Atmos. Chem. Phys., 13, 2153–2164, 2013
www.atmos-chem-phys.net/13/2153/2013/
doi:10.5194/acp-13-2153-2013
© Author(s) 2013. CC Attribution 3.0 License.

Atmospheric Chemistry and Physics Open Access

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

L. Riuttanen[1], M. Hulkkonen[1], M. Dal Maso[2,1], H. Junninen[1], and M. Kulmala[1]

[1]Department of Physics, University of Helsinki, P.O. Box 48, 00014 Helsinki, Finland
[2]Department of Physics, Tampere University of Technology, P.O. Box 692, 33101 Tampere, Finland

Correspondence to: L. Riuttanen (laura.riuttanen@helsinki.fi)

Received: 28 October 2011 – Published in Atmos. Chem. Phys. Discuss.: 19 January 2012
Revised: 31 January 2013 – Accepted: 5 February 2013 – Published: 25 February 2013

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 Hyytiälä (61°51′ N, 24°17′ E). Our method did not reproduce the EMEP emission soures, 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 Hyytiälä, 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 Hyytiälä.

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., 2007); 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 homogenous 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_x ($NO + NO_2$) 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

HYSPLIT_4 (HYbrid Single-Particle Lagrangian Integrated Trajectory) trajectories (Draxler and Hess, 1998; Heinzerling, 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 ($1° \times 1°$) 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 HYSPLIT_4 trajectories has been estimated to be 10–30 % of the distance travelled by the air parcel (15–30 % by Heinzerling (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

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

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

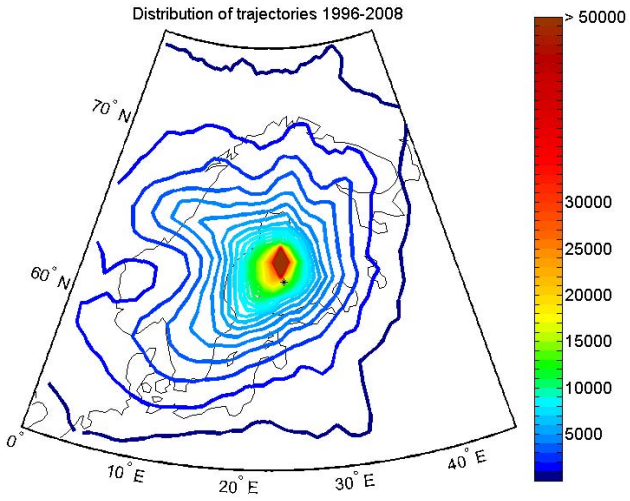

Fig. 1. The distribution of trajectories 1996–2008. The amount of hourly trejectories having passed each grid cell is shown with coloured contour lines.

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.

				Hyytiälä measurement statistics 1996–2008		
Compound	τ	Sources	Sinks	Median	Minimum	Maximum
NO_x [ppb]	1.5 d	Fossil fuel (combustion); Biomass burning; Soils; Lightning; Aircrafts	Photochemistry; Oxidation to HNO_3 and PAN; Dry deposition	1.3	0.2	10.0
SO_2 [ppb]	2 d	Fossil fuel (combustion + indstry); Biomass burning; Volcanoes; Oxidation of DMS	Dry deposition; Wet deposition; Chemistry (reactions with OH radical)	0.2	< 0.1	4.4
O_3 [ppb]	8 d (summer) – 100 d (winter)	In situ chem. prod.; Transport from the stratosphere; Interhemispheric transport	In situ chem. loss (photochem.); Dry deposition	32	7	62
Particle number concentration (N) (D_p = 3–25 nm) [cm^{-3}]	< 1 d	Nucleation	Brownian coagulation; Condensational growth	239	6	8080
N (D_p = 25–90 nm) [cm^{-3}]	0.5–2 d	Condensational growth of nucleation mode particles; Emissions	Inter- and intramodal coagulation; Dry deposition	756	64	5410
N (D_p = 90–1000 nm) [cm^{-3}]	4–6 d	Traffic; Growth of Aitken mode particles	Wet deposition; Intramodal coagulation	446	36	2970
N (D_p = 3–1000 nm) [cm^{-3}]	5–7 d	–	–	1790	211	12 000

concentrations are low, and elevated values are typically registered in episodes. There are point sources of SO_2, NO_x 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 SO_2 and NO_x 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 SO_x, 3200 t a^{-1} for NO_x and 900 t a^{-1} for particulate matter (PM_{10}) (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 northern Estonia, about 500 km away from Hyytiälä: 47 400 t a^{-1}, 8440 t a^{-1} and 2500 t a^{-1} for SO_x, NO_x and PM_{10}, 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 NO_x 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 NO_x. 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

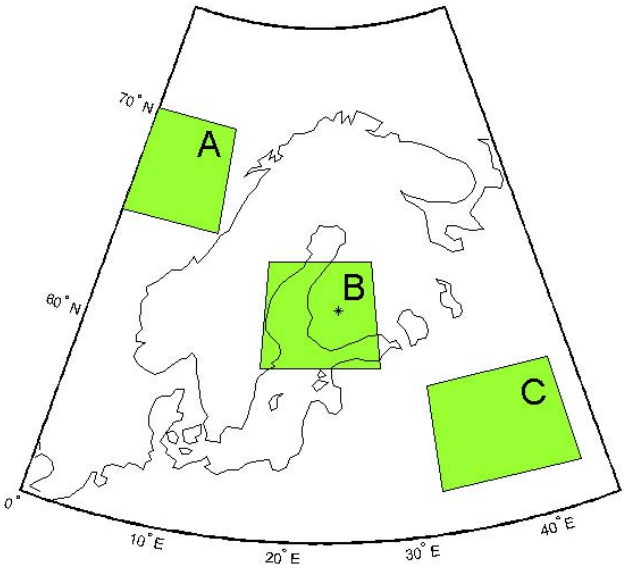

Fig. 2. Three sectors were selected to study concentration trends. Sector A represents marine environment, sector B the vicinity of Hyytiälä measurement station and sector C continental environment.

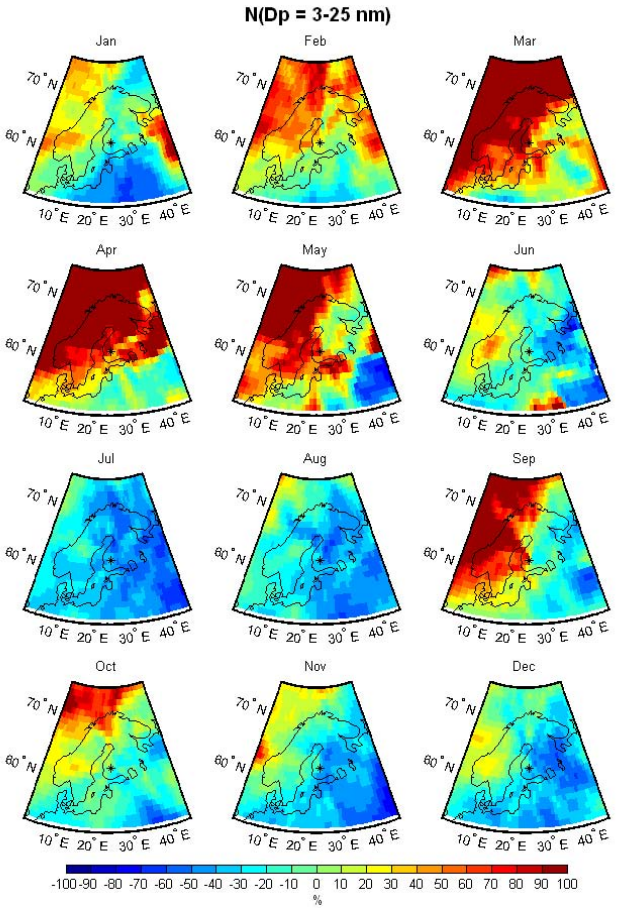

Fig. 3. Deviation from measured average number concentration of nucleation mode particles ($D_p = 3$–25 nm) in Hyytiälä according to transport directions. Monthly concentration fields are produced for years 1996–2008. Fields are normalized to the geometric mean concentration (239 cm^{-1}) of the whole measurement period. Hyytiälä is marked with a star.

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

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

	Sector A	Sector B	Sector C
$N_{D=3-25\,\mathrm{nm}}$	−0.8 %	−1.3 %	−1.6 %
$N_{D=25-90\,\mathrm{nm}}$	−0.0 %	−0.8 %	+1.3 %
$N_{D=90-1000\,\mathrm{nm}}$	−1.1 %	−0.9 %	+1.2 %
$N_{D=3-1000\,\mathrm{nm}}$	−0.4 %	−0.9 %	+1.3 %
SO_2	−6.0 %	−7.9 %	−6.5 %
NO_x	−2.5 %	−3.0 %	−1.8 %
O_3	+0.4 %	+0.7 %	+1.7 %

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 sector A, −1.3 % per year in the Hyytiälä sector B and −1.6 % per year in the continental sector C between 1996–2008 (Table 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 concentrations in Hyytiälä it is the air masses with north-western and Atlantic origin that are favourable. Clean arctic and marine air masses have been shown to be optimal for new particle 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 accumulation mode particles), leading to high condensation and coagulation sinks and removal of nucleation precursor vapours. This can also be deduced from the CF maps produced for particles of different sizes. For example the dominant source sector for accumulation mode particles can indeed be found in the south-east, indicating continental origin, 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 photochemically produced hydroxyl radicals, is a major contributor 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 critical inhibiting factor for particle formation is the pre-existing aerosol's ability to scavenge vapors and small particles from air is characterized by the condensation sink (CS) (see e.g. Hyvönen et al., 2005; Dal Maso et al., 2007).

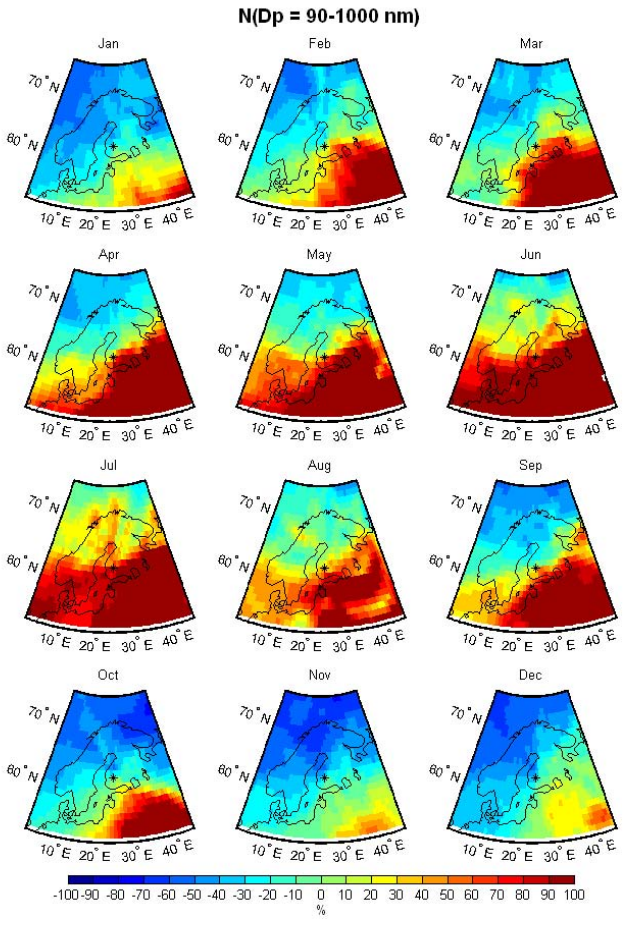

Fig. 4. Deviation from measured average number concentration of accumulation mode particles ($D_p = 90$–1000 nm) in Hyytiälä according to transport directions. Monthly concentration fields are produced for years 1996–2008. Fields are normalized to the geometric mean concentration (419 cm^{-1}) of the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

Condensation sink, the ability of an aerosol population to remove condensable vapour from the air, was calculated based on the particle size distribution information received from DMPS measurements in Hyytiälä. Air masses that lead to high condensation sink values are carrying a large particle surface area, typically dominated by particles belonging to the accumulation mode. Therefore, the studied concentration fields of the CS have similar patterns as those for accumulation mode (Fig. 4).

Seasonal variation of CF for accumulation mode particles is shown in Fig. 4 and can be thought as a balance between wintertime combustion-related sources and summertime forest fires. There is a slight decrease in accumulation mode

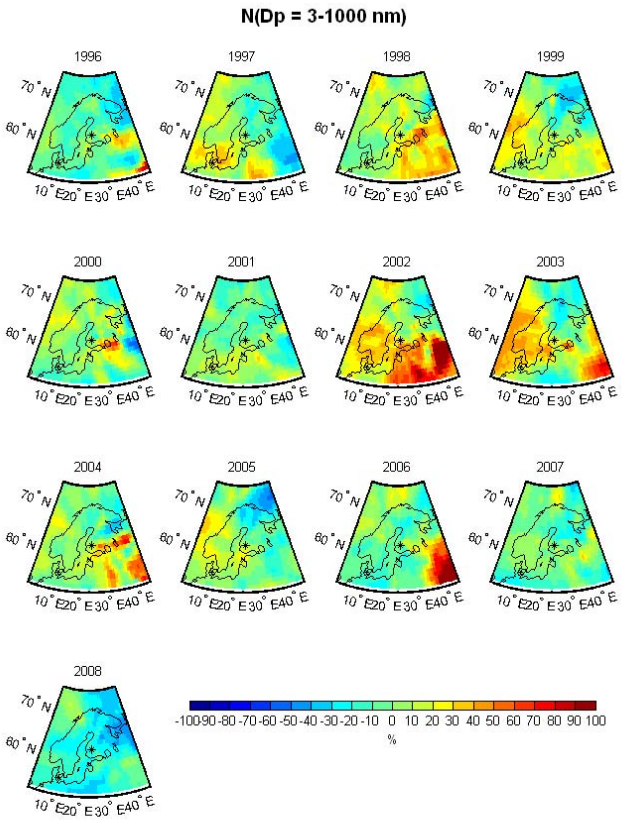

Fig. 5. Deviation from measured average number concentration of total number concentration of particles ($D_p = 3$–1000 nm) in Hyytiälä according to transport directions. Yearly concentration fields are produced for years 1996–2008. Fields are normalized to the geometric mean concentration (1707 cm^{-1}) of the whole measurement period. Hyytiälä is marked with a star.

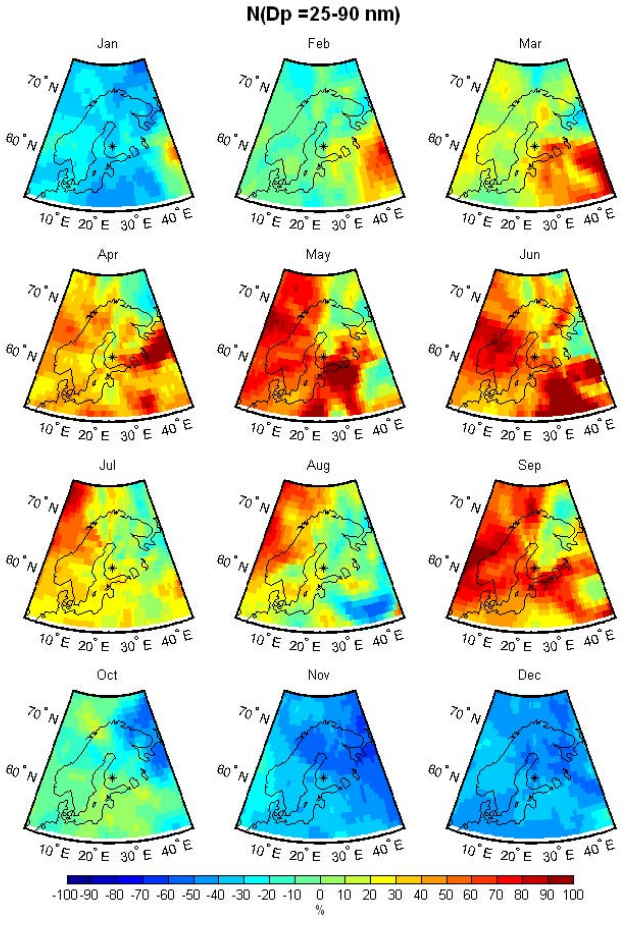

Fig. 6. Deviation from measured average number concentration of Aitken mode particles ($D_p = 25$–90 nm) in Hyytiälä according to transport directions. Monthly concentration fields are produced for years 1996–2008. Fields are normalized to the geometric mean concentration (725 cm^{-1}) of the whole measurement 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 (1997–008). A general decreasing trend of $-2.2\,\%\,yr^{-1}$ (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 south-east 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

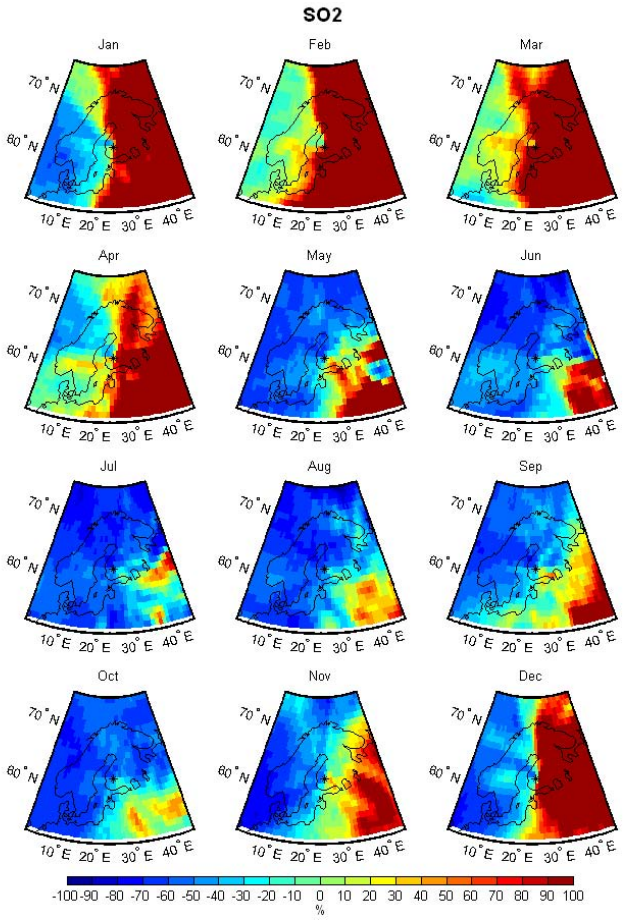

Fig. 7. Deviation from measured average SO_2 concentration in Hyytiälä according to transport directions. Monthly concentration fields are produced for years 1996–2008. Fields are normalized to the geometric mean concentration (0.18 ppb) of the whole measurement period. Hyytiälä is marked with a star.

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 Värriö 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

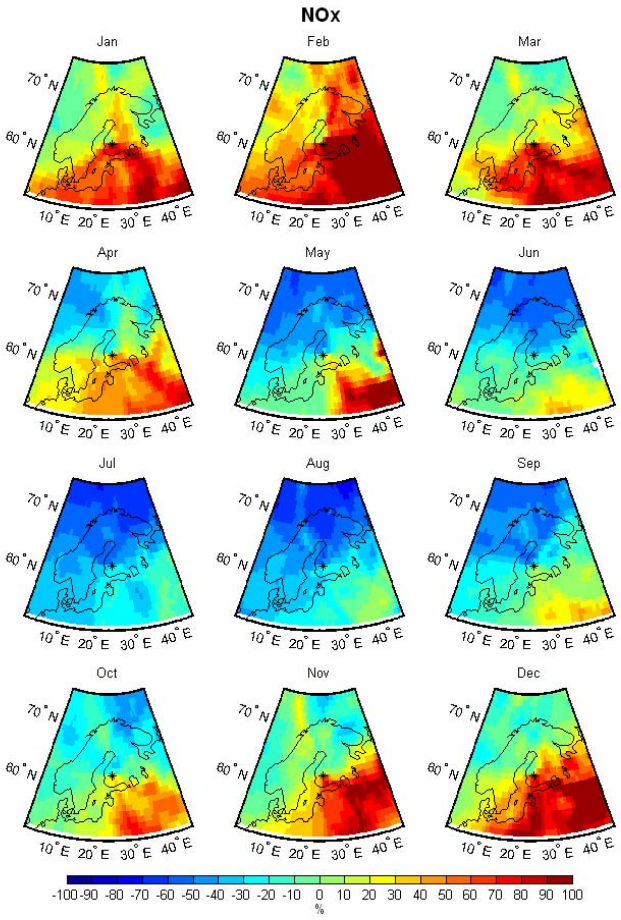

Fig. 8. Deviation from measured average NO_x concentration in Hyytiälä according to transport directions. Monthly concentration fields are produced for years 1996–2008. Fields are normalized to the mean concentration (1.78 ppb) of the whole measurement period. Hyytiälä is marked with a star.

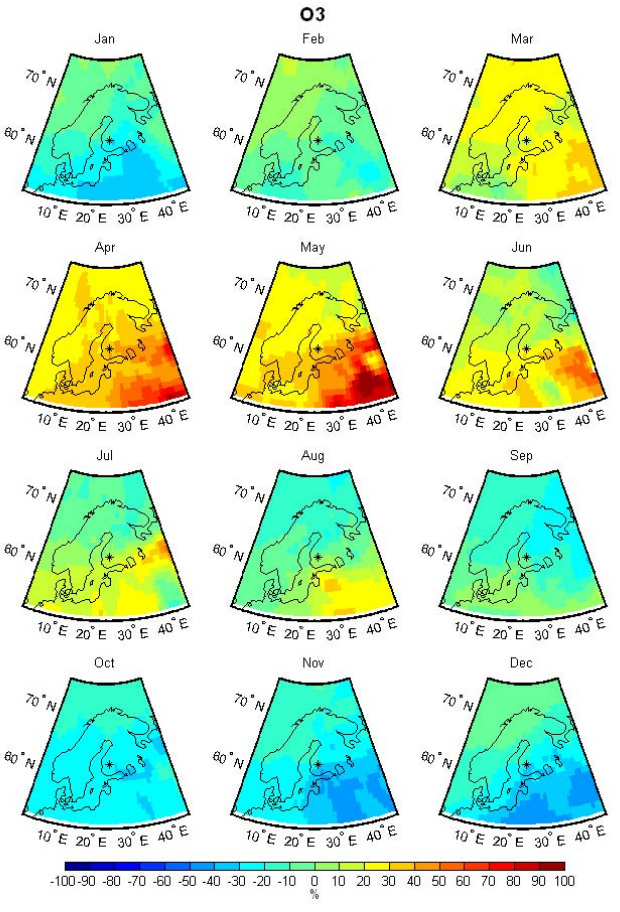

Fig. 9. Deviation from measured average O_3 concentration in Hyytiälä according to transport directions. Monthly concentration fields are produced for years 1996–2008. Fields are normalized to the mean concentration (32.6 ppb) of the whole measurement period. Hyytiälä is marked with a star.

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.

Acknowledgements. This research was supported by the Academy of Finland (Project No. 128731) and the Academy of Finland Center of Excellence program (Project No. 1118615).

Edited by: K. Lehtinen

References

Aalto, P., Hämeri, K., Becker, E., Weber, R., Salm, J., Mäkelä, J., Hoell, C., O'Dowd, C., Karlsson, H., Hansson, H.-C., Väkevä, M., Koponen, I., Buzorius, G., and Kulmala, M.: Physical characterization of aerosol particles during nucleation events, Tellus B, 53, 344–358, 2001.

Aalto, T., Hatakka, J., Paatero, J., Tuovinen, J., Aurela, M., Laurila, T., Holmén, K., Trivett, N., and Viisanen, Y.: Tropospheric carbon dioxide concentrations at a northern boreal site in Finland: basic variations and source areas, Tellus B, 54, 110–126, 2002.

Anttila, P. and Tuovinen, J.-P.: Trends of primary and secondary pollutant concentrations in Finland in 1994–2007, Atmos. Environ., 44, 30–41, 2010.

Apadula, F., Gotti, A., Pigini, A., Longhetto, A., Rocchetti, F., Cassardo, C., Ferrarese, S., and Forza, R.: Localization of source and sink regions of carbon dioxide through the method of the synoptic air trajectory statistics, Atmos. Environ., 37, 3757–3770, 2003.

Ashbaugh, L., Malm, W., and Sadeh, W.: A residence time probability analysis of sulfur concentrations at grand Canyon National Park, Atmos. Environ. (1967), 19, 1263–1270, 1985.

Dal Maso, M., Sogacheva, L., Aalto, P. P., Riipinen, I., Komppula, M., Tunved, P., Korhonen, L., Suur-Uski, V., Hirsikko, A., Kurten, T., Kerminen, V.-M., Lihavainen, H., Viisanen, Y., Hansson, H.-C., and Kulmala, M.: Aerosol size distribution measurements at four Nordic field stations: identification, analysis and trajectory analysis of new particle formation bursts, Tellus B, 59, 350–361, 2007.

Dal Maso, M., Hyvärinen, A., Komppula, M., Tunved, P., Kerminen, V.-M., Lihavainen, H., Viisanen, Y., Hansson, H.-C., and Kulmala, M.: Annual and interannual variation in boreal forest aerosol particle number and volume concentration and their connection to particle formation, Tellus B, 60, 495–508, 2008.

Draxler, R. R. and Hess, G. D.: An Overview of the HYSPLIT_4 Modelling System for Trajectories, Dispersion and Deposition, Austr. Met. Mag., 47, 295–308, 1998.

Engler, C., Lihavainen, H., Komppula, M., Kerminen, V.-M., Kulmala, M., and Viisanen, Y.: Continuous measurements of aerosol properties at the Baltic Sea, Tellus B, 59, 728–741, 2007.

Hamed, A., Birmili, W., Joutsensaari, J., Mikkonen, S., Asmi, A., Wehner, B., Spindler, G., Jaatinen, A., Wiedensohler, A., Korhonen, H., Lehtinen, K. E. J., and Laaksonen, A.: Changes in the production rate of secondary aerosol particles in Central Europe in view of decreasing SO_2 emissions between 1996 and 2006, Atmos. Chem. Phys., 10, 1071–1091, doi:10.5194/acp-10-1071-2010, 2010.

Hari, P. and Kulmala, M.: Station for Measuring Ecosystem-Atmosphere Relations (SMEAR II), Boreal Environ. Res., 10, 315–322, 2005.

Heinzerling, D.: Automation of HYSPLIT trajectory generation and subsequent analyses, Washington university, Research for Undergraduates Program 2004, 2004.

Hellén, H., Hakola, H., Reissell, A., and Ruuskanen, T. M.: Carbonyl compounds in boreal coniferous forest air in Hyytiälä, Southern Finland, Atmos. Chem. Phys., 4, 1771–1780, doi:10.5194/acp-4-1771-2004, 2004.

Hulkkonen, M.: Pitoisuuskenttämenetelmän käytettävyys lähdealueanalyysissä: testausta ja arviointia SO_2-pitoisuusmittausten ja HYSPLIT 4 -trajektorien avulla, Master's thesis, University of Helsinki, 2010.

Hyvönen, S., Junninen, H., Laakso, L., Dal Maso, M., Grönholm, T., Bonn, B., Keronen, P., Aalto, P., Hiltunen, V., Pohja, T., Launiainen, S., Hari, P., Mannila, H., and Kulmala, M.: A look at aerosol formation using data mining techniques, Atmos. Chem. Phys., 5, 3345–3356, doi:10.5194/acp-5-3345-2005, 2005.

Junninen, H., Lauri, A., Keronen, P., Aalto, P., Hiltunen, V., Hari, P., and Kulmala, M.: Smart-SMEAR: on-line data exploration and visualization tool for SMEAR stations., Boreal Environ. Res., 14, 447–457, 2009.

Kabashnikov, V. P., Chaikovsky, A. P., Kucsera, T. L., and Metelskaya, N. S.: Estimated accuracy of three common trajectory statistical methods, Atmos. Environ., 45, 5425–5430, 2011.

Kaiser, A., Scheifinger, H., Spangl, W., Weiss, A., Gilge, S., Fricke, W., Ries, L., Cemas, D., and Jesenovec, B.: Transport of nitrogen oxides, carbon monoxide and ozone to the Alpine Global Atmosphere Watch stations Jungfraujoch (Switzerland), Zugspitze and Hohenpeissenberg (Germany), Sonnblick (Austria) and Mt. Krvavec (Slovenia), Atmos. Environ., 41, 9273–9287, 2007.

Karvosenoja, N.: Emission scenario model for regional air pollution, Monographs of the Boreal Environment Research, 32, 55 pp., 2008.

Kulmala, M., Rannik, U., Pirjola, L., Dal Maso, M., Karimäki, J., Asmi, A., Jäppinen, A., Karhu, V., Korhonen, H., Malvikko, S.-P., Puustinen, A., Raittila, J., Romakkaniemi, S., Suni, T., Yli-Koivisto, S., Paatero, J., Hari, P., and Vesala, T.: Characterization of atmospheric trace gas and aerosol concentrations at forest sites in southern and northern Finland using back trajectories, Boreal Environ. Res., 5, 315–336, 2000.

Lauer, A. and Hendricks, J.: Simulating aerosol microphysics with the ECHAM4/MADE GCM – Part II: Results from a first multiannual simulation of the submicrometer aerosol, Atmos. Chem. Phys., 6, 5495–5513, doi:10.5194/acp-6-5495-2006, 2006.

Lyubovtseva, Y. S., Sogacheva, L., Dal Maso, M., Bonn, B., Keronen, P., and Kulmala, M.: Seasonal variations of trace gases, meteorological parameters, and formation of aerosols in boreal

forests, Boreal Environ. Res., 10, 493–510, 2005.

Niemi, J. V., Saarikoski, S., Aurela, M., Tervahattu, H., Hillamo, R., Westphal, D. L., Aarnio, P., Koskentalo, T., Makkonen, U., Vehkamäki, H., and Kulmala, M.: Long-range transport episodes of fine particles in southern Finland during 1999–2007, Atmos. Environ., 43, 1255–1264, 2009.

Nilsson, E. D., Paatero, J., and Boy, M.: Effects of air masses and synoptic weather on aerosol formation in the continental boundary layer, Tellus B, 53, 462–478, 2001.

Paasonen, P., Nieminen, T., Asmi, E., Manninen, H. E., Petäjä, T., Plass-Dülmer, C., Flentje, H., Birmili, W., Wiedensohler, A., Hõrrak, U., Metzger, A., Hamed, A., Laaksonen, A., Facchini, M. C., Kerminen, V.-M., and Kulmala, M.: On the roles of sulphuric acid and low-volatility organic vapours in the initial steps of atmospheric new particle formation, Atmos. Chem. Phys., 10, 11223–11242, doi:10.5194/acp-10-11223-2010, 2010.

Riipinen, I., Sihto, S.-L., Kulmala, M., Arnold, F., Dal Maso, M., Birmili, W., Saarnio, K., Teinilä, K., Kerminen, V.-M., Laaksonen, A., and Lehtinen, K. E. J.: Connections between atmospheric sulphuric acid and new particle formation during QUEST III–IV campaigns in Heidelberg and Hyytiälä, Atmos. Chem. Phys., 7, 1899–1914, doi:10.5194/acp-7-1899-2007, 2007.

Riuttanen, L., Dal Maso, M., de Leeuw, G., Riipinen, I., Sogacheva, L., Vakkari, V., Laakso, L., and Kulmala, M.: Long-range transport of biomass burning smoke to Finland in 2006, Atmos. Chem. Phys. Discuss., 13, 4289–4330, doi:10.5194/acpd-13-4289-2013, 2013.

Saarikoski, S., Sillanpää, M., Sofiev, M., Timonen, H., Saarnio, K., Teinilä, K., Karppinen, A., Kukkonen, J., and Hillamo, R.: Chemical composition of aerosols during a major biomass burning episode over northern Europe in spring 2006: Experimental and modelling assessments, Atmos. Environ., 41, 3577–3589, 2007.

Scheifinger, H. and Kaiser, A.: Validation of trajectory statistical methods, Atmos. Environ., 41, 8846–8856, 2007.

Seibert, P., Kromp-Kolb, H., Baltensperger, U., Jost, D., Schwikowski, M., Kasper, A., and Puxbaum, H.: Trajectory analysis of aerosol measurements at high alpine sites, in: Transport and Transformation of Pollutants in the Troposphere, edited by: Borrel, P. M., Puxbaum, H., Cvitas, T., and Seiler, W., 689–693, Academic Publishing, Den Haag, 1994.

Seinfeld, J. H and Pandis, S. N.: Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, Wiley-Interscience, New York, 1998.

Sipilä, M., Berndt, T., Petäjä, T., Brus, D., Vanhanen, J., F., S., Patokoski, J., Mauldin III, R. L., Hyvärinen, A.-P., Lihavainen, H., and Kulmala, M.: The Role of Sulfuric Acid in Atmospheric Nucleation, Science, 327, 1243–1246, 2010.

Sogacheva, L., Dal Maso, M., Kerminen, V.-M., and Kulmala, M.: Probability of nucleation events and aerosol particle concentrations in different air mass types arriving at Hyytiälä, southern Finland, based on back trajectories analysis, Boreal Environ. Res., 10, 479–491, 2005.

Sogacheva, L., Saukkonen, L., Nilsson, E. D., Dal Maso, M., Schultz, D. M., De Leeuw, G., and Kulmala, M.: New aerosol particle formation in different synoptic situations at Hyytiälä, Southern Finland, Tellus B, 60, 485–494, 2008.

Stohl, A.: Trajectory statistics – a new method to establish source-reseptor relationships of air pollutants and its application to the transport of particulate sulfate in Europe, Atmos. Environ., 30, 579–587, 1996.

Stohl, A.: Computation, accuracy and applications of trajectories - a review and bibliography, Atmos. Environ., 32, 947–966, 1998.

Stohl, A., Hittenberger, M., and Wotawa, G.: Validation of the lagrangian particle dispersion model FLEXPART against large-scale tracer experiment data, Atmos. Environ., 32, 4245–4264, 1998.

Vasconcelos, L. A. d. P., Kahl, J. D. W., Liu, D. S., Macias, E. S., and White, W. H.: A tracer calibration of back trajectory analysis at the Grand Canyon, J. Geophys. Res., 101, 19329–19335, 1996.

Vestreng, V., Myhre, G., Fagerli, H., Reis, S., and Tarrasón, L.: Twenty-five years of continuous sulphur dioxide emission reduction in Europe, Atmos. Chem. Phys., 7, 3663–3681, doi:10.5194/acp-7-3663-2007, 2007.

Virkkula, A., Mäkinen, M., Hillamo, R., and Stohl, A.: Atmospheric aerosol in the Finnish Arctic: particle number concentrations, chemical characteristics and source analysis, Water Air Soil Pollut., 85, 1997–2002, 1995.

Virkkula, A., Backman, J., Aalto, P. P., Hulkkonen, M., Riuttanen, L., Nieminen, T., dal Maso, M., Sogacheva, L., de Leeuw, G., and Kulmala, M.: Seasonal cycle, size dependencies, and source analyses of aerosol optical properties at the SMEAR II measurement station in Hyytiälä, Finland, Atmos. Chem. Phys., 11, 4445–4468, doi:10.5194/acp-11-4445-2011, 2011.

Wotawa, G. and Kröger, H.: Testing the ability of trajectory statistics to reproduce emission inventories of air pollutants in cases of negligible measurement and transport errors, Atmos. Environ., 33, 3037–3043, 1999.

Zhou, L., Hopke, P., and Liu, W.: Comparison of two trajectory based models for locating particle sources for two rural New York sites, Atmos. Environ., 38, 1955–1963, 2004.