Trajectory analysis of atmospheric transport of fine particles, SO$_2$, NO$_x$ and O$_3$ to the SMEAR II station in Finland in 1996–2008

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Abstract. Trajectory statistical methods that combine in situ measurements of trace gas or particle concentrations and back trajectories calculated for corresponding times have proven to be a valuable approach in atmospheric research; especially in investigating air pollution episodes, but also in e.g. tracing the air mass history related to high vs. low concentrations of aerosol particles of different sizes at the receptor site. A concentration field method was fine-tuned to take the presumable horizontal error in calculated trajectories into account, tested with SO$_2$ and validated by comparison against EMEP (European Monitoring and Evaluation Programme) emission data. In this work we apply the improved method for characterizing the transport of atmospheric SO$_2$, NO$_x$, O$_3$ and aerosol particles of different size modes to a Finnish measurement station located in Hyytiala (61°51'N, 24°17'E). Our method did not reproduce the EMEP emission sources, but proved useful for qualitative analysis on where the measured compounds come from, from one measurement station point of view. We applied it to study trends and seasonal variation in atmospheric pollutant transport during 13 yr at the SMEAR II (Station for Measuring Ecosystem-Atmosphere Interactions) station.

1 Introduction

Statistical analysis of a large set of trajectories has been a popular tool for identifying the regions that serve as source areas of selected compounds and thus contribute to the concentrations measured at the receptor site (Stohl, 1996, 1998; Scheifinger and Kaiser, 2007). Different methods have been developed for the purpose of tracing back registered concentrations.

Ashbaugh et al. (1985) introduced a method that was later named the potential source contribution function (PSCF). Similar concepts were developed by Vasconcelos et al. (1996) and Zhou et al. (2004). Instead of calculating conditional probabilities for high concentrations to occur as a result of certain air mass paths, actual concentration values for each grid cell are obtained with the Concentration Field (CF) method introduced by Seibert et al. (1994) and developed further by Stohl (1996). The results of both PSCF and CF methods can be interpreted as the distribution of either potential sources and sinks or the concentration of the compound. These methods have been applied in several studies run over Central Europe (e.g. Wotawa and Kröger, 1999; Kaiser et al., 2007; Apadula et al., 2003), most often with the intention of reproducing known emission fields. Trajectory statistical methods have been seen to construct characteristics of the emission fields with a good statistical significance, but only in idealised conditions where the effects of dispersion, deposition and chemical conversion can be excluded (Scheifinger and Kaiser, 2007; Kabashnikov et al., 2011).

Source area analysis done in previous studies for different trace gases and aerosol particles measured in Hyytiala, Finland, has been based on classifying trajectories according to their origin (Kulmala et al., 2000; Hellén et al., 2004). By finding a set of trajectories with similar history and the average of concentration values measured at times corresponding to trajectory arrival times it has been possible to coarsely identify “clean” and “polluted” sectors from the perspective of Hyytiala.
Redistribution concentration field method developed by Stohl (1996) has been utilized from the perspectives of other Finnish stations: to study the arrival of CO\(_2\), SO\(_2\), O\(_3\), black carbon and condensation nuclei to Pallas (Aalto et al., 2002); to find the areas contributing to O\(_3\), SO\(_2\) and particle concentrations registered in Utö at the Baltic Sea (Engler et al., 2002); and to find the origins of sulphate, ammonium and sodium measured at Sevettijärvi (Virkkula et al., 1995). Since the flow climatology and background conditions are different at each site, the results can not be generally applied to Hyytiälä as well. Furthermore, we have a longer data set than in any previous study, which decreases the impact of exceptional years (e.g. years with strong forest fires) and episodes, and increases the statistical significance of the result. Still, it is sensible to do some comparison between studies to possibly find features that are visible in all. Sogacheva et al. (2005) applied a similar method to aerosol particles of different size modes measured in Hyytiälä, but trace gas concentrations measured at SMEAR II have not been investigated with this kind of an approach.

In this study we use an improved Concentration Field method to study air pollution transport to the measurement site SMEAR II (Station for Measuring Ecosystem-Atmosphere Interactions) in Hyytiälä, Finland, whose data is widely used as a reference of background air in boreal areas. We want to see where the air comes from regarding high vs. low concentrations in our data at SMEAR II. Since we have not taken any dynamical nor chemical processes into account, we do not expect our figures to represent the actual emission fields, but only the air mass transport direction related to statistically higher or lower concentrations at our measurement station. We did not take the mean atmospheric residence time into account since we were also conducting the study on compounds of secondary type, like freshly nucleated secondary particles and ozone. They are not formed at the surface, but are instead likely to be produced in the atmosphere, the source strength depending on the properties of air as it passes over different regions.

Changes in anthropogenic activities and natural phenomena can result in trends in atmospheric composition. One aspect of this study is to find whether there has been an occurrence of strengthening or weakening in the contribution that different areas have on values observed in Hyytiälä over the 13-yr measurement period. Human influence, biogenic factors and changes in transport patterns are also likely to cause monthly, seasonal and yearly variation in the results. We expect to detect these and discuss the reasons behind them.

2 Materials and methods

We have used continuous concentration measurements from a measurement tower together with four days’ back trajectories to study the effect of air mass history on measured concentrations at our measurement station.

2.1 Atmospheric data from SMEAR II

SMEAR II (Station for Measuring Ecosystem-Atmosphere Interactions) measurement site is located in a rather homogeneous Scots pine (Pinus sylvestris) stand on a flat terrain at the Hyytiälä Forestry Field Station of the University of Helsinki (61°51’N, 24°17’E, 181 m above sea level), 220 km northwest from Helsinki. The largest city near the SMEAR II station is Tampere, located about 60 km south-east from the measurement site and having about 200,000 inhabitants.

In an instrumented 73-m-tall mast there are monitors to measure several trace gas concentrations, temperature and wind speed profiles, the properties of solar and thermal radiation of the stand, and the fluxes between the canopy and atmosphere (Hari and Kulmala, 2005). Measurements have been run continuously since 1996. The data used in this study belongs to an extensive set of atmospheric measurements during 13 yr (1996–2008) at SMEAR II. SO\(_2\) concentration is measured with a fluorescence analyser (TEI 43 BS, Thermo Environmental), NO\(_3\) (NO + NO\(_2\)) concentration with a chemiluminescence analyser (TEI 42C TL, Thermo Environmental) and O\(_3\) concentration with an ultraviolet light absorption analyser (TEI 49, Thermo Environmental); all at a height of 67.2 m above the mast base. Measured values are reported as 30-min means. Data coverage of the 13-yr measurement set is good, from 89 to 92 %. Particle number size distributions are measured with a Differential Mobility Particle Sizer (DMPS) that consists of two DMA’s and two CPC’s and scans the size distribution of particles between 3–1000 nm in 10-min intervals (Aalto et al., 2001). Number concentrations for total particulate matter, nucleation mode (3–25 nm), Aitken mode (25–90 nm) and accumulation mode (90–1000 nm) particles are used.

2.2 Trajectories and data processing

HYSLPLIT,4 (HYbrid Single-Particle Lagrangian Integrated Trajectory) trajectories (Draxler and Hess, 1998; Heinerling, 2004) were calculated for an arrival height of 100 m above ground level at hourly intervals, going 96 h back in time using NOAA FNL-archive data (1° horizontal resolution, 13 pressure levels) for 1998–2007 and NCEP/NCAR reanalysis data (2.5° horizontal resolution, 17 pressure levels) for years 1996–1997 and 2008.

At each time step the measured concentration value is assigned to the grid cells (1°×1°) along the corresponding back trajectory. Gas and particle concentrations were interpolated to the trajectory arrival times (on the hour) by using nearest neighbour interpolation. The horizontal uncertainty related to calculated HYSLPLIT,4 trajectories has been estimated to be 10–30 % of the distance travelled by the air parcel (15–30 % by Heinerling (2004), 10–20 % by Draxler and Hess (1998)). It is taken into account by using a weighted mean, where cells closer than 10 % of the trajectory travelling distance are given a weight factor of 0.70 and those farther than
10 % but closer than 20 % of the travelled distance get a weight factor of 0.30. The choice of factors was made assuming a normally distributed probability of trajectory error.

Weighted arithmetic or geometric mean of values accumulated to each grid cell is calculated to get a concentration field

$$\text{CF}_{ij} = \left( \frac{\sum_{n=1}^{N} c_n w_n}{\sum_{n=1}^{N} w_n} \right)_{ij},$$

where $i$ and $j$ are the indices of the latitude/longitude grid, $n$ the index of the trajectory and $N$ the total number of trajectories, $c_n$ is the concentration associated with the trajectory and $w_n$ is the weight factor derived from the trajectory inaccuracy. The method differs from the so-called nine point filter suggested by Stohl (1996), where the first guess concentration field is followed by an iterative redistribution procedure to improve the spatial resolution.

In the end the percentual difference from the mean or geometric mean concentration of the whole measurement period is calculated.

In order to ensure the statistical significance of the result, values are calculated only if a minimum number of trajectories, set to 10 in this study, crossed a grid cell. CF maps were produced for all compounds, yearly and monthly, over all years.

2.2.1 Testing procedure of the trajectory method

Different formulations of the trajectory method were tested by Hulkkonen (2010). Weighting of trajectory inaccuracy was tested for a few ways and different inaccuracies. We ended up using the method described in Sect. 2.2, since it best takes into account the trajectory inaccuracies reported in the literature. Mixing height of the boundary layer and precipitation along each trajectory (i.e. wet deposition), modelled by HYSPLIT, were taken into account for SO$_2$ in an attempt to reproduce EMEP emission source fields. However, the trajectory method was not able to produce the reported emission fields in a remote Finnish environment. Combining data sets from different Finnish measurement stations (SMEAR I-III, http://www.atm.helsinki.fi/SMEAR/) did not bring improvements to the correlations with EMEP, although the number of trajectories was tripled and the subjective view of each station got less weight. Therefore we chose to concentrate on the transport climatology of the measured concentrations.

3 Site-specific features

The amount of hourly trajectories having passed each grid cell (within 50–75° N, 0–45° E) during 1996–2008 varies from 112 to 111 369. The dominant air mass flow direction from Hyytiälä’s perspective is 220–310° (Fig. 1). The majority of trajectories received in Hyytiälä cross over the coast of Norway and the Scandis where orographic precipitation may occur. Continental air can be expected to bring the highest concentrations of trace gases and particles for which wet deposition is an important sink.

The median wind speed along trajectories varies between 2.8–14 m s$^{-1}$, with elevated values in winter months as a result of stronger temperature and pressure gradients. There is also significant variation in the flow speed along each trajectory: the difference between maximum and minimum flow speeds along a trajectory is as high as 5.6–17 m s$^{-1}$, again with larger values in the winter. Varying flow speeds result in the variation of residence times over different areas and the possibility for short-lived compounds to travel long distances.

Also the altitude of the followed air parcel shows variation both along the trajectory and seasonally. The median altitude along trajectories calculated for an arrival height of 100 m increases steadily when receding from Hyytiälä and reaches approximately 350 m after 96 h. In winter months air parcels travel further and reach higher altitudes than in the summer: the maximum height achieved along a −96 h trajectory is approximately 5000 m in the winter and 1500 m in the summer. But in all seasons the majority of trajectories stay all the way under the altitude of 1000 m. The distance travelled by an air parcel in 96 h varies between 500–6000 km.

Hyytiälä can be considered as a background station in terms of air pollution. This becomes evident when looking at the median, minimum and maximum concentrations of atmospheric SO$_2$, NO$_x$, O$_3$ and particles of different size modes presented in Table 1. Seasonal variation exists (Lyubovtseva et al., 2005), but in general the background...
### Table 1. Investigated compounds, their typical sources, sinks and estimated atmospheric lifetimes (according to Seinfeld and Pandis (1998) for trace gases and Lauer and Hendricks (2006) for particles). Median, minimum (median of values < 1-percentile limit) and maximum (median of values > 99-percentile limit) concentrations registered in Hyytiälä 1996–2008.

<table>
<thead>
<tr>
<th>Compound</th>
<th>τ</th>
<th>Sources</th>
<th>Sinks</th>
<th>Hyytiälä measurement statistics 1996–2008</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOx [ppb]</td>
<td>1.5 d</td>
<td>Fossil fuel (combustion); Biomass burning; Soils; Lightning; Aircrafts</td>
<td>Photochemistry; Oxidation to HNO₃ and PAN; Dry deposition</td>
<td>Median: 1.3, Minimum: 0.2, Maximum: 10.0</td>
</tr>
<tr>
<td>SO₂ [ppb]</td>
<td>2 d</td>
<td>Fossil fuel (combustion + industry); Biomass burning; Volcanoes; Oxidation of DMS</td>
<td>Dry deposition; Wet deposition; Chemistry (reactions with OH radical)</td>
<td>Median: 0.2, Minimum: &lt; 0.1, Maximum: 4.4</td>
</tr>
<tr>
<td>O₃ [ppb]</td>
<td>8 d (summer) – 100 d (winter)</td>
<td>In situ chem. prod.; Transport from the stratosphere; Interhemispheric transport</td>
<td>In situ chem. loss (photochem.); Dry deposition</td>
<td>Median: 32, Minimum: 7, Maximum: 62</td>
</tr>
<tr>
<td>Particle number concentration (N) ($D_p = 3–25$ nm) [cm⁻³]</td>
<td>&lt; 1 d</td>
<td>Nucleation</td>
<td>Brownian coagulation; Condensational growth</td>
<td>Median: 239, Minimum: 6, Maximum: 8080</td>
</tr>
<tr>
<td>N ($D_p = 25–90$ nm) [cm⁻³]</td>
<td>0.5–2 d</td>
<td>Condensational growth of nucleation mode particles; Emissions</td>
<td>Inter- and intramodal coagulation; Dry deposition</td>
<td>Median: 756, Minimum: 64, Maximum: 5410</td>
</tr>
<tr>
<td>N ($D_p = 90–1000$ nm) [cm⁻³]</td>
<td>4–6 d</td>
<td>Traffic; Growth of Aitken mode particles</td>
<td>Wet deposition; Intramodal coagulation</td>
<td>Median: 446, Minimum: 36, Maximum: 2970</td>
</tr>
<tr>
<td>N ($D_p = 3–1000$ nm) [cm⁻³]</td>
<td>5–7 d</td>
<td>–</td>
<td>–</td>
<td>Median: 1790, Minimum: 211, Maximum: 12 000</td>
</tr>
</tbody>
</table>

Concentrations are low, and elevated values are typically registered in episodes. There are point sources of SO₂, NOx and particulate matter in the vicinity of the measurement station, for example the UPM Kymmene paper mills approximately 80 km and 100 km away (visualized by Smart-SMEAR: Junninen et al., 2009). The SO₂ and NOx emissions from these, however, are three to four times smaller than those of the strongest point sources in Finland (e.g. Rautaruukki steelworks about 300 km away from Hyytiälä or powerplants in Helsinki, 230 km away). The highest values of Finnish point source emissions are of the order of 4000 t a⁻¹ for SO₂, 3200 t a⁻¹ for NOx and 900 t a⁻¹ for particulate matter (PM₁₀) (E-PRTR – European Pollutant Release and Transfer Register, http://prtr.ec.europa.eu/). These values can be compared with those of a power plant located in northeastern Estonia, about 500 km away from Hyytiälä: 47 400 t a⁻¹, 8440 t a⁻¹ and 2500 t a⁻¹ for SO₂, NOx and PM₁₀, respectively. The St. Petersburg region, with several point sources, is approximately 700 km from Hyytiälä measurement site: if we assume an average flow speed of 20 km h⁻¹, an air parcel passing over St. Petersburg arrives in Hyytiälä in 35 h. This should be borne in mind together with the average atmospheric lifetimes of different compounds presented in Table 1. E.g. the amount of NOx emitted in St. Petersburg would decline to 1/e: th (assuming an exponential removal function) by the time it gets to the measurement site, since the travelling time approximately equals the atmospheric lifetime of NOx. Dilution during atmospheric transport reduces the observed concentration further.

The sectors used in trend analysis are presented in Fig. 2. They were chosen to represent homogeneously marine (A) and continental (C) areas, and the vicinity of Hyytiälä (B). Trends were calculated by fitting a linear regression curve to yearly median CF values of sectors A–C.

### 4 Results and discussion

#### 4.1 Interpretation of the concentration fields

The produced concentration fields (CFs, Figs. 3–9) show the change in measured concentrations in Hyytiälä according to air mass statistics during a particular month. We see that certain directions bring higher concentrations on average than
Three sectors were selected to study concentration trends. Sector A represents marine environment, sector B the vicinity of Hyytiälä measurement station and sector C continental environment.

Others. Principally the CF’s are a representation of the combination of the flow dynamics relevant for Hyytiälä and the emission sources and sinks along air mass paths. However, no removal processes are taken into account, nor is the back trajectory length scaled to any estimation of atmospheric residence time of the compound in study. It needs to be kept in mind that these fields may not present actual emission fields, but the climatology of air pollution transport to the remote site.

Since the concentrations have not been scaled by the travelling time, the grids further away from the receptor site may get higher values than their actual significance. If there is a very repetitive path crossing a grid cell with a strong emission source, the method gives erroneous weight to the grid cells along the trajectory farther from the actual source area.

The −96 h trajectory length exceeds the average atmospheric residence time of some of the compounds in question (Table 1). Thus the concentration fields should not be interpreted as source areas but rather as statistical information on air masses bringing high vs. low concentrations to a certain place. Especially for compounds of secondary type, like freshly formed secondary particles or ozone, the concentration fields can not be interpreted as source areas, but rather as areas where the precursors come from.

The effect of wet deposition was tested (Sect. 2.2.1) but not taken into account, like no other decay processes. Generally the western air masses are bringing more rain to Finland than the eastern ones, and the western pollution sources seem to be concealed from our measurement site point of view.

In general the maps are assumed to be more unreliable the further away from the receptor site. These caveats have to be kept in mind when interpreting the CF maps.

4.2 Transport climatology of aerosol particles of different size modes

The results for different size modes of aerosol particles are in line with previous studies (Kulmala et al., 2000; Sogacheva et al., 2005; Dal Maso et al., 2007), but reveal more detailed characteristics of the origins and pathways of air masses leading to observing high and low particle concentrations in Hyytiälä. Monthly, seasonal and annual variations, intermodal differences and weakening or strengthening of different source areas over the 13-yr measurement period are detected.

For the number concentration of nucleation mode particles ($D_p = 3–25$ nm) the produced CF shows well-outlined
features that have seasonal variation (Fig. 3). Figure 3 also
gives indication of the relative number concentration levels
in different months. The frequency of new particle formation
has been shown to peak in March–April and September
(Dal Maso et al., 2007).

The features of the transport climatology of nucleation
mode particles remain similar over years, but a decrease in
the levels of CF-values can be detected: an average decrease
of −0.8 % per year in the median value in the marine sec-
tor A, −1.3 % per year in the Hyytiälä sector B and −1.6 %
per year in the continental sector C between 1996–2008 (Ta-
ble 2). This is in line with other studies, since nucleation
mode particle concentrations have been detected to decrease
in Europe possibly due to decreased SO$_2$ emissions (Hamed
et al., 2010).

For measuring high nucleation mode particle number con-
centrations in Hyytiälä it is the air masses with north-western
and Atlantic origin that are favourable. Clean arctic and ma-
rine air masses have been shown to be optimal for new par-
ticle formation in Hyytiälä (Dal Maso et al., 2007), while
polluted continental air tends to prevent it due to a large
pre-existing particle surface area (especially Aitken and ac-
cumulation mode particles), leading to high condensation
and coagulation sinks and removal of nucleation precursor
vapours. This can also be deduced from the CF maps pro-
duced for particles of different sizes. For example the dom-
inant source sector for accumulation mode particles can in-
deed be found in the south-east, indicating continental ori-
gin, which is the source sector of air masses connected to the
lowest nucleation mode particle concentrations measured in
Hyytiälä (comparing Figs. 3 and 4).

The source areas of new nucleation mode particles have to
be considered in the light of the processes that are producing
these particles. The exact mechanism of atmospheric particle
formation is yet unknown, but it has been established that
sulphuric acid, resulting from the oxidation of SO$_2$ by pho-
tochemically produced hydroxyl radicals, is a major contrib-
utor to the formation process (Riipinen et al., 2007; Sipilä
et al., 2010). Additionally, oxidised organic compounds that
are emitted from forested areas are probably also required to
form observable particles (e.g. Paasonen et al., 2010). A crit-

![Fig. 4. Deviation from measured average number concentration of accumulation mode particles ($D_p = 90–1000$ nm) in Hyytiälä according to transport directions. Monthly concentration fields are produced for years 1996–2008. Fields are normalized to the geometric mean concentration (419 cm$^{-1}$) of the whole measurement period. Hyytiälä is marked with a star.](image)

Table 2. Average yearly change in median RSC-values of atmo-
spheric constituents in sectors represented in Fig. 2. Linear regres-
sion line is fitted to the yearly CFs between years 1996–2008.

<table>
<thead>
<tr>
<th>Sector</th>
<th>Sector A</th>
<th>Sector B</th>
<th>Sector C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_{D=3–25}$ nm</td>
<td>−0.8 %</td>
<td>−1.3 %</td>
<td>−1.6 %</td>
</tr>
<tr>
<td>$N_{D=25–90}$ nm</td>
<td>−0.0 %</td>
<td>−0.8 %</td>
<td>+1.3 %</td>
</tr>
<tr>
<td>$N_{D=90–1000}$ nm</td>
<td>−1.1 %</td>
<td>−0.9 %</td>
<td>+1.2 %</td>
</tr>
<tr>
<td>$N_{D=3–1000}$ nm</td>
<td>−0.4 %</td>
<td>−0.9 %</td>
<td>+1.3 %</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>−6.0 %</td>
<td>−7.9 %</td>
<td>−6.5 %</td>
</tr>
<tr>
<td>NO$_x$</td>
<td>−2.5 %</td>
<td>−3.0 %</td>
<td>−1.8 %</td>
</tr>
<tr>
<td>O$_3$</td>
<td>+0.4 %</td>
<td>+0.7 %</td>
<td>+1.7 %</td>
</tr>
</tbody>
</table>
Fig. 5. Deviation from measured average number concentration of total number concentration of particles ($D_p = 3-1000$ nm) in Hyytiälä according to transport directions. Yearly concentration fields are produced for years 1996–2008. Fields are normalized to the geometric mean concentration ($1707 \text{ cm}^{-1}$) of the whole measurement period. Hyytiälä is marked with a star.

Fig. 6. Deviation from measured average number concentration of Aitken mode particles ($D_p = 25-90$ nm) in Hyytiälä according to transport directions. Monthly concentration fields are produced for years 1996–2008. Fields are normalized to the geometric mean concentration ($725 \text{ cm}^{-1}$) of the whole measurement period. Hyytiälä is marked with a star.

Particle sources over the Atlantic ocean ($-1.1\%$ per year, sector A) and in trend in the vicinity of Hyytiälä ($-0.9\%$ per year, sector B), and a slight increase over the continent ($+1.2\%$ per year, sector C) (Table 2).

In terms of total particle concentration, the transport climatology is not consistent from year to year. Marine and continental air masses alike are able to bring high concentrations. This is visible in Fig. 5, where the yearly variation in the contribution of different areas to the total particle number concentrations measured in Hyytiälä is presented. For example years 2002 and 2003 (with an exceptionally high fraction of days with new particle formation occurring) stand out with the north-western sector having a strong contribution to the values measured in Hyytiälä. On the other hand, in the CFs of 2002, 2003 and 2006 the south-eastern corner clearly dominates as forest fire smoke was transported from those areas to Finland those years (Niemi et al., 2009; Riuttanen et al., 2013; Saarikoski et al., 2007).

A slight decrease in the total fine particle ($D_p = 3-1000$ nm) concentration sources is detected in the oceanic origin and in the vicinity of the station in Table 2. The continental sector, however, shows an increase of $1.3\%$ per year, with the years of biomass burning smoke episodes standing out. Previous studies (e.g. Dal Maso et al., 2008) have found no clear trend in fine particle concentrations in Hyytiälä. A trajectory study gives new understanding to the factors affecting the measured total fine particle concentration.

A strong yearly variation applies also for the source areas of Aitken mode particles. It is both nucleation mode particles related to clean marine air masses and combustion-related particles with continental origin that contribute to the number concentrations in Aitken mode. The two main pathways of Aitken mode particles to Hyytiälä are evident in the CF presented in Fig. 6, which shows the seasonal variation averaged over 13 yr. From April to September we observe elevated values throughout the field, which highlights the biogenic origin of Aitken mode particles. The north-west sector stands out,
which possibly indicates ongoing nucleation and growth of particles as a result of condensing organic vapours along the way towards Hyytiälä, where we observe these grown particles instead of freshly nucleated ones throughout the summer. No significant trend in the marine source has been detected, but the continental source (sector C) has increased by 1.3 % per year on average (Table 2), with years 2002 and 2006 standing out.

4.3 Transport climatology of trace gases

4.3.1 SO$_2$

A clear decrease in the SO$_2$ concentration level, presumably as a result of pollution control and the change in the East European industry in the late 1990s (Vestreng et al., 2007), can be detected when comparing the yearly concentration fields. Average changes of $-6 \%$ to $-8 \%$ per year are observed (Table 2). The general decreasing trend of $-5.2$ per year in SO$_2$ concentrations is observed in Hyytiälä measurements (1997–2008). A general decreasing trend of $-2.2 \% \text{yr}^{-1}$ (1994–2006) of SO$_2$ emissions in Finland has been estimated by Anttila and Tuovinen (2010).

Seasonal variation in the source areas of SO$_2$ is clearly visible in the CFs presented in Fig. 7: winter months from December to April are connected with the highest values as a result of emissions due to higher demand for heating in the cold season, less photochemical loss of SO$_2$ and frequent temperature inversions leading to trapping of pollution. The most polluted transport directions bring concentrations several folds higher than the others.

The highest SO$_2$ concentrations are measured in Hyytiälä when the air is coming from the south-east sector of the CF map. Clusters of anthropogenic emission sources in St. Petersburg, Baltic countries, Kola Peninsula and the southeast corner of the White Sea tend to stand out. Comparison against EMEP emission data (Hulkkonen, 2010) shows that the regions with the highest emissions are located in the south-west of the domain, but their relative contribution to the concentrations in Hyytiälä remains insignificant. There is more rain and wet removal in air masses arriving to Finland from the west, which means Atlantic origin. We assume this is the reason why the Central European sources are not seen at our measurement station, not even when the wet deposition is taken into account (Hulkkonen, 2010).

Study of Karvosenoja (2008) shows that 70 point sources contribute 64 % of SO$_2$ emissions in Finland. These point sources certainly contribute to the obtained CFs to some extent, but they can not explain the strong eastern contribution to the measured concentrations. The north-eastern emission sector seen, especially in February (Fig. 7) probably includes a contribution from a couple of power plants and paper mills 50–300 km in that direction. Also the point sources of southern Finland are seen in the Fig. 7. However, there are also several strong point sources in the western coast of Finland that are not visible in these figures.

Previous studies of SO$_2$ concentration fields from Finnish perspective by Virkkula et al. (1995) and Aalto et al. (2002) are conducted for the stations in very northern Finland. The CFs are clearly dominated by eastern flows, most probably originating from the Nikel industrial area. The same pattern was noted by Hulkkonen (2010) for Vääräö SMEAR I station in northern Finland. Hulkkonen (2010) also studied SO$_2$ CFs for Helsinki, southern Finland. The results showed higher concentrations in eastern and southern air masses, as in Fig. 7. Therefore it can be concluded that the results of this study can to some extent be applied to southern Finland in general, if no strong local sources are nearby.

4.3.2 NO$_x$

The atmospheric lifetime of NO$_x$ is typically of the order of 1 day, which means that the emission domain reliably seen by
the method is smaller than shown in the CF figures. The areas with high anthropogenic NO$_x$ emissions in St. Petersburg region and the northern Baltic are at the edge of this domain determined by the lifetime of NO$_x$, which explains the broadening “tail” of high values behind them from Hyytiälä’s perspective. High concentrations in Hyytiälä are often related to air masses passing over St. Petersburg and the Baltic countries. The majority of the NO$_x$ emissions of Finland are produced in southern Finland, the sources being the strongest south and west to Hyytiälä (Karvosenoja, 2008). The importance of local sources in southern Finland to measured NO$_x$ concentrations in Hyytiälä may be seen in Fig. 8, but western sources are again hidden.

The seasonal variation of air mass origins connected with high NO$_x$ concentrations follows a very similar pattern as that for SO$_2$ described above. NO$_x$ concentrations are the highest during winter months and early spring, because of combustion sources and weakness of the photochemical sink.

Also the climatology supports long-range transport of short-lived compounds in the wintertime, when the wind speeds are higher and they can travel further.

A decreasing trend in the general concentration level can be observed (Table 2: −2.5 % in sector A coming from the sea, −3.0 % in the vicinity of Hyytiälä and −1.8 % in the most polluted sector C), while the dominating sector remains very similarly delimited over the years.

### 4.3.3 O$_3$

The concentration fields of ozone should be interpreted with caution, since ozone is not directly emitted to the atmosphere and has complicated chemistry related to amount of light and other compounds, like NO$_x$ and VOCs. The majority of the measured O$_3$ is probably formed in the vicinity of the measurement site, but clear differences related to different air mass pathways are seen in Fig. 9.
Air masses coming from marine areas (North Atlantic and the Arctic Sea), where ozone deposition and the concentrations of ozone-destroying pollutants are low, are connected with higher O$_3$ concentrations measured in Hyytiälä in the wintertime. When approaching the summer, photolysis is gaining ground and there is a spring maximum of ambient ozone concentration. Also a shift of origin of air masses bringing high concentrations occurs between north-west and south-east, the latter sector being dominant in the summer and relatively stronger than the wintertime source areas. The transport patterns bringing the highest spring concentrations from the south-east have similar pattern than those of NO$_x$, SO$_2$ and accumulation mode particles. Similar general features of higher concentrations of O$_3$ from the north in winter and from the south in summer are also shown in the CFs of Aalto et al. (2002) for the northern Finland.

Observed trends in ozone concentrations show an increase in ozone sources in the continental sector C (+1.7 % per year, Table 2).

5 Conclusions

The relatively simple trajectory-based method applied in this study was evaluated with the conclusion that it can well be used for analysing the origins and paths of air masses related to high vs. low concentrations of atmospheric constituents monitored at the receptor site. The concentration field method was not able to reproduce EMEP emission fields, but results obtained in this study disclose the contribution that air masses passing different areas have on the values monitored in Hyytiälä, supporting earlier studies and reinforcing our conception of the regions that influence the measurement site in terms of different atmospheric constituents. The improved CF method has already been used to study origins of aerosols with different optical properties (Virkkula et al., 2011). Possibilities for applications remain.

The origin of air masses that statistically bring high particle concentrations to Hyytiälä depends highly on which particle size mode is focused on. North-west dominates as the origin of air masses that relates to high nucleation mode particle concentrations, whereas air masses from the south-east bring high concentrations of combustion-related accumulation mode particles. Particles belonging to Aitken mode get contribution from both directions. Seasonal variations in the CF fields tell more about the nature of particles in each mode: for example, CFs for Aitken mode particles show elevated values from April to September, highlighting the biogenic origin, whereas for accumulation mode particles from both wintertime combustion and summertime forest fires can be deduced as factors defining the seasonal variation in the CFs. A slight weakening of Atlantic origin and a slight increase of continental origin of fine particles was detected.

Combustion-related trace gases SO$_2$ and NO$_x$ are transported to Hyytiälä mainly from Eastern Europe, with winter months dominating. Local sources are also strong. A rather sharply outlined sector in the south-east has the strongest contribution to the high concentrations measured in Hyytiälä. This is presumably due to the fact that there are relatively strong emission sources in the industrial areas of northern Estonia and St. Petersburg, which are located such that for an air parcel passing over them, on average, it takes about 1–2 days to arrive in Hyytiälä. Being at the upper limit of the lifetime of the compounds in question, the travelling time from regions beyond the above-mentioned is so long as to make it impossible to see them as source areas from Hyytiälä’s perspective. These regions are thus interpreted as areas passed by trajectories that eventually also crossed, e.g. St. Petersburg, and brought high concentrations to Hyytiälä. Emissions from the western sources, both local in south-western Finland and remote in Western Europe, are not seen in Hyytiälä, probably due to climatological reasons, i.e. more rain and wet deposition in the western air masses of Atlantic origin. Furthermore, an average decreasing yearly trend of 6–8 % in the general concentration levels of SO$_2$ and 2–3 % of NO$_x$ is observed in the CF fields.

Studying the concentration fields shows that SO$_2$ and CS source contributions seem to originate from roughly the same geographical areas, namely continental (Eastern) Europe (Figs. 4 and 7), possibly even from partly the same sources. The air masses contributing to higher nucleation mode particle concentrations, however, seem to originate from a different area, e.g. sparsely populated Scandinavian areas and the Arctic Ocean. This result is similar to results obtained in previous studies (e.g. Sogacheva et al., 2008; Nilsson et al., 2001). The comparison of the different contributing process indicators (CS for loss processes, SO$_2$ for sources) also supports the idea that for the Hyytiälä station, particle formation is controlled by the particle loss processes rather than the particle source processes (as already suggested by Dal Maso et al., 2007). This might have consequences for aerosol formation in the future, if air pollution regulations lead to reductions in either (or both) SO$_2$ and particulate matter and thus CS.

The origin of air masses that bring high concentrations of O$_3$ to Hyytiälä shifts between north-west and south-east, the latter sector being dominant in the summer and relatively stronger than the wintertime source areas that are congruent with areas characterized by low concentrations of ozone destroying pollutants. Opposite to SO$_2$ and NO$_x$, a slight increase in the general concentration level of tropospheric O$_3$ is observed over the 13-yr measurement period in Hyytiälä.

We have studied air pollution transport climatology from Hyytiälä background measurement site point of view, using concentration measurements and air mass back trajectories. We have found this relatively simple method useful in understanding the measured time series at Hyytiälä measurement site. To produce emission source maps, all sink processes should be taken into account, including dispersion, wet and dry deposition, photo-chemistry and chemical...
transformation. Some difficulties related to the method may still remain, especially when investigating compounds with varying lifetimes and those with strong sources in the proximity of the measurement site. Also the reliability of HYSPLIT trajectories in Northern Europe context should be studied in more detail. Potential emission sensitivity or so-called footprints calculated by e.g. FLEXPART (Stohl et al., 1998) could lead to a better description of the actual source areas than single trajectories. The extent of the data set used in this study (9000–113 000 trajectories per figure) is, however, good enough to produce results with statistical significance – and with less computational capacity needed.

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