Low cost measurements of nitrogen and sulphur dry deposition velocities at a semi-alpine site: Gradient measurements and a comparison with deposition model estimates

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Abstract

The conditional time averaged gradient method was used to measure air-surface exchange of nitrogen and sulphur compounds at a semi-alpine site in Southern Norway. Dry deposition velocities were then obtained from the bi-weekly concentration gradient measurements. Annual deposition velocities were found to be 1.4, 11.8 and 4.0 mm s⁻¹ for NH₃, HNO₃ and SO₂, respectively, if all data were included, and to be 10.8, 11.8 and 13.0 mm s⁻¹, respectively, if only positive values were included. Measured deposition velocities were compared to two sets of values estimated from a big-leaf dry deposition module applying to two different land types (short grass and forbs, and tundra), driven by measured micrometeorological parameters. The deposition module gives reasonable values 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 studied area.

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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, 2004; Fowler and Duyzer, 1990; Krupa, 2003; Tørseth, 2003). Monitoring and modelling of air pollutant deposition are essential to develop and evaluate policies to abate the effects related to air pollution and to determine sinks of pollutants from the atmosphere.

While the concentration field and wet deposition of different atmospheric compounds are well monitored and modelled e.g. in the EMEP² program, long term dry deposition data are 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 long term deposition data are available for a number of different land cover classes and regions. Nitrogen compounds, ammonia and nitrate in particular, cause eutrophication and their relative importance in acidification is

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increasing since sulphur concentrations in air and precipitation are decreasing. Decreasing sulphur concentrations also influence the surface affinity to N compounds (Erisman and Wyers, 1993; Erisman et al., 2005). New initiatives such as the COST 729 action (www.cost729.org) and the NitroEurope integrated project (www.nitroeurope.eu) seek to better quantify the nitrogen balance and to get a more complete overview of atmosphere—biosphere fluxes in Europe.

Within the ACCENT-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 with high resolution are necessary, but the instrumentation required is expensive and labour intensive. 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). CoTAG measurements (Famulari et al., submitted for publication) 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).

Dry deposition accounts for about 20% of the total deposition in Europe, with a range of 10—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 Finmark county (less than 500 mm precipitation per year) (Hole and Tørseth, 2002). Here we present 18 months of dry deposition measurements for the main N and S atmospheric compounds from a semi-alpine moor in southeast Norway. The annual precipitation here is around 1200 mm, so it is expected that dry deposition accounts for a significant part of the total deposition. For three of the compounds (ammonia (NH3), nitric acid (HNO3) and sulphur dioxide (SO2)), results were compared with output from an updated big-leaf deposition module (Zhang et al., 2003), using local meteorology as input.

2. Description of the field experiment

A five-year project on N balance and the influence of climate changes has been carried out in Norway in 2003—2007.3 Modelling activities such as N deposition scenarios in Scandinavia under possible future climate regimes and modelling of the nitrogen ecosystem cascade are carried out together with an extensive fieldwork program and analysis of long term data series. The main field site is Storgama in Telemark county (59°01´N 8°32´E, 600 m asl), 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 (3—4 m) Scots Pine trees. The CoTAG system was established on a grass covered patch with a flat fetch of about 100 m in the sector studied. Soil depth to solid bedrock was only between 10 and 20 cm. There is some agricultural activity in village Treungen about 10 km down valley to the west, but local sources are expected to be ignorable at this site.

The CoTAG systems have traditionally 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 we expected values not far from the detection limit, we decided to use more powerful pumps with a capacity of approximately 51 air min⁻¹ 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. The system was equipped with the standard Campbell 23X data logger and micrometeorological sensors. Compounds analysed for and presented here were SO2—S, HNO3—N, NH3—N, SO2—S, NO3—N, NH4—N, “sum NO3—N” (NO3—N + HNO3—N) and “sum NH4—N” (NH3—N + NH4—N). We also analysed for Cl, Na, K, Ca and Mg concentrations but these results are not presented here.

The CoTAG system was set up in Storgama in mid June 2004 and was run until the end of 2005. Chemical sampling was disrupted from mid January to mid April 2005 due to deep snow. The sampling interval was set to two weeks to ensure that enough air volume was sampled. Air chemistry sampling heights were 0.45, 1.25 and 1.75 m while the meteorological sampling heights for estimation of dynamical stability were 0.5 and 1.5 m. A sketch of the experimental lay-out is shown in Fig. 1.

Fig. 1. Sketch of the experimental site. The sector of interest was west of the CoTAG system, since the topography to the east was very complex.
3. Brief description of the dry deposition module

Using the well-known resistance analogy to dry deposition, 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 aerodynamic resistance, $R_a$, quasi-laminar sublayer resistance, $R_b$, and surface or canopy resistance, $R_c$. $R_a$ is only a function of micrometeorological conditions and the roughness characteristics of the underlying surface, so it is independent of chemical species. $R_b$ is a function of friction velocity and the molecular diffusivity of each chemical species. The simple approach as used in Padro (1996) is adopted here to determine $R_a$ and $R_b$.

$R_c$ is calculated according to Zhang et al. (2003):

$$\frac{1}{R_c} = \frac{1 - W_{st}}{R_{st} + R_m} + \frac{1}{R_{ns}}$$

(1)

$$\frac{1}{R_m} = \frac{1}{R_{ac} + R_g} + \frac{1}{R_{cut}}$$

(2)

Note that $R_c$ is divided into two parallel paths: one is stomatal resistance ($R_{st}$) with its associated mesophyll resistance ($R_m$), and the other is non-stomatal resistance ($R_{ns}$). $R_{ns}$ is further decomposed into resistance to soil uptake, which includes incanopy 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. $R_{st}$ is calculated using a sunlit/shade stomatal resistance submodule and $R_m$ is treated as dependent only on the chemical species. $R_{ac}$ and $R_{cut}$ are parameterized as functions of friction velocity, relative humidity and leaf area index. $R_g$ is given different values for different chemical species and over different surfaces. Detailed descriptions of $R_{st}$ and $R_m$ can be found in Zhang et al. (2002), and of the rest terms, in Zhang et al. (2003).

4. Data processing

For the period studied, the overall CoTAG data coverage was 38.3%, varying from 20 to 60% for each sampling period (about two weeks) (Fig. 2). This means that the micrometeorological

Fig. 2. Friction velocity ($u^*$), sensible heat flux ($H$) and air temperature ($T$) wind speed and CoTAG data coverage at the Storgama site.
dynamical stability close to ground was close to neutral (Richardson number $R_i$ in the interval $-0.05$ to 0.05) and the wind was from the desired sector. The meteorological sampling interval was 15 min and $R_i$ was recalculated for each sampling.

Micrometeorological data (wind speed, air temperature, air humidity, friction velocity and sensible heat flux) from the CoTAG system were interpolated to hourly values and used as input to the dry deposition module. Since detailed precipitation data were not present, a typical precipitation of 0.1 mm h$^{-1}$ was used 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. A snow cover was included in December–March.

The average temperature was never below zero in the sampling periods and there was a tendency for higher wind speeds in late autumn (Fig. 2). It also appears as expected from Fig. 2 that the CoTAG system has been sampling in cases with high wind speed and low sensible heat flux (close to neutral stability). There were snowfall episodes starting in November 2004, but no significant and lasting snow deposition occurred until mid January 2005 when the measurements were discontinued until mid April. The winter in Southern Norway was about 1°C warmer than average in 2004–2005 (www.met.no). Annual precipitation, measured between July 2004 and June 2005, was 1121 mm and the monthly average temperature ranged from $-1.9$ °C in February to 17.6 °C in July (Brunner and Hole, 2007).

Fig. 3 shows all analysed concentrations for N and S compounds through the sampling period. For some of the compounds it seems to be a seasonal pattern in concentrations. Sampled air volumes were between 27 and 120 m$^3$ for each sampling period and the measurement accuracy was then very high (0.01 µg m$^{-3}$ for SO$_2$, 0.005 µg N m$^{-3}$ for HNO$_3$ and 0.01 µg m$^{-3}$ for NH$_3$). However, in some cases the gradient was smaller than the detection limit for the compound. These cases have not been included in the calculation of deposition velocities from the CoTAG measurements (Brunner and Hole, 2007). We focus here on three gases with different properties: gaseous nitric acid (HNO$_3$), ammonia (NH$_3$) and sulphur dioxide (SO$_2$).

Since we had three measuring heights available, four concentration gradients were calculated for each CoTAG sampling period (top–bottom, top–middle, middle–bottom and least square slope top–middle–bottom (reference value)). This enables us to remove outliers and gradients that are not representative for the measuring period (Brunner and Hole, 2007; Famulari et al., submitted for publication). The data presented here are the least square slope which was very similar to the top–bottom gradient.

5. Results and discussion

In Fig. 4 and in Tables 1 and 2 the CoTAG values are compared with module calculations from using two different land use categories (LUC): “LUC 13: short grass and forbs” and “LUC 22: tundra”. Although measured micrometeorological parameters were used to drive the module, other parameters (e.g., leaf area index (LAI), and roughness length) were taken from the default module values. The studied area has a very low productivity and is no longer used as pasture land. The default LAI in the module has a constant value of 1 for LUC 13 and ranges from 0 to 1 for LUC 22 during one-year period. These values seem to be reasonable considering the very low productivity of the area.

Modeled values were well within the range of the measurements. However, the large variability found in the measurement was not reproduced by the module. For example, modeled deposition velocities ranged from 2 to 8 mm s$^{-1}$ for SO$_2$ and NH$_3$, and from 7 to 14 mm s$^{-1}$ for HNO$_3$ (Fig. 4, right column) while measured values ranged from negative to higher than 50 mm s$^{-1}$. The difference between the module estimations and measurements can be explained in two aspects: (1) the module does not include some processes, such as co-deposition of SO$_2$/NH$_3$ and bi-directional exchange of NH$_3$, and (2) some extreme values in measurements were possibly caused by measurement uncertainties (e.g., advection from heterogeneous surface) can either increase or decrease the vertical concentration gradients (more discussions below).

It is noted that there is no clear seasonal pattern in the measured deposition velocities, although for ammonia there is enhanced uptake in summer and spring. Estimations from the module show no apparent seasonal variations either. LAI is the dominant parameter for stomatal uptake of gaseous species. Considering the very small LAI values at the measurement site and the fact that the three gaseous species (SO$_2$, NH$_3$ and HNO$_3$) can also deposit easily to external surfaces (non-stomatal pathways), the deposition velocities would be mainly decided by meteorological conditions. This largely explains the very small seasonal variation of deposition velocities. Such a phenomenon was also found from 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 (Horváth et al., 2005) 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).

A sulphur dioxide deposition episode in late November 2005 seemed to correspond with high wind speeds (Fig. 2); 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 (Fig. 3). 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$_2$ might have decreased SO$_2$ deposition while at the same time enhanced NH$_3$ deposition. With no co-deposition included 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.

The deposition maxima in late fall are reasonable considering the climatic conditions during the two measurement years.
Fig. 3. Concentrations (μg m⁻³) at three heights for the whole sampling period.
Dry 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, the surface was not frozen but the temperatures were relatively low (Fig. 2), 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 (Wichnik Kruit et al., 2007). Fowler et al. (1998) report an average value of 25 mm s$^{-1}$ 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 mm s$^{-1}$ 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 (Fig. 3). 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).

Other studies (e.g. Sutton et al., 1993; Wichnik 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

![Fig. 4. Measured and modelled deposition velocities at Storgama. The model results are averaged over the CoTAG sampling intervals.](image-url)

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Annual average deposition velocities for the CoTAG system and two parameterisations of the AURAMS deposition module</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>$V_{\text{all}}$</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>1.44</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>11.80</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>3.99</td>
</tr>
</tbody>
</table>

$V_{\text{all}}$ = Mean deposition velocity calculated from the measurements (including all values after removing erroneous data); $V_{\text{pos}}$ = mean deposition velocity calculated from the measurements, just positive values; $V_{\text{grass}}$ = mean deposition velocity model parameterisation “short grass”; $V_{\text{tundra}}$ = mean deposition velocity model parameterisation “tundra”. All values are given in mm s$^{-1}$. 

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compensation point. Despite a highly unreasonable minima in winter 2005 that remain 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 (Fig. 2). Several authors (e.g. Spindler et al., 2001; Wichnik Kruit et al., 2007) report ammonia emission events in diurnal cycles and averages. Over the already introduced non-fertilized grassland in the Netherlands a \( \text{NH}_3 \)-Flux of 4 ng m\(^{-2}\) s\(^{-1}\) (i.e. a net emission), averaged over a 28-day sampling period in warm summer conditions was observed (Wichnik Kruit et al., 2007) and the average \( \text{NH}_3 \)-Flux during the vegetation period (five months) over a Hungarian grassland was 3.4 ng m\(^{-2}\) s\(^{-1}\) (Horváth et al., 2005). The mean ammonia flux for a comparable two months period at Storgama (29th June 2005 until 30th August 2005) is 3.4 ng m\(^{-2}\) 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 was 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 rain water from which the ammonium (\( \text{NH}_4^+ \)) in the surface water releases \( \text{NH}_3 \) to the atmosphere as the water evaporates. Another major effect is that of temperature on the solubility of \( \text{NH}_3 \) 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). The module only considered deposition (i.e., compensation point is included) and thus cannot produce upward fluxes.

More difficult to explain are the negative deposition velocities in the sulphur dioxide record. Feliciano et al. (2001) who monitored \( \text{SO}_2 \)-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 \( c(\text{SO}_2) < 1 \) \( \mu \text{g m}^{-3} \), i.e. \( c(\text{SO}_2) - S < 0.5 \) \( \mu \text{g m}^{-3} \). Since higher ambient air concentrations were measured in Portugal than at Storgama, these low concentrations were removed

<table>
<thead>
<tr>
<th>Gas</th>
<th>( (V_{all} - V_{grass}) )</th>
<th>( (V_{all} - V_{tundra}) )</th>
<th>Data points</th>
<th>( (V_{pos} - V_{grass}) )</th>
<th>( (V_{pos} - V_{tundra}) )</th>
<th>Data points</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NH}_3 )</td>
<td>0.32</td>
<td>0.25</td>
<td>23</td>
<td>0.59</td>
<td>0.27</td>
<td>15</td>
</tr>
<tr>
<td>( \text{HNO}_3 )</td>
<td>0.29</td>
<td>0.16</td>
<td>23</td>
<td>0.29</td>
<td>0.16</td>
<td>23</td>
</tr>
<tr>
<td>( \text{SO}_2 )</td>
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<td>0.17</td>
<td>20</td>
<td>0.16</td>
<td>0.19</td>
<td>15</td>
</tr>
</tbody>
</table>

Table 2

Correlations between CoTAG values and modelled values

Fig. 5. CoTAG deposition velocities at Storgama for total nitrate (particle + gas) and total ammonium.
through selection criteria when calculating deposition fluxes. As can be seen in Fig. 3, the measured concentrations at Storgama were constantly 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. One possibility for the observed negative deposition velocities could be caused by advection effects. 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.

Partitioning between gas phase and particle phase is not necessarily correctly measured with a filter pack. Unlike high apparent deposition velocity for particulate ammonium or nitrate could be due to evaporation of ammonia and nitric acid as the particles approach the ground. We therefore also calculated deposition velocities for total NO$_3$ (NO$_3^-$ as the particles approach the ground. We therefore also calculated deposition velocities for total NO$_3$ (NO$_2^+$ + HNO$_3^-$) and total NH$_4$ (NH$_4^+$ + NH$_3$) (Fig. 5), but the deposition velocity of these species varied within the same range as HNO$_3$ and NH$_3^-$, respectively, and negative deposition velocities for total NH$_4$ were also present.

6. Concluding remarks

Deposition velocity measurements for nitrogen and sulphur compounds have been carried out at a semi-alpine site in Southern Norway by the use of the conditional time averaged gradient method. The measurements have been compared with module-estimated values using two different land types with measured micrometeorological parameters as input. There is no clear annual pattern in measured or modelled data due to the very small canopy leaf area index. The module can generally produce the measured values, but not those extremely high values or negative values. Very high deposition velocities were found to be mainly caused by strong wind conditions and co-deposition of SO$_2$NH$_3$.

Comparisons between the CoTAG system and more sophisticated instrumentation 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 are 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. The deposition module used here seem to be able to provide long term average dry deposition estimates, however, improvements are needed to include more processes such as bi-directional exchange of NH$_3$ and co-deposition of SO$_2$ and NH$_3$.

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