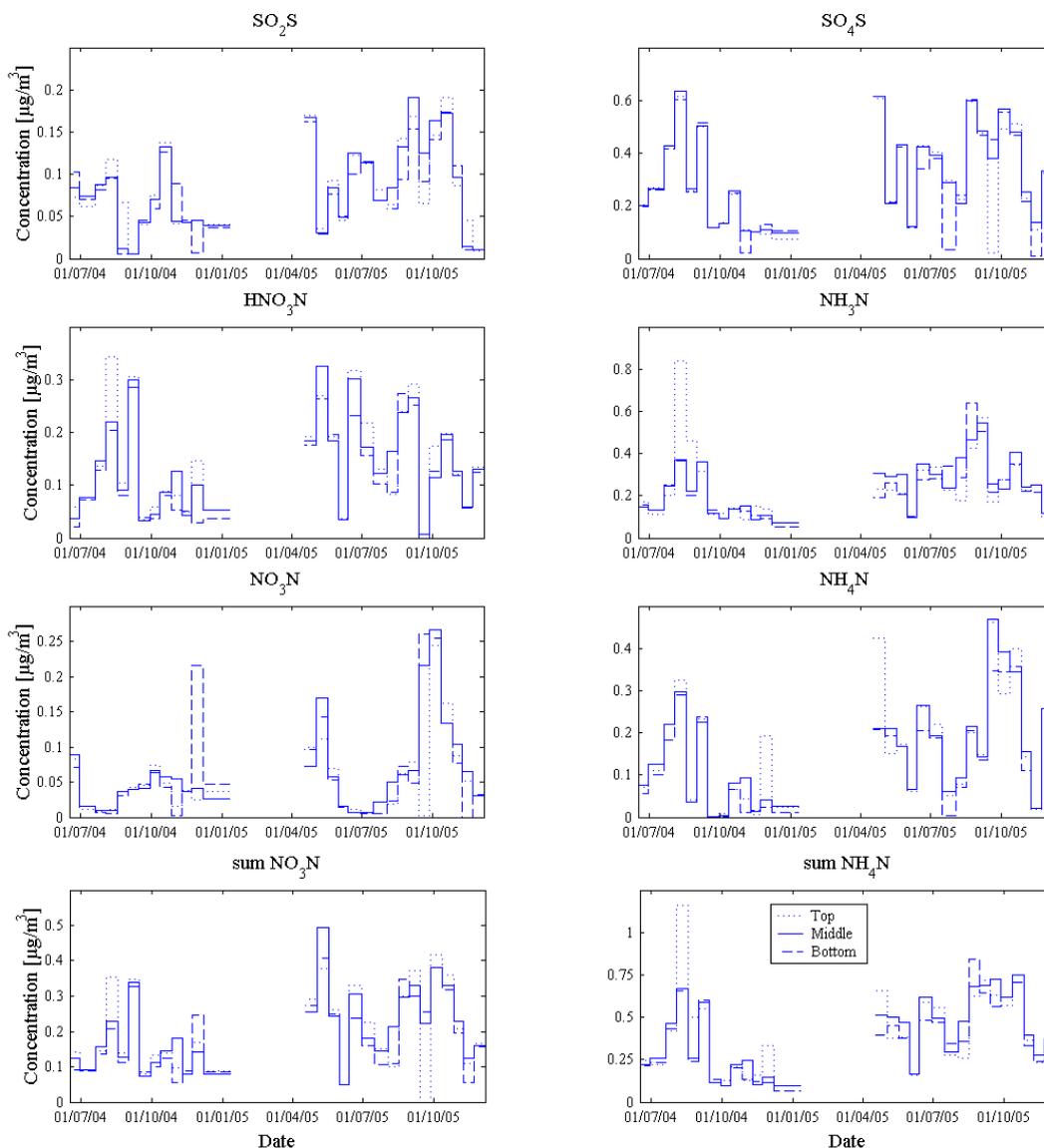


Figure 5: Concentrations of the measured compounds at three heights during the sampling period.

The compounds in common between the CoTAG measurements and the deposition module and thus available for comparison and focused on, are ammonia, gaseous nitric acid and sulphur dioxide. Figure 6 shows the dry deposition velocities (bi-weekly averages) of the three trace gases at the top measurement height, resulting from the CoTAG system after removing erroneous values according to the procedure described in chapter 4.1. The data presented here are the least-square slope, which were very similar to the profiles calculated from the top-bottom gradient. No clear seasonal pattern in the estimated deposition velocities is dedectable, although there seems to be a tendency for enhanced uptake in fall and minima in the summer months. For ammonia and

sulphur dioxide the average values even become negative, representing periods of upward fluxes, i.e. emission of the gas from the soil and vegetation to the atmosphere. Highest velocities above 50 mms^{-1} are reported for SO_2 and HNO_3 , while the maximum values for NH_3 are around 20 mms^{-1} . A further discussion of the profiles is presented later on in chapter 6.1.

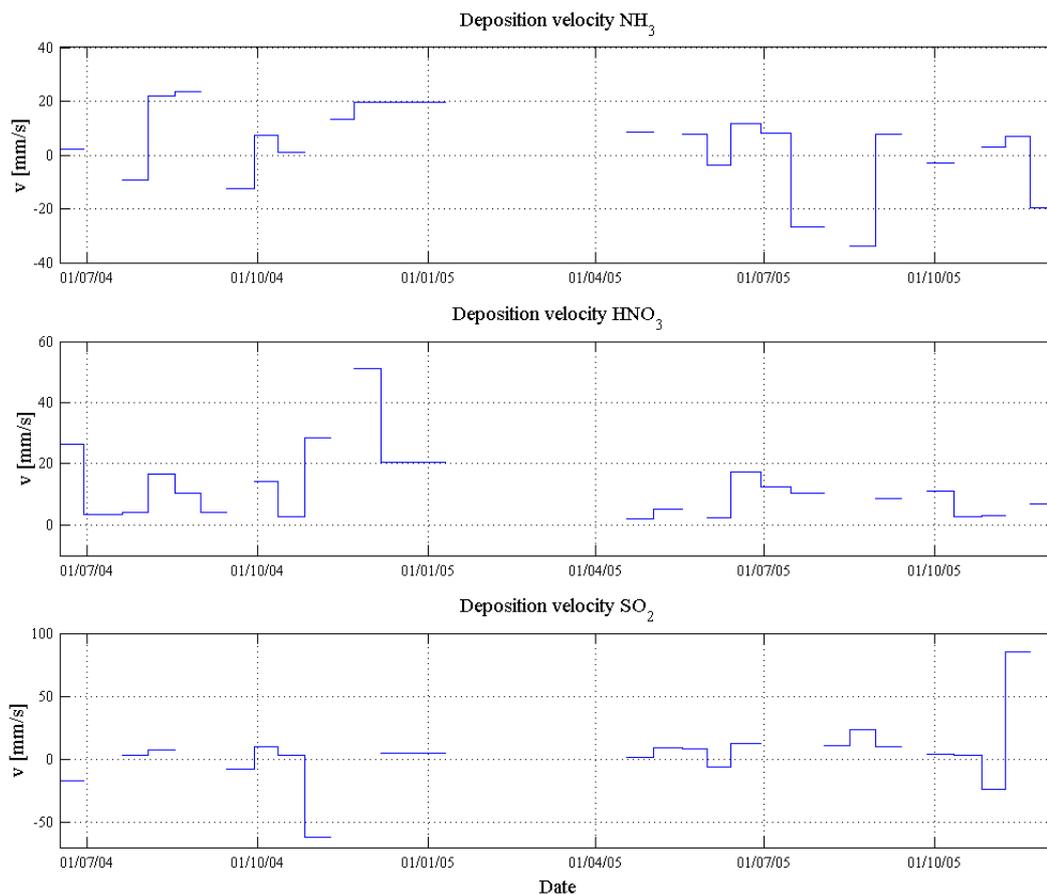


Figure 6: Dry deposition velocities of ammonia, nitric acid and sulphur dioxide at 1.75 m.

To picture the total atmospheric deposition at Storgama, wet deposition fluxes of the compounds measured in the rain samples, ammonium, nitrate and sulphate are compared with their dry deposition fluxes (Figure 7). Since at the pH of the collected precipitation (averagely 4.8) wet deposited NH_3 and HNO_3 dissipate to the basic respectively acidic species ($\text{pK}_{\text{NH}_4}=9.25$, $\text{pK}_{\text{HNO}_3}=-2$), the ammonium and nitrate wet deposition flux is likely to be the sum flux of the alkaline and acidic compounds and therefore also compared to the dry deposition of $\text{sumNH}_4\text{-N}$ ($\text{NH}_4\text{-N} + \text{NH}_3\text{-N}$) and $\text{sumNO}_3\text{-N}$ ($\text{NO}_3\text{-N} + \text{HNO}_3\text{-N}$). The sulphur content of precipitation includes dissolved SO_2 gas (as sulphite) and sulphate from particles and gas. In rain water samples the dissolved SO_2 is oxidised rapidly to sulphate and it cannot be determined from precipitation analysis which fraction of sulphate concentration is caused by SO_2 and which by sulphate itself (Brueggemann and Spindler, 1999). Therefore Figure 7 also includes a comparison between the wet flux of $\text{SO}_4\text{-S}$ and the dry flux of the summarized sulphur compounds, i.e. $\text{SO}_4\text{-S} + \text{SO}_2\text{-S}$, denoted as $\text{sumSO}_x\text{-S}$. By convention the flux is negative when

examined from the atmosphere downwards to the ecosystem and positive in case of emission from soil and plants.

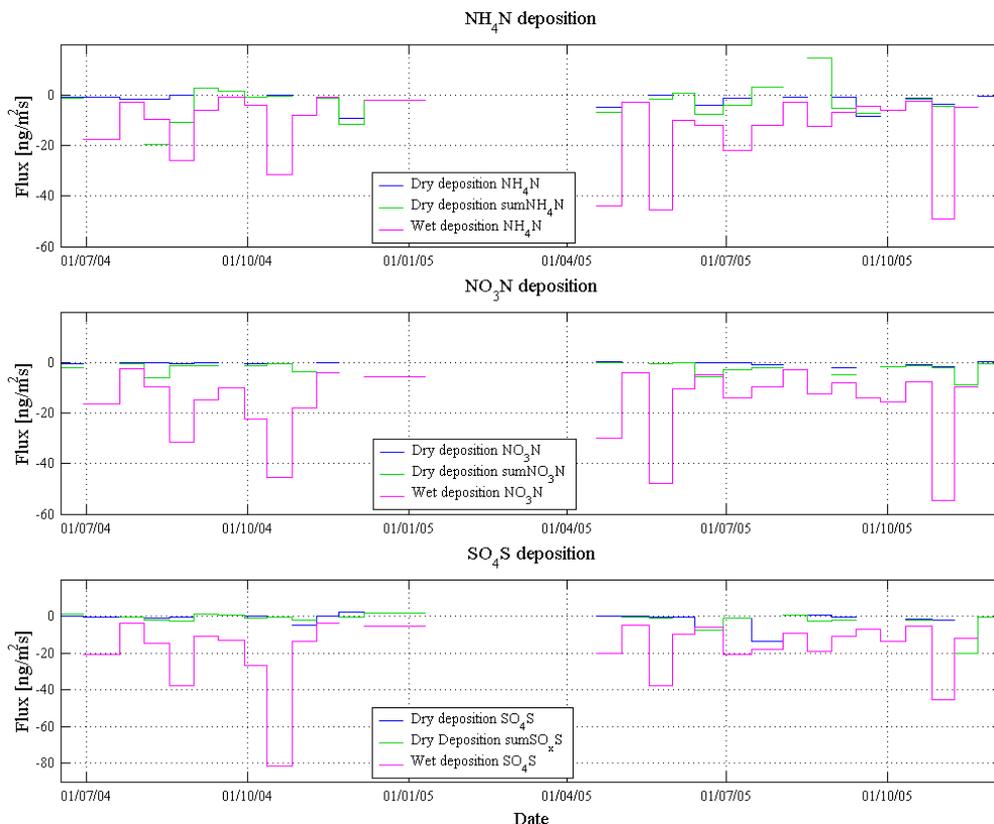


Figure 7: Comparison between dry and wet deposition fluxes of ammonium, nitrate and sulphur, where $sumNH_4N = NH_4N + NH_3N$, $sumNO_3N = HNO_3N + NO_3N$ and $sumSO_xS = SO_4S + SO_2S$.

The wet deposition profiles of the three compounds show similar minima and maxima and correspond well with the measured precipitation amount (Figure 4). It seems that the wet deposition is the dominant process accounting for most of the removal of pollutants from the atmosphere. However in less humid conditions the dry flux can contribute a significant percentage to the total deposition as can be seen in certain sampling periods between July and October 2005 (Figure 7). Table 1 is an overview of the average net flux of the trace gases as well as of the yearly nitrogen and sulphur input to the ecosystem. Highest wet and lowest dry deposition rates are estimated for the sulphur compounds with a difference of nearly factor 10 in their importance. Regarding the nitrogen compounds, nitrate/nitric acid are deposited more efficiently by rain, while the input to the ecosystem by dry deposition is highest from ammonia/ammonium even though still less than the wet deposited amount. It has to be kept in mind that the deposition of $sumNH_4-N$ is a net flux, also including the presented ammonia emissions during summer months. The contribution of the dry to the total deposition flux ranges from around 19% for $sumNH_4-N$ to 12% for $sumNO_3-N$ and less than 10% for $sumSO_x-S$. The total burden on the ecosystem is 1.1 g N and 0.63 g S per year and square meter.

Table 1: Average dry and wet deposition fluxes and yearly input to the ecosystem.

Gas	Deposition	Average net flux [ngm ⁻² s ⁻¹]	Yearly deposition [gm ⁻² y ⁻¹]
sum NH ₄ -N	dry	- 3.13	0.10
NH ₄ -N	wet	- 13.37	0.42
sum NO ₃ -N	dry	- 2.33	0.07
NO ₃ -N	wet	- 16.39	0.51
sum SO _x -S	dry	- 1.98	0.06
SO ₄ -S	wet	- 18.20	0.57

5.2 Comparison between CoTAG measurements and the dry deposition module

To investigate the applicability of the big-leaf deposition module to model for the Storgama site, two different land use categories (LUC) have been used, “LUC 13: short grass and forbs” and “LUC 22: tundra”, to model the dry deposition velocities of the trace gases (Figure 8). Although measured micrometeorological parameters were used to drive the module, other parameters (e.g. leaf area index (LAI), roughness length) were taken from the default module values. For LUC 13 the default LAI is constantly 1 and for LUC 22 it ranges from 0 to 22 during one-year period, which seem reasonable considering the very low productivity of the area.

Modelled values are well within the range of the measurements, even though the deposition module did not reproduce the large variability. For example, modelled deposition velocities ranged from 2 to 8 mms⁻¹ for SO₂ and NH₃, and from 7 to 15 mms⁻¹ for HNO₃ (Figure 8, right column), while the corresponding measured values ranged from negative to higher than 50 mms⁻¹. Similar to the CoTAG results estimations from the model show no apparent seasonal variations either.

Table 2 compares annual average deposition velocities for the CoTAG system and the two module parameterisations. Since the module only considered deposition and thus cannot produce upward fluxes, the measured mean values have also been calculated using only positive velocities (V_{pos}). The modelled deposition is less, using the LUC 13: short grass and forbs parameterisation, and the mean velocities compare better with the results from the CoTAG calculations including the whole record, which is confirmed by a performed correlation analysis (Table 3). As can be seen in Table 3, the available data points are few and decrease the significance of the statistical evaluation.

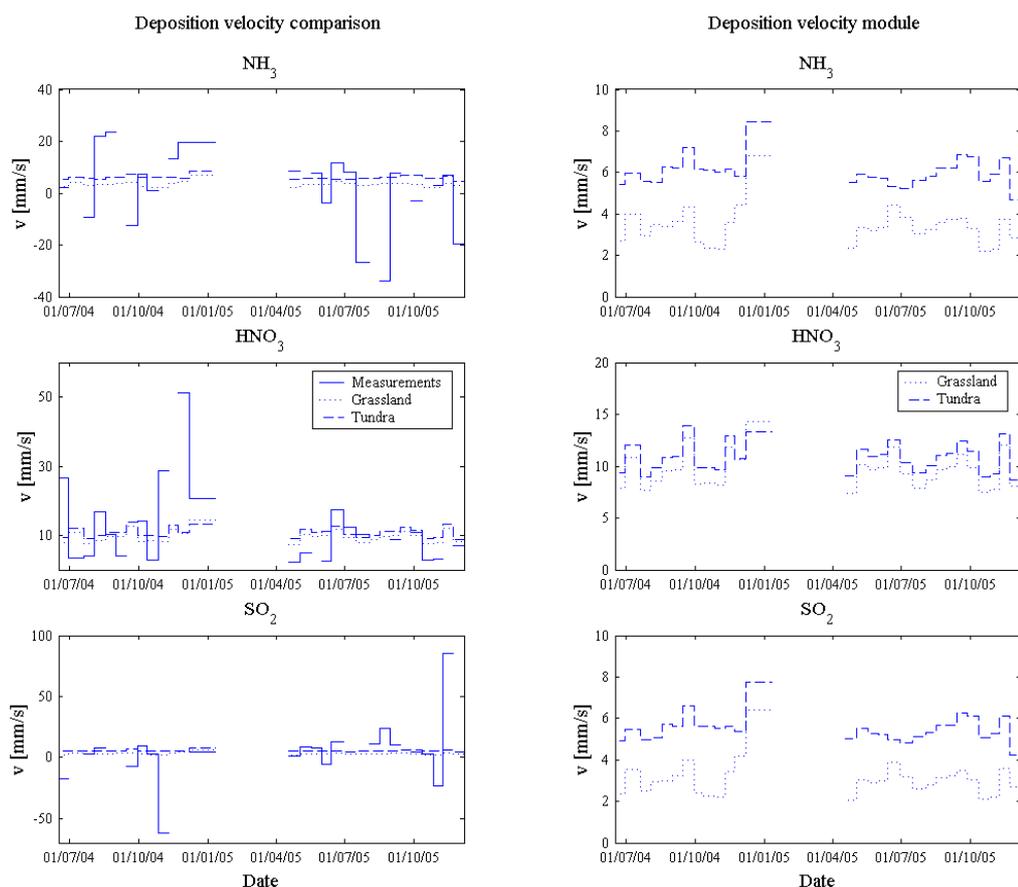


Figure 8: Measured and modelled deposition velocities at Storgama.

Table 2: Annual average deposition velocities for the CoTAG system and two module parameterisations. V_{all} = mean V_d calculated from the measurements including all values, V_{pos} = mean V_d from the measurements, just positive values, V_{grass} = mean V_d model parameterisation “short grass and forbs”, V_{tundra} = mean V_d model parameterisation “tundra”.

Gas	\bar{V}_{all} [mms ⁻¹]	\bar{V}_{pos} [mms ⁻¹]	\bar{V}_{grass} [mms ⁻¹]	\bar{V}_{tundra} [mms ⁻¹]
NH ₃	1.44	10.76	3.39	5.98
HNO ₃	11.80	11.80	9.58	10.74
SO ₂	3.99	13.04	3.07	5.47

Table 3: Correlations between CoTAG and modelled values.

Gas	$\langle V_{all} V_{grass} \rangle$	$\langle V_{all} V_{tundra} \rangle$	Data points	$\langle V_{pos} V_{grass} \rangle$	$\langle V_{pos} V_{tundra} \rangle$	Data points
NH ₃	0.32	0.25	23	0.59	0.27	15
HNO ₃	0.29	0.16	23	0.29	0.16	23
SO ₂	0.28	0.17	20	0.16	0.19	15

6 Discussion and conclusions

6.1 CoTAG measurements

Deposition velocity measurements for nitrogen and sulphur compounds have been carried out at a semi-alpine site in Southern Norway using the conditional time averaged gradient method in order to monitor fluxes of the trace gases. The studied area has a very low productivity and is not used as pasture land any longer. Variability of deposition velocities through the year is consequently probably to a large degree governed by meteorological conditions. As can be seen in Figure 7, the profile of sulphur dioxide shows a period of enhanced deposition in late November 2005, corresponding well with higher friction velocities (Figure 3). It may also be caused by co-deposition of SO_2/NH_3 (Erisman and Wyers, 1993), since the concentration ratio of NH_3 to SO_2 is higher compared to other times (Figure 9). A smaller peak in the wind record is also observable in late November 2004 which seems to be related with higher deposition velocities of the nitrogen compounds NH_3 and HNO_3 . However such a peak was not found for SO_2 during the same period. The relative low concentration ratio of NH_3/SO_2 (Figure 9) might have decreased sulphur dioxide deposition while at the same time enhanced ammonia deposition.

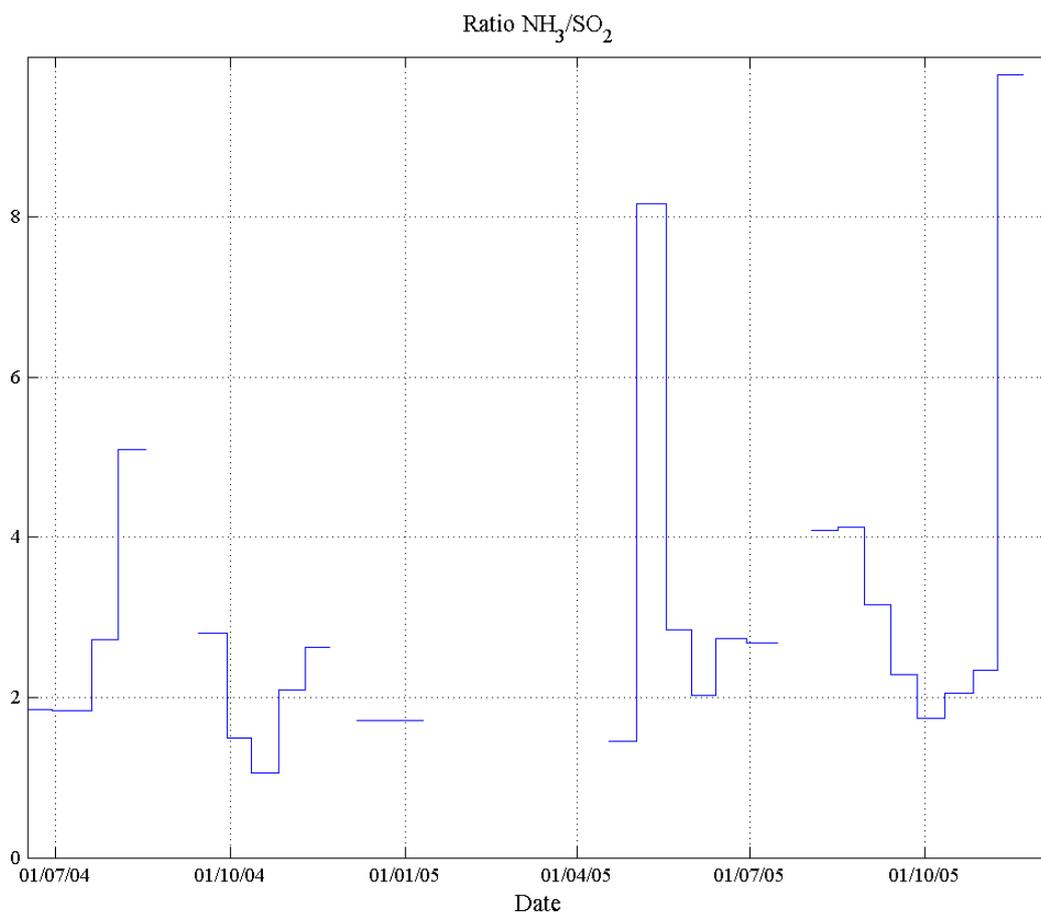


Figure 9: Ratio of air concentration of NH_3 to SO_2 (average of the three measurement heights).

The deposition maxima in late fall are reasonable considering the climatic conditions during the two measurement years. Deposition is most rapid in cool and humid conditions (Sutton et al., 2001) and as there were no major snow events in early winter in both years (www.met.no), the surface was not frozen but the temperatures low, providing ideal conditions for high deposition rates. Especially for ammonia similar enhanced deposition velocities during cool and wet fall months were observed at comparable sites, e.g. above a Dutch non-fertilized grassland (Wichink Kruit et al., 2007). Fowler et al. (1998) report an average value of 25 mms^{-1} for the deposition velocity of NH_3 in mild winter conditions above a Scottish moorland which is in good agreement with the estimated maxima of 20 mms^{-1} at Storgama. Even though the timing of the peak of SO_2 is appropriate, the size order exceeds the moderate range of the Storgama records as well as observed deposition velocities of the trace gas above short vegetation at least by a factor 7 (e.g. Feliciano et al., 2001; Erisman et al., 1991), and is probably an overestimation resulting from the low concentrations near detection limit measured during the sampling interval (Figure 5). The reported high deposition velocities imply efficient adsorption to aqueous layers of leaf surfaces or soil particles, since neither stomatal uptake nor diffusion through the cuticle is rapid enough to explain the observed fluxes (Sutton et al., 1993).

The absence of a clear seasonal cycle for all substances is supported by other European studies measuring trace gas deposition over short vegetation. The difference between seasonal ammonia deposition velocities above a Hungarian grassland site was not significant (Horv ath et al., 2004) and over a cold humid meadow in Portugal only a slight variation in the seasonality of the sulphur dioxide fluxes is observed, but without any regular pattern (Feliciano et al., 2001). Beside the fact that the deposition velocities are mainly decided by meteorological conditions, the very small seasonal variation can also be explained by the fact that the three gaseous species SO_2 , NH_3 and HNO_3 easily deposit to external surfaces (non-stomatal pathways) and thus are not dependent on vegetation cycles.

Studies (e.g. Sutton et al., 1993; Wichink Kruit et al., 2007) have shown, that regarding ammonia fluxes a compensation point concentration exists for plants, which is the ammonia air concentration in equilibrium with plant tissue ammonium ions. When air concentrations are larger than the compensation point, deposition is expected, whereas emission is expected when air concentrations are smaller than the compensation point. Despite a highly unreasonable minima in winter 2005 that remains unexplained, the negative deposition velocities (i.e. ammonia emissions from the surface) at Storgama are observed in the vegetation period between June and October which is the season characterized by highest temperatures and sensible heat flux (Figure 3). Several authors (e.g. Spindler et al, 2000; Wichink Kruit et al., 2007) report ammonia emission events in diurnal cycles and averages, however positive deposition fluxes averaged over longer periods as found at Storgama have also been observed elsewhere. Over the already introduced non-fertilized grassland in the Netherlands a NH_3 -Flux of $4 \text{ ngm}^{-2}\text{s}^{-1}$ (i.e. a net emission), averaged over a 28-day sampling period in warm summer conditions was observed (Wichink Kruit et al., 2007) and the average NH_3 -Flux during the vegetation period (5 months) over a Hungarian grassland was $3.4 \text{ ngm}^{-2}\text{s}^{-1}$ (Horv ath et al., 2005). The mean ammonia flux for a comparable two months period at Storgama (29. June 2005 until 30. August 2005) is $3.35 \text{ ngm}^{-2}\text{s}^{-1}$ and

therefore in good agreement with the references. Fowler et al. (1998) report a fraction of 18% of emission fluxes within a month in the growing season which were consistent with gradual changes in the compensation point. The conditions leading to net emission of ammonia from the canopy include the drying of dew or rainwater from which the ammonium (NH_4) in the surface water releases NH_3 to the atmosphere as the water evaporates. Another major effect is that of temperature on the solubility of NH_4 and the opening of stomata, both of which lead to the periods of ammonia emission being the period of temperature and radiation maxima (Fowler et al., 1998).

More difficult to explain are the negative deposition velocities in the sulphur dioxide record and no studies of evident bi-directional fluxes of the trace gas were found. However, Feliciano et al. (2001) who monitored SO_2 -Fluxes above a humid grassland in Portugal found that upward sulphur dioxide fluxes calculated by the gradient technique are a common feature at low concentrations, especially for $c(\text{SO}_2) < 1 \mu\text{gm}^{-3}$, i.e. $c(\text{SO}_2-S) < 0.5 \mu\text{gm}^{-3}$. Since higher ambient air concentration than at Storgama were measured, these low concentrations were removed through selection criteria when calculating deposition fluxes. As can be seen in Figure 5, the measured concentrations at Storgama were permanently below this limit and the appearance of negative deposition velocities therefore a possible occurrence when applying the gradient method. However the reliability of the results may be restricted due to the low concentrations in the atmosphere and the limits of the CoTAG system for remote and unpolluted sites may be discussed. Advection events could cause negative deposition velocities. When there are horizontal gradients in concentrations (i.e. heterogeneous surfaces caused by different canopies or terrain), the measured concentrations at high-levels could represent the upwind conditions, while at lower levels, represent the local conditions. If the upwind concentration is lower than at the measurement location, negative deposition will be observed. This is also the reason why negative deposition velocities were usually observed when concentrations were very low. On the other hand, when the upwind concentration is higher, the observed deposition velocity can also be overestimated.

Comparisons between the CoTAG system and more sophisticated instrumentations are rare and presented in terms of fluxes averaged over half-yearly periods (Fowler et al., 2001; Erisman et al., 2005). For this extended time span the agreement between the low cost method and the more expensive instrumentation was excellent, but no higher resolution data is available in literature. It is therefore difficult to estimate how reliable the short term averages at Storgama are and more detailed comparisons between monitoring systems especially for low concentrations and shorter intervals are needed.

6.2 Dry and wet deposition fluxes

To estimate the relative importance of the processes responsible for removing trace gases and particles from the atmosphere, and to get an idea of the total pollutant input to the ecosystem, the dry deposition calculations have been compared to wet deposition fluxes reported at Storgama. Which of the two mechanisms of deposition prevails, depends on a combination of a number of parameters which include atmospheric concentration of the trace components,

synergistic effects with other gases, the roughness of the surface, the geographical site, the wind velocity and the distance from the sources (Erisman and Wyers, 1993; Brüeggemann and Spindler, 1999). In Storgama the wet deposition flux was the dominant process during most of the monitoring period and strongly governed by the measured rain amount. As can be seen from Figure 4 and Figure 7, especially the flux peaks in early fall 2004 and November 2005 can be ascribed to big rain events during the sampling intervals.

In Norway in general the deposition pattern of nitrogen and sulphur species is mostly influenced by the precipitation frequency and amount and wet deposition is far more important than dry deposition (Hole and Tørseth, 2002). Anyway since the average rain volume collected in the monitoring period was in a rather moderate range, higher contributions from the dry to the total deposition could be expected. Above a Japanese grassland with comparable precipitation amount the mean fraction of the monthly dry to total deposition was with 63% for $\text{NH}_3\text{-N}$ and 23% for $\text{NO}_3\text{-N}$ much higher than in Storgama (Hayashi et al., 2007), where the corresponding percentages were 19% and 12%, respectively. Above a German grassland site Brüeggemann and Spindler (1999) report monthly fractions of dry sulphur to total sulphur deposition varying between 3% and 80% with corresponding intensity of precipitation between 158 mm and 13 mm and illustrate therefore again the influence of the rain amount for the relative importance of the two processes. However when comparing the Storgama results to other studies the relatively uncertain rain measurements with lack of values in several periods and overflow of the tank have to be taken into account as well as the low air concentrations of the pollutants. Low concentrations decrease the importance of dry deposition (Tørseth et al., 2000) and are thought to be at least partly responsible for the dominant wet elimination of pollutants from the atmosphere at the Storgama site.

The total yearly mean input to the ecosystem was around $1.10 \text{ g nitrogen m}^{-2}\text{yr}^{-1}$ and $0.63 \text{ g sulphur m}^{-2}\text{yr}^{-1}$ which is in good agreement with results from a Norwegian study that estimated total depositions of critical compounds with a higher resolution in the whole country (Hole and Tørseth, 2002). For the years 1997 – 2001 and the region studied here, a mean nitrogen burden of $0.8 - 1.2 \text{ gm}^{-2}\text{yr}^{-1}$ and a sulphur burden of $0.5 - 0.7 \text{ gm}^{-2}\text{yr}^{-1}$ are reported.

6.3 Comparison between measured and modelled dry deposition

Dry deposition velocities have also been estimated by a big-leaf module using two different land use categories which resulted in values that were well within the range of measurements. However the large variability found in the CoTAG calculations was not reproduced by the module. This can mainly be explained in two aspects. First the module does not include some processes, such as co-deposition of SO_2/NH_3 and bi-directional exchange of NH_3 . Second some extreme values in measurements were possibly caused by measurement uncertainties (see discussion chapter 6.2.). Spindler et al. (2001) also found similar explanations for obvious differences between micrometeorological flux-gradient measurements and calculations using an inferential model over a German grassland. For ammonia fluxes the best agreement they found between the measured and modelled data was a correlation of $r=0.23$. Additionally an overestimation of

mean dry deposition velocity can be expected when applying several rejection criteria to select data for gradient flux calculations, especially for averages over longer periods. This is partly because only concentrations above detection limit and with appreciable turbulence are sampled and thus the average concentration from the selected data is higher than from the complete data set (Erisman et al., 1993).

As described in chapter 6.2., very high deposition velocities from the measured data were found to be mainly caused by strong wind conditions and co-deposition of SO₂/NH₃. With no co-deposition incorporated in the module, the peaks produced by the module, which only included effects of strong wind speed, were not as high as seen in the measurements. In addition the module only considers deposition (i.e. compensation point is included) and thus cannot produce upward fluxes. Thus, even if the deposition module seems to be able to provide long-term average dry deposition estimates, improvements are needed to incorporate these important processes also in the modelling activities.

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References

- Aas, W. (ed.) (2006) Data quality 2004, quality assurance and field comparisons. Kjeller, Norwegian Institute for Air Research (EMEP/CCC-Report 4/2006). Downloadable at <http://www.nilu.no/projects/ccc/reports.html>.
- Aneja, V.P., Roelle, P.A., Murray, G.C., Southerland, J., Erisman, J.W., Fowler, D., Asman, W.A.H. and Patni, N. (2001) Atmospheric nitrogen compound II: Emissions, transport, transformation, deposition and assessment. *Atmos. Environ.*, 35, 1903-1911.
- Brueggemann, E. and Spindler, G. (1999) Wet and dry deposition of sulphur at the site Melpitz in East Germany. *Water, Air, Soil Poll.*, 109, 81-99.
- Erisman, J.W. and Wyers, G.P. (1993) Continuous measurements of surface exchange of SO₂ and NH₃: Implications for their possible interaction in the deposition process. *Atmos. Environ.*, 27A, 1937-1949.

- Erisman, J.W., Versluis, A.H., Verplanke, T.J.A.W., de Haan, D., Anink, D., van Elzakker, B.G., Mennen, M.G. and van Aalst, R.M. (1993) Monitoring the dry deposition of SO₂ in the Netherlands: Results for grassland and heather vegetation. *Atmos. Environ.*, 27A, 1153-1161.
- Erisman, J.W., Van Pul, A. and Wyers, P. (1994) Parameterization of surface resistance for the quantification of atmospheric deposition of acidifying pollutants and ozone. *Atmos. Environ.*, 28, 2595–2607.
- Erisman, J.W., Hensen, A., Fowler, D., Flechard, C.R., Grüner, A., Spindler, G., Duyzer, J.H., Weststrate, H., Römer, F., Vonk, A.W. and Jaarsveld, H.V. (2001) Dry deposition monitoring in Europe. *Water, Air, Soil Poll., Focus 1*, 17-27.
- Erisman, J.W., Vermeulen, A., Hensen, A., Flechard, C., Dämmgen, U., Fowler, D., Sutton, M., Grünhage, L. and Tuovinen, J.P. (2005) Monitoring and modelling of biosphere/atmosphere exchange of gases and aerosols in Europe. *Environ. Poll.*, 133, 403-413.
- Erisman, J.W., Hensen A., Mosquera, J., Sutton, M. and Fowler, D. (2005) Deposition monitoring networks: what monitoring is required to give reasonable estimates of ammonia/ammonium? *Environ. Poll.*, 135, 419 – 431.
- Famulari, D., Fowler, D., Storeton-West, R.L., Nemitz, F., Hargreaves, K., Rutherford, G., Tang, Y.S., Sutton, M.A. and Weston, K.J. (2007) Development of a low-cost system for measuring SO₂ and NH₃ deposition fluxes on the field scale by micrometeorology. Submitted to *Environ. Poll.*
- Feliciano, M.S., Pio, C.A. and Vermeulen, A.T. (2001) Evaluation of SO₂ dry deposition over short vegetation in Portugal. *Atmos. Environ.*, 35, 3633-3643.
- Fowler, D., Coyle, M., Flechard, C., Hargreaves, K., Storeton-West, R., Sutton, M. and Erisman, J.W. (2001) Advances in micrometeorological methods for the measurement and interpretation of gas and particles nitrogen fluxes. *Plant Soil*, 228, 117–129.
- Hayashi, K., Komada, M. and Miyata, A. (2007) Atmospheric deposition of reactive nitrogen on turf grassland in central Japan: Comparison of the contribution of wet and dry deposition. *Water, Air, Soil Poll., Focus 7*, 119-129.
- Hensen, A., Erisman, J.W., Fowler, D., Flechard, C.R., Gruener, A., Spindler, G., Duyzer, J.H., Weststrate, H., Roemer, F.G., Vonk, A.W. and van Jaarsveld, H. (1999) Towards development of a deposition monitoring network for air pollution in Europe: low-cost monitoring methods: LIFE96ENV/NL/215: final technical report. Petten, Energy Research Centre of the Netherlands (ECN-C-99-075).
- Hole, L.R. and Tørseth, K. (2002) Deposition of major inorganic compounds in Norway 1978-1982 and 1997-2001: Status and trends. Kjeller (NILU OR 61/2002). URL: www.nilu.no/data/inc/leverfil.cfm?id=4625&type=6

- Hole, L.R., Brunner, S.H., Hanssen, J.E. and Zhang, L. (2007) Low cost measurements of nitrogen and sulphur deposition velocities at a semi-alpine site: Gradient measurements and a comparison with deposition model estimates. Submitted to *Environ. Poll.*
- Horvath, L., Asztalos, M., Führer, E., Mészáros, R. and Weidinger, T. (2005) Measurement of ammonia exchange over grassland in the Hungarian Great Plain. *Agr. Forest Meteorol.*, 130, 282-298.
- Krupa, S.V. (2003) Effects of atmospheric ammonia (NH₃) on terrestrial vegetation: a review. *Environ. Poll.*, 124, 179-221.
- Massman, W.J. (1999) A model study of $k_B H^{-1}$ for vegetated surfaces using 'localized near-field' Lagrangian theory. *J. Hydrol.*, 223, 27-43.
- Padro, J. (1996) Summary of ozone dry deposition velocity measurements and model estimates over vineyard, cotton, grass and deciduous forest in summer. *Atmos. Environ.*, 30, 2363-2369.
- Philips, S.B., Arya, S.P. and Aneja, V.P. (2004) Ammonia flux and dry deposition velocity from near-surface concentration gradient measurements over a grass surface in North Carolina. *Atmos. Environ.*, 38, 3469-3480.
- Spindler, G., Teichmann, U. and Sutton, M.A. (2001) Ammonia dry deposition over grassland – micrometeorological flux-gradient measurements and bidirectional flux calculations using an inferential model. *Q.J.R. Meteorol. Soc.*, 127, 795-814.
- Sutton, M.A., Fowler, D. and Moncrieff, J.B. (1993) The exchange of atmospheric ammonia with vegetated surfaces. I: Unfertilized vegetation. *Q.J.R. Meteorol. Soc.*, 119, 1023-1045.
- Sutton, M.A., Milford, C., Nemitz, E., Theobald, M.R., Hill, P.W., Fowler, D., Schjoerring, J.K., Mattson, M.E., Nielsen, K.H., Husted, S., Erisman, J.W., Otjes, R., Hensen, A., Mosquera, J., Cellier, P., Loubet, B., David, M., Genermont, S., Neftel, A., Blatter, A., Hermann, B., Jones, S.K., Horvath, L., Führer, E.C., Mantzanas, K., Koukoura, Z., Gallagher, M., Williams, P., Flynn, M. and Riedo, M. (2001) Biosphere-atmosphere interactions of ammonia with grasslands: Experimental strategy and results from a new European initiative. *Plant Soil*, 228, 131-145.
- Tørseth, K., Semb, A., Schaug, J., Hanssen, J.E. and Aamlid, D. (2000) Processes affecting deposition of oxidised nitrogen and associated species in the coastal areas of Norway. *Atmos. Environ.*, 34, 207-217.
- Tørseth, K. and Hov, Ø. (eds.) (2003) The EMEP monitoring strategy 2004-2009. Background document with justification and specification of the EMEP monitoring programme, 2004-2009. Kjeller, Norwegian Institute for Air Research (EMEP/CCC report 9/2003). Downloadable at <http://www.nilu.no/projects/ccc/reports.html>.

- Uggerud, H.T., Hanssen, J.E., Schaug, J. and Skjelmoen, J.E. (2003) The twentieth intercomparison of analytical methods within EMEP. Kjeller, Norwegian Institute for Air Research (EMEP/CCC report 8/2003). Downloadable at <http://www.nilu.no/projects/ccc/reports.html>.
- Wesely, M.L. (1989) Parametrisation of surface resistances to gaseous dry deposition in regional-scale numerical models. *Atmos. Environ.*, *23*, 1293-1304.
- Wesely, M.L. and Hicks, B.B. (2000) A review of the current status of knowledge in dry deposition. *Atmos. Environ.*, *34*, 2261–2282.
- Wichnik Kruit, R.J., van Pul, W.A.J., Otjes, R.P., Hofschreuder, P., Jacobs, A.F.G. and Holtslag, A.A.M. (2007) Ammonia fluxes and derived canopy compensation points over non-fertilized agricultural grassland in The Netherlands using the new gradient ammonia-high accuracy-monitor (GRAHAM). *Atmos. Environ.*, *41*, 1275-1287.
- Wyers, G.P., Otjes, R.P. and Slanina, J. (1993) A continuous flow denuder for the measurement of ambient concentrations and surface fluxes of ammonia. *Atmos. Environ.*, *27A*, 2085-2090.
- Zhang, L., Moran, M.D., Makar, P.A., Brook, J.R. and Gong, S. (2002) Modelling gaseous dry deposition in AURAMS: a unified regional air-quality modelling system. *Atmos. Environ.*, *36*, 537–560.
- Zhang, L., Brook, J.R. and Vet, R. (2003) A revised parametrization for gaseous dry deposition in air-quality models. *Atmos. Chem. Phys.*, *3*, 2067-2082.

