Atmos. Chem. Phys. Discuss., 15, 14593–14641, 2015
www.atmos-chem-phys-discuss.net/15/14593/2015/
doi:10.5194/acpd-15-14593-2015

Atmospheric Chemistry and Physics Discussions
Open Access

Sources of long-lived atmospheric VOCs at the rural boreal forest site, SMEAR II

J. Patokoski[1], T. M. Ruuskanen[1], M. K. Kajos[1], R. Taipale[1], P. Rantala[1], J. Aalto[2], T. Ryyppö[3], T. Nieminen[1,4], H. Hakola[5], and J. Rinne[1,5,6]

[1]Division of Atmospheric Sciences, Department of Physics, University of Helsinki, P.O. Box 64, 00014 University of Helsinki, Finland
[2]Department of Forest Sciences, University of Helsinki, Finland
[3]Finnish Meteorological Institute, Arctic Research Centre, Tähteläntie 62, 99600 Sodankylä, Finland
[4]Helsinki Institute of Physics, P.O. Box 64, 00014 University of Helsinki, Finland
[5]Finnish Meteorological Institute, P.O. Box 503, 00101 Helsinki, Finland
[6]Department of Geosciences and Geography, University of Helsinki, Finland

Received: 19 February 2015 – Accepted: 26 April 2015 – Published: 26 May 2015

Correspondence to: J. Patokoski (johanna.patokoski@helsinki.fi)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

In this study a long-term volatile organic compounds (VOCs) data set, measured at the SMEAR II (Station for measuring Ecosystem–Atmosphere Relations) boreal forest site at Hyytiälä, Finland during the years 2006–2011, was investigated. VOC mixing ratios were measured using proton transfer reaction mass spectrometry. Four-day backward trajectories and the Unmix 6.0 receptor model were used for source area and source composition analysis. Two major forest fire events, one in Eastern Europe and one in Russia, took place during the measurement period. The effect of these fires was clearly visible in the trajectory analysis, lending confidence to the method employed with this data set. Elevated volume mixing ratios (VMRs) of non-biogenic VOCs, e.g. acetonitrile and aromatic VOCs, related to forest fires were observed. Ten major source areas for long-lived VOCs (methanol, acetonitrile, acetaldehyde, acetone, benzene and toluene) were identified at the SMEAR II site. The main source areas for all the targeted VOCs were Western Russia, Northern Poland, Kaliningrad and Baltic countries. Industrial areas in Northern Continental Europe were also found to be source areas for certain VOCs. Both trajectory and receptor analysis showed that air masses from Northern Fennoscandia were less polluted with both the VOCs studied and with other trace gases (CO, SO_2 and NO_x) than areas of Eastern and Western Continental Europe, Western Russia and Southern Fennoscandia.

1 Introduction

Volatile organic compounds (VOCs) in the atmosphere have several sources, both biogenic and anthropogenic. On a global scale the emissions of biogenic VOCs are estimated to be an order of magnitude higher than anthropogenic ones (Guenther et al., 1995). The main biogenic sources are forests (Simpson et al., 1999), and to a lesser degree crops (Guenther et al., 1995) and algae in aquatic ecosystems (Fink et al., 2007). However, in the northern latitude winter and during air pollution events, anthropogenic emissions can be dominant. The most important non-biogenic VOC sources are traffic, biomass burning (especially forest fires), the extraction and refining of fossil fuels, and the evaporation of solvents (Blake et al., 2009). Once emitted, the VOCs may be transported and oxidized in photochemical processes during this transport. The main oxidants for VOCs in the atmosphere are ozone (O_3), and the hydroxyl (OH) and nitrate (NO_3) radicals (Atkinson and Arey, 2003). Depending on their reactivity with these oxidants, some VOCs have a relatively long lifetime from a few days to a few months, and can be transported over long distances. In order to study this atmospheric transport and to identify the source areas of the measured concentrations, trajectory analysis has been widely used (Stohl, 1996; Stohl and Seibert, 1998).

In source areas, VOCs are emitted, for example, from forest fires (de Gouw et al., 2006) or industrial sources or, on the other hand, from densely-populated urban areas: these have a mixture of various source elements such as industry, power plants and vehicles (Baker et al., 2008). The locations of source areas may vary temporally and spatially, due to e.g. seasonal variations in the biogenic activity of plants or variations in anthropogenic activity or meteorological conditions.

The SMEAR II (Station for measuring Ecosystem–Atmosphere Relations) site, located in a rural environment in boreal forest in Southern Finland, has been used for two decades to investigate atmospheric processes leading to aerosol particle formation and growth. There is ample evidence that biogenic VOCs contribute to these processes at this site (e.g. Tunved et al., 2006; Ehn et al., 2014). However, there is also evidence that emissions and atmospheric concentrations of some VOCs, such as monoterpenes, are occasionally affected by anthropogenic processes (Liao et al., 2011; Haapanala et al., 2012). Many VOCs with a relatively long lifetime have both biogenic and anthropogenic sources. These VOCs include e.g. methanol, acetone and acetaldehyde which lifetimes for Southern Finland have been estimated to be in spring 16, 33 and 4 days, respectively by Patokoski et al. (2014). As these compounds can be transported over thousands of kilometres, their atmospheric concentrations observed at SMEAR II are likely to be influenced by distant anthropogenic emissions in addition to more local sources. Previously, Ruuskanen et al. (2009) have observed that there is an indication of long-range transport of VOCs from continental Europe to Finland. Hellén et al. (2006) studied the source areas of VOCs in Helsinki urban air, and found out that most of the benzene was from distant sources. During long-range transport, the VOCs in air masses coming to the SMEAR II site are often at least partly oxidized. The observed VOCs may thus have both primary and secondary sources.

The volume mixing ratios (VMRs) of VOCs have earlier been studied at SMEAR II e.g. by Rinne et al. (2005); Ruuskanen et al. (2009); Hakola et al. (2009, 2012) and Hellèn et al. (2004). These studies have only made use of short data sets, with the exception of that by Hakola et al. (2009, 2012), thus not allowing a study of annual to inter-annual variations. Hakola et al. (2012) made continuous measurements using an in situ gas-chromatograph and Hakola et al. (2009) using noon-time samples and laboratory analysis, but in both measured only terpenoids. The analysis of source areas has not been possible without employing larger data sets comprising several compounds.

Thus our aim in this study is to use VOC VMR data covering several years (2006–2011) and to investigate the source profiles and source areas of relatively long-lifetime VOCs (methanol, acetaldehyde, acetone, toluene, benzene) observed at the SMEAR II site. Winters are characterized by stronger anthropogenic influence e.g. from heating whereas biogenic activity is more pronounced in the summer. The specific aims of this study are (1) to investigate long term changes in sources affecting the VOC concentrations and to quantify their trends (biogenic and anthropogenic) over a six-year period, (2) to determine the biogenic vs. the anthropogenic influence from defining the source profiles of VOCs in relation to other trace gases for SMEAR II, (3) to identify the source areas of VOCs in air masses arriving from Northern Fennoscandia, Northern Continental Europe and Western Russia within the lifetime of the long-lived VOCs, such as acetone and benzene, observed at SMEAR II, (4) to investigate how these sources coincide with e.g. wildfires and biomass burning, and major urban and industrial areas. The SMEAR II's focus is atmosphere biosphere interaction and define aerosol formation and growth processes in boreal climate zone. While many studies have focused on the influence of local to regional sources on the observed trace gases concentrations (Patokoski et al., 2014; Liao et al., 2011; Eerdekens et al., 2009; Hakola et al., 2009, 2012), this study aims at identifying regional to continental source areas and focuses on characterizing the effect of long range transport.

2 Methods

2.1 Measurements site

VOCs VMRs were measured at the SMEAR II site in Finland during the years 2006–2011. SMEAR II is a rural measurement station located in boreal forest at Hyytiälä, Southern Finland (61°51′ N, 24°17′ E, 180 m a.s.l.). A detailed description of the site is given by e.g. Hari and Kulmala (2005). The site is located 220 km north-west of Helsinki and 60 km north-east of Tampere which with a population of about 200 000 is the largest city near the site. Continuous long-term measurements of trace gases, aerosol particles and gas exchange between the atmosphere and the biosphere have been carried out at SMEAR II since the mid-1990's (Vesala et al., 1998). The forest surrounding the station is dominated by Scots pine (*Pinus sylvestris*), sown in 1962 (Bäck et al., 2012). There is also some Norway spruce (*Picea abies*), aspen (*Populus tremula*) and birch (*Betula* sp.) at the site (Hari and Kulmala, 2005). Within a square of 40 km × 40 km centred on the station 23 % of the area is covered by pine forests, 26 % by spruce forest, and 21 % by mixed forest (Haapanala et al., 2007). Agriculture and water bodies cover 10 and 13 %, respectively.

2.2 Instrumentation and sampling

The VOC VMRs were measured with a quadrupole proton transfer reaction mass spectrometer (PTR-MS, Ionicon Analytik GmbH, Austria, Lindinger et al., 1998a). PTR-MS uses the hydronium ion (H_3O^+) as a primary reactant ion. VOCs with a larger proton affinity than that of water will readily react with H_3O^+ (Lindinger et al., 1998a, b). The PTR-MS uses a soft ionization technique and most compounds hardly fragment at all (Tani et al., 2003). The reactant and the product ions are mass filtered with a quadrupole mass spectrometer and detected with a secondary electron multiplier (SEM). Product ions are protonated and thus e.g. methanol is identified at molecular mass m 33. During the measurements, the PTR-MS was calibrated with a VOC calibration gas mixture at regular weekly or biweekly intervals. During the period 2006–2011 four different VOC mixtures, which all included 16–18 VOCs and were all manufactured by Apel-Riemer Environmental Inc., USA, were used. A detailed description of the calibration procedure and the VMR calculation methodology is presented by Taipale et al. (2008). The following settings were used during the measurements: U_{drift} varied from 450 to 525 V (mean value 479 V), temperature of drift tube was 50 °C, E/N range varied from 105 to 130 Td (mean value 110 Td) and normalized sensitivity for e.g. acetone varied from 18 to 40 ncps ppb_v^{-1} (mean value 28 ncps ppb_v^{-1}). Detection limits for studied VOCs are presented in Table 1. The instrument was calibrated every time when settings were changed, taking into account the changes in the sensitivity and cancelling effects on the measured VMRs.

Seven masses: m 33, m 42, m 45, m 59, m 79, m 93 and m 137 a.m.u, which have been identified as methanol, acetonitrile, acetaldehyde, acetone, benzene, toluene and monoterpenes, respectively (de Gouw and Warneke, 2007), were measured. PTR-MS and GC-MS concentration measurements in Hyytiälä have agreed well for monoterpenes (Ruuskanen et al., 2005) as well as of methanol, acetaldehyde, acetone, benzene and toluene (Kajos et al., 2015). These VOCs, excluding monoterpenes, have relatively long lifetimes, and the behaviour of their VMRs was investigated with trajectory analysis and the Unmix 6.0 receptor model. One-hour median mixing ratios were calculated for the analysis. All the data are presented in local standard time (UTC +2 h). There are some gaps in the data due to maintenance, some technical problems and the usage of the PTR-MS in other measurement campaigns (Fig. 1). Data quality was checked and data were filtered by removing values below the detection limit. The detection limits for the measurement periods are presented in Table 1.

During the years 2006–2009 the VMRs of the VOCs were measured from a scaffolding tower at a height of 22 m above the ground. From summer 2006 to spring 2007 the measurement sequence consisted of one-hour VMR measurements followed by one-hour disjunct eddy covariance measurements (Rinne et al., 2007). Thus VMR data were obtained every second hour. The sampling protocol changed in March 2007 when a chamber with a Scots pine shoot enclosed was included in the measurement cycle; VOC VMRs were then measured every third hour instead of every second hour. In May 2010 the sampling protocol changed again when the instrument was transported to another measurement hut. At the same time the sampling inlet was moved about 50 m to another tower, 33.6 m above ground. These measurement heights were chosen for analysis because they are more representative for depicting concentrations due to transport, rather than concentrations inside the canopy. The canopy height was about 16 m.

Nitrogen oxides (NO_x), carbon monoxide (CO), sulphur dioxide (SO_2) and ozone (O_3) mixing ratio data were used in the analysis as ancillary data. The mixing ratios of NO_x were measured with a chemiluminescence technique (TEI 42C TL, Thermo Environmental Instruments, MA, USA) and CO was measured by an infrared light absorption analyzer (HORIBA APMA 360, Horiba, Japan). SO_2 was measured with a fluorescence analyzer (TEI 43 BS, Thermo Environmental Instruments, MA, USA) and O_3 by an ultraviolet light absorption technique (TEI 49, Thermo Environmental Instruments, MA, USA). CO, NO_x, O_3 and SO_2 were also measured at a height of 33 m except in 2010, when CO was measured at 16.8 m.

2.3 Trajectory analysis

HYSPLIT 4 (HYbrid Single Particle Lagrangian Intergrated Trajectory) was used for air mass trajectories (Draxler and Hess, 1998). The arrival height of the calculated trajectories at SMEAR II was 100 m a.g.l., thus representing air masses arriving in the surface layer, in which the VOC VMR measurements were made. Backward trajectories of 96 h (4 days) were calculated for every hour from 2006 to 2011. For the purposes of the trajectory analysis the VOC VMR data were interpolated using a Piecewise Cubic Hermite Interpolating Polynomial (PCHIP) to cover every hour and thus match the trajectory data. Each time measured VOC VMR data were available at SMEAR II, they were associated with a trajectory arriving at the site at the same time. The path of the back trajectories was considered with a 1° × 1° spatial resolution. The VMRs were assumed to remain constant during the whole transport time. The grid cells over which trajectories traversed prior to the observation of high VMR values at SMEAR II were associated with high values in the source field. Thus the trajectory maps are interpreted so that there is a color code corresponding to VMRs e.g. if there is an area in a map where methanol is observed to be 3 $\mathrm{ppb_v}$ this means that the measured value 3 $\mathrm{ppb_v}$ at the site is assumed to come from that area (see Figs. 3–5). The trajectory analysis was limited to the area between 50 and 75° N in latitude; 12 and 50° E in longitude. For reasons of statistical significance, at least 25 trajectories had to cross a grid cell in order for that grid cell to be accepted into the analysis, i.e., grid cells with less than 25 traverses were omitted from the analysis. Finally, all the VOC VMRs at each grid cell were averaged to yield the VOC source field (Stohl et al., 1995; Stohl and Seibert, 1998).

2.4 Forest fire locations from satellite observations

The forest fire location data are obtained from FIRMS (Fire Information Resource Managements System), which delivers fire locations and hotspots as globally observed by MODIS (Moderate Resolution Imaging Spectroradiometer). Data have been collected by NASA's Earth observing system (EOS) Terra and Aqua satellites. With these two satellites global data coverage is achieved every 1 to 2 days.

2.5 Unmix 6.0

Source compositions and contributions were investigated with the multivariate receptor model EPA Unmix 6.0 (Norris et al., 2007), developed by Ronald Henry at the University of Southern California. A basic problem of multivariate receptor models is how to determine the optimal number of sources, the source fingerprints and their contribution from the ambient air VOC measurement data alone. Some additional constraints must be added in order to obtain unique solutions. In Unmix, the composition and contribution of the sources must be non-negative. In addition to this, Unmix searches for periods when the data indicate that the contribution of one of the sources is missing completely or its contribution is minor. The application of Unmix to VOC data obtained by gas chromatographic methods at an urban site in Helsinki is described by Hellén et al. (2003). According to the recommendations for the model, the regression of each of the species explained by the sources (R^2) should be over 0.8, while the signal-to-noise ratio should be over 2. In this study, Unmix was applied for inorganic trace gas and VOC data, except monoterpenes that were excluded from the source area trajectory analysis (see Sect. 3.5). One-hour medians of trace gases and VOCs were used as input data. Data were filtered by horizontal wind speed, excluding from analysis observations (30 % of data were excluded from analysis) with wind speed below 1 $\mathrm{m\,s^{-1}}$. All the results exceeded the recommended R^2 and signal-to-noise values, indicating receptor modelling results that were applicable and valid.

3 Results and discussion

The VOC VMRs of most compounds which were studied have maxima in summertime and minima in winter (Fig. 1). However, benzene behaves in the opposite way. This is due to a lack of significant biogenic sources of benzene and its shorter atmospheric lifetime in summer. Of the other studied VOCs, methanol, acetone, acetaldehyde and the monoterpenes also have biogenic sources around the measurement site (Rinne et al., 2007), and acetonitrile is emitted by biomass burning.

3.1 Lifetimes of the observed VOCs

To estimate the VOC chemical lifetimes (e-folding times), OH and NO_3 radical concentrations, were estimated, based on data from Hakola et al. (2003). The summertime OH concentration presented by Hakola et al. (2003) agreed well with the observations (Rinne et al., 2012), except in the case of summertime NO_3, whose radical concentration is at least twice as high as the observations. Thus, for this study, the annual cycle of NO_3 as presented by Hakola et al. (2003) was scaled by dividing it by two. Summer- and wintertime median O_3 concentrations were calculated from O_3 measurements at SMEAR II. Photolysis values for summer- and wintertime were calculated following Hellén et al. (2004). Actinic flux values corresponding to the albedo for snow-covered forest in winter ($\alpha = 0.8$) were used when photolysis values were calculated. The concentrations of oxidants and reaction rate coefficients are presented in Tables 2 and 3.

The calculated atmospheric lifetimes of the studied VOCs (methanol, acetaldehyde, acetone, benzene and toluene) in summer- and wintertime are presented in Table 4. Compared to the lifetimes of monoterpenes (about one day in winter and one hour in summer) these lifetimes were much longer. For most compounds, the atmospheric lifetimes exceed the duration of the back-trajectories used in this analysis. However, in summertime both toluene and acetaldehyde have a lifetime below four days. Thus, for these compounds, the results of the four-day backward trajectory analysis should be interpreted with caution.

The following sections describe the source areas of the studied VOCs: (1) during long-range transport episodes from forest fires, (2) for all VOC VMR data and (3) for summers and winters separately.

3.2 Forest fire episodes in Russia in the summers of 2006 and 2010

During the measurement periods two particularly active forest fire episodes with several fire hotspots occurred in Russia, one in summer 2006 and the other in summer 2010.

They also influenced air quality in Finland (Leino et al., 2014). These fires provide temporally and spatially well-defined sources that can be used to evaluate the ability of the trajectory analysis to identify the source areas.

Biomass burning has previously been observed to be a source of VOCs in several field and laboratory studies (e.g. Crutzen and Andreae, 1990; Holzinger et al., 1999; de Gouw et al., 2006; Virkkula et al., 2014). Acetonitrile has commonly been used as a marker compound for emissions from biomass burning (de Gouw et al., 2003, 2006; Holzinger et al., 1999). The oxygenated VOCs (OVOCs) and aromatic VOCs (benzene and toluene) have also been linked to biomass burning in different studies (Koppmann and Wildt, 2007; de Gouw et al., 2006). Forest fires affect air quality; and the biggest smoke plumes can be seen in satellite images and even reduce visibility in the plume areas.

Forest fires, which were observed during these measurements, occurred in the year 2006 in the Vyborg area near the Finnish–Russian border and in year 2010 in the Moscow area (Fig. 2). The sum of all observed fires during the two episodes are shown in Fig. 2; in order to be visible on the map, the forest at the given location was not necessarily burning all the time. Lappalainen et al. (2009) observed an exceptional drought at SMEAR II during summer of 2006. During the summer of 2010 an unusually high temperature anomaly was observed in Eastern Europe (Twardosz and Kossowska-Cezak, 2013). Williams et al. (2011) also reported unusually high temperatures at SMEAR II during summer 2010. These circumstances can be favourable for the ignition and development of major forest fires.

In summer 2006 the largest fires were south of Moscow and in Belarus. There were also fires in Karelia, in Vyborg area near St. Petersburg and the Finnish-Russian border. The first forest fire episode occurring within the time-frame of this study was in the period 4–31 August 2006. The trajectory analysis shows the high VOC mixing ratios observed at SMEAR II during this period to have originated from that area (Fig. 3). Unfortunately, acetonitrile was not being measured during this period. During this period Anttila et al. (2008) also observed elevated amounts of particulate matter mass (PM_{10},

$PM_{2.5}$) and higher polycyclic aromatic hydrocarbon (PAH) concentrations at Virolahti, located on the Finnish south coast near the Finnish-Russian border.

During summer 2010 a large number of forest fires were located in Northwest Russia. The second forest fire episode within the time frame of this study was in 20 July–31 August 2010. During this period acetonitrile data too was being measured at SMEAR II. Comparing the forest fire locations (Fig. 2) and acetonitrile's mean VMR field from trajectory analysis, one can see that acetonitrile is originating from the general direction of the maximum burning area (Fig. 4). All the other VOCs and trace gases studied also had similar source area distributions to acetonitrile.

For comparison between fire and non-fire VOC VMRs, the mean VMR values of methanol, acetonitrile, benzene, SO_2 and CO were calculated for periods both before and during the forest fire episodes in both years (Table 5). In, 2006 the period from 1 to 31 July 2006 was selected to represent the situation before the forest fires. In, 2010 the period from 25 June to 15 July 2010 was used for the same purpose. In both cases concentrations were calculated using data, filtered by trajectories, of air which had traversed the burning areas. In this study, the forest fire areas were selected to be [27–36° E, 58–62° N] (area 1) in 2006 and [28–34° E, 56–61° N] (area 2) in 2010. Before the forest fire episode in year 2010, the VMR of acetonitrile was 0.06 ppb_v, while during the episode it was 0.13 ppb_v. Benzene too had elevated VMR levels in arriving air masses that had travelled over forest fires. In, 2006, benzene's VMR before the forest fires was 0.08 ppb_v and during the episode 0.17 ppb_v; in 2010 the values were 0.05 and 0.09 ppb_v, respectively. Acetonitrile and benzene have earlier been observed to be emitted from biomass burning (Holzinger et al., 1999; Simpson et al., 2011; Virkkula et al., 2014). Elevated CO concentrations were also observed in air masses associated with forest fires. Before the forest fire episodes, CO was measured at 128 ppb_v in 2006 and 111 ppb_v in 2010. During the episodes, CO concentrations were 154 and 152 ppb_v, respectively. However, the mean VMRs of methanol did not increase during the fire episodes, which indicates that methanol at SMEAR II has other dominant sources, such as biogenic emissions from vegetation. SO_2 is usually linked to fossil fuel combustion

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◀| |▶
◀ ▶
Back | Close
Full Screen / Esc

Printer-friendly Version
Interactive Discussion

processes rather than biomass burning (Seinfeld and Pandis, 1998). In this study, too, the SO_2 concentration in 2006 was actually lower during the forest fire episode than before it; in 2010 it was only slightly elevated during the episode.

3.3 Differences in source areas for the whole measurement period

The mean trajectory fields of the VOCs studied (methanol, acetonitrile, acetaldehyde, acetone, benzene and toluene), as well as CO, NO_x and SO_2 from the year 2006 to the year 2011 are presented in Fig. 5. From this figure it can be seen that methanol, acetone and acetaldehyde had very similar source areas. There was very good correlation between methanol and acetone ($r = 0.86$, $p = 0$). Methanol and acetaldehyde were also correlated to each other ($r = 0.66$, $p = 0$). On the other hand, the source areas of benzene, toluene, CO and NO_x were also similar to each other and correlated well. Acetonitrile had similarities with both methanol and benzene, correlating, however, better with the methanol group than with the benzene group. The correlation matrix and Pearson's correlation coefficients between all compounds are presented in Fig. A1. All p values were below 0.05 except those for the correlations between methanol and benzene, NO_x and CO which were statistically insignificant. Anthropogenically-influenced source areas (benzene, toluene, NO_x, CO) were observed in the northern part of Continental Europe and Eastern Europe, Fennoscandia, Western Russia, and marine and coastal areas (Baltic Sea, Barents Sea, White Sea, Norwegian Sea and North Sea) (Fig. 4). Northern Fennoscandia seemed to be quite free of anthropogenic sources of VOCs. NO_x, CO and SO_2 concentrations were also low in air masses arriving from the north. Except methanol and acetonitrile, the other VOCs do not have any elevated source areas in the Northern area. The occurrence of forest fires in Eastern Europe is visible in the mean trajectory fields of all data. In addition to biomass burning, some small local emissions e.g. from traffic, wood combustion and biogenic emissions may also have had an effect on the results.

The source areas of SO_2 were similar to those of NO_x and CO. The main source areas of SO_2 were Western Russia, Northern Poland and Kaliningrad, while NO_x and CO had additional source areas in Western Europe. Riuttanen et al. (2013) found a similar sharp distinction in SO_2 concentrations between air masses arriving from Eastern and Western Europe. They also found that air masses coming from Central Europe were exposed to more rain and thus wet removal of SO_2. They speculate that this may be one reason why SO_2 source areas in Central Europe were not separable in the trajectory fields. However, in this study we found that water-soluble methanol and also NO_x were not totally washed away, as there were visible source areas for methanol in the North Sea, Skagerrak and the northern Germany areas, and for NO_x in Northern Continental Europe (Fig. 5). We propose that wet deposition does not fully explain the absence of SO_2 in the air masses arriving from Western Europe, as interpreted by Riuttanen et al. (2013), but that the observed difference in SO_2 is probably due to more rigorous emission regulations in the western part of Europe than the eastern part. This interpretation is supported by Vestreng et al. (2007), who observed a difference in the reduction of emissions of SO_2 between Western and Eastern Europe during years 1980–2004. According to the EMEP database SO_2, emissions in the European Union have decreased from about 25.8 to 4 Gg over the period 1990–2012. Emission data from Eastern Europe for the same time period is scarce. Riuttanen et al. (2013) also observed a general decreasing trend of SO_2 of −5.2 % per year at SMEAR II during 1997–2008. Anttila and Tuovinen (2010) observed a decreasing trend of SO_2 of −2.2 % per year for the whole of Finland during the years 1994–2006.

3.4 Source areas and their seasonal difference

In order to study the possible seasonal changes in the VOC source areas, these were determined separately for the summer (June–August) and the winter (December-February) periods. Data of the short forest fire episodes were removed prior to this analysis so that they would not mask other source areas. Although there was some inter-annual variation in the observed VMRs of VOCs, no clear trends of VMRs were observed during the whole measurement period (Fig. 1). The long-term trends of selected VOCs based on the summertime medians of the VMRs of VOCs studied are presented in Table 6. These trends are all slightly negative except for that of monoterpenes that seemed to be slightly positive. For monoterpenes the VMR change was 8 % per year for the summer monthly medians. However, one should interpret these trends with care, because they were calculated based on measured summer monthly medians whose trends were not, in fact, statistically significant (i.e. the confidence intervals included zero). Summers were different from each other, e.g. the median temperature between summers in Finland at Hyytiälä were observed to vary from 12.9 to 17 °C, which may have an effect on the emissions of VOCs e.g. methanol, acetone and monoterpenes. Additionally, in the case of monoterpenes' VMRs the change of the sampling location may bias the trend calculated over the whole observation period, as monoterpenes have a short life time (1 h; Table 4).

The source areas of the VOCs also varied slightly between years due to variations in the VOC VMRs, deposition and the prevailing paths of arriving air masses. Despite these differences, all five summers (2006–2008, 2010–2011) and two winters (2006–2007 and 2008–2009) were combined in this study, to get as good an areal trajectory data coverage as possible for summers and winters separately. Summer, 2009 was not included in the trajectory analysis because VOC VMR data was then only available for 18 days.

For the evaluation of the VMR source areas, ten rectangular areas were selected for separate analysis of the trajectory fields of both main seasons (summer, winter) (Fig. 6). These areas differ from each other in having e.g. different industry and population densities.

The ten selected areas were as follows: (1) Western Russia [54–61° N, 29–40° E]. In this area there are two densely-populated cities, Moscow and St. Petersburg, and also harbours on the Baltic Sea. The area includes many different industries as described in detail in Table A1, (2) Northern Poland, Kaliningrad and Baltic countries (Estonia, Latvia and Lithuania) [53–59° N, 18–28° E]. This area includes the port of Gdansk, which is one of the important harbors in the Baltic Sea. Similarly to Western Russia there is also a lot of industry in this area, (3) Karelia and the White Sea [63–66° N, 31–

40° E]. This area is a significant Russian industrial area, also including large forests and the coastal areas of White Sea. Compared to the Western Russia source area, the Karelia and White Sea area is more sparsely populated, (4) The Kola Peninsula and Barents Sea [66–70° N, 29–42° E]. This area is rich in minerals and is therefore an important Russian industrial area. Around the Barents Sea there is an active petroleum industry (Austvik, 2007) with several oil drilling sites and oil tankers present on the Norwegian and Russian coasts. Four different source areas for VOCs were then defined in Fennoscandia (Denmark, Finland, Norway and Sweden): (5) The Bay of Bothnia [64–67° N, 20–25° E] was separated off as its own source area, as there are several metallurgy plants there (Skellefteå, Luleå, Tornio, Raahe) and also wood and timber industry, (6) The coast of the Norwegian Sea and Northern Sweden [67–69° N, 13–20° E]. In this area the notable cities in industrial point of view are Kiruna and Narvik. Kiruna has rich iron ore deposits and Narvik has a large port, (7) The Stockholm region [58–61° N, 15–20° E] is one of the most important industrial areas in Sweden. Stockholm is also the largest city in Fennoscandia, with an important harbour, (8) The Skagerrak area [54–60° N, 8–14° E] includes the surroundings of Goteborg, Malmö, Copenhagen and Oslo. In addition to the Stockholm area, the Skagerrak region is also significant from an industrial point of view. There are many important ports and diverse industry in this area, (9) In the North Sea and coastal areas [52–58° N, −1–6° E] are situated Europe's important offshore oil and gas fields. Norway, Denmark, Germany, the Netherlands and the UK are involved in oil production in the North Sea (EIA, International Energy Outlook, 2014). The coastal areas of the North Sea are also very densely populated; (10) Northern Germany [52–54° N, 8–15° E]. This is one of Germany's main industry areas, with several important harbours such as Hamburg, Lübeck and Rostock.

To evaluate the source areas for the studied VOCs during summer and winter, two different VOC VMR trajectory fields were calculated for each compound. The momentary VOC VMR trajectory field was calculated directly from the measured one-hour median values. The interpolated VOC VMR trajectory field was calculated from a linear interpolation of the monthly median values corresponding to the same time period.

This interpolated VOC VMR trajectory field is called the background field in the following discussion. By subtracting the latter from the momentary field a differential source field was obtained, with the seasonal trend removed from the source area analysis. The average values of the differential source field for the ten areas listed above are presented in Fig. 7. Acetonitrile was included in the source area analysis in summer only, when forest fires occurred.

In urban areas, VOCs mostly originate from traffic, but are also evaporated from fuels and combustion processes (Reimann and Lewis, 2007; Hellén et al., 2006) and from various industrial processes. The ten areas investigated here were mainly located in similar areas having a lot of industry and/or dense population. The strongest source areas for all the VOCs studied were located in Eastern Europe including Western Russia, Northern Poland, Kaliningrad and the Baltic countries, Karelia and the White Sea. In these areas, calculated mean VMR values differed significantly from values based on monthly medians (Fig. 7). In addition to these source areas, which are common to most of the studied compounds, certain compounds have specific source areas of their own. Methanol is known to be a very abundant VOC in the atmosphere having many different sources, both biogenic and anthropogenic (Jacob et al., 2005). From Fig. 7, it can be seen that nearly all of the selected areas are sources of methanol. Eastern Europe was observed to be a large emitter of OVOCs (methanol, acetaldehyde and acetone) in general. This is in line with earlier observations by Hellén et al. (2004), who reported Eastern Europe to be an important emitter of carbonyls. In addition to these source areas, acetone and acetaldehyde also arrived from the areas of Stockholm, the Skagerrak, the North Sea and the coastal areas and northern Germany: all these areas have traffic emissions and solvent use related to various different industries. The oxidation of hydrocarbons and the primary biogenic emission of acetaldehyde are known to be the major global source of acetaldehyde (Singh et al., 2004); these sources have not, however, been taken to account into this study. Acetaldehyde also has relatively short lifetime (2 days) during summer. These factors can add some uncertainty to this analysis of acetaldehyde. Benzene was also found to have sources in the Kola Peninsula area, connected with the petrochemical industry and mining. However, the North Sea area with its active petrochemical industry did not appear as a distinguishable source area for aromatic VOCs in this study.

As seen earlier, when comparing the VMRs of VOCs before and during forest fires, the mixing ratios at SMEAR II for benzene and acetonitrile were found to be elevated during these episodes (Table 5). In Fig. 7, forest fires seem to be sources of all VOCs, and especially for acetonitrile. Acetonitrile's VMR difference from the background field values was in the year 2010 0.07 $\mathrm{ppb_v}$. In other source areas, acetonitrile's VMR difference from values based on the background field was indistinguishable (Fig. 7).

The strongest source areas in the trajectory maps seemed to be of anthropogenic origin, and eight out of ten were located in an easterly or southerly direction from Finland. However, there is a vast boreal forest zone in Northern Europe that is an important emitter of biogenic VOCs (BVOCs). Most BVOCS emitted from boreal forests are short-lived terpenoids, whose high atmospheric reactivity keeps their concentrations relatively low (Hakola et al., 2003) compared to those of e.g. OVOCs, with longer atmospheric lifetimes. In this study, the forest regions were not identifiable as well-defined source areas, but probably contributed to background levels. During summer there were minor source areas in the Baltic Sea, where there should be no anthropogenic sources. These interesting source areas could be producing VOCs from e.g. algae or cyanobacteria. However, the VMR levels of VOCs originating from algae are low (Kansal et al., 2009) compared to anthropogenic sources. With the current data and analysis it is not possible to identify the source of these marine emissions. In the future, their origin could be clarified by using shorter trajectories and making measurements near the Baltic Sea or by collecting samples from over the Baltic Sea.

3.5 Low concentrations from the north, urban influences from continents and seas

VOC sources were analyzed with the Unmix 6.0 receptor model. For the Unmix analysis, VOC VMR and trace gas data were divided into three sectors according to the wind direction at SMEAR II. The division was made based on the findings of the VOC source areas described above. The sectors were: (1) North (0–5 and 300–360°), Urbanized continental (5–210°) and Urban and sea (210–300°). In all sectors, three distinctive sources were identified: (1) A source containing mainly SO_2; this was named the SO_2 source, (2) A source containing toluene, benzene, NO_x and CO. These compounds are typical of anthropogenic emissions, and thus the source was named the anthropogenic source, (3) A source containing oxygenated VOCs (OVOCs, methanol, acetone and acetaldehyde), acetonitrile and a portion of CO. This source was related to biomass burning and other biogenic emissions, and was named to biogenic/combustion source.

The mean contributions of all these sources in the different sectors were similar in both seasons. The contribution of the anthropogenic source was dominant in winter and the biogenic/combustion source in summer (Fig. 8). The dominance of the biogenic/combustion source in summer can be attributed to two processes. First, the biogenic/combustion source included acetonitrile, and high mixing ratios of acetonitrile were observed during forest fire episodes in summer; secondly, this source included OVOCs which also have biogenic sources and thus higher VMRs during summer (Fig. 1). Biogenic emissions are dominant at SMEAR II in summer. The monoterpenes measured at SMEAR II are mostly emitted from biogenic sources. However, from the time series of monoterpenes it can be seen that there are occasionally notably high VMR peaks, which are known to have an anthropogenic origin (Liao et al., 2011) (Fig. 1). Monoterpenes were not included in the trajectory and Unmix analysis because they differ from the other VOCs in this study in having a short lifetime from one hour to several hours and mainly local sources. A comparison of diurnal cycles of the anthropogenic source and monoterpenes is presented in Fig. 9. Data in Fig. 9 are from the urbanized continental sector. Monoterpenes had a considerable diurnal variation during summer, with higher mixing ratios at night, and no variation in winter, as also observed in previous studies in similar ecosystems (Hakola et al., 2000; Rinne et al., 2005). This is due to the diurnal cycle in surface layer mixing and the night-time emissions of monoterpenes from coniferous trees. The aromatic VOCs have shorter summertime lifetimes as compared to winter, leading to lower anthropogenic source levels in summer. The contribution of the anthropogenic source in winter was about three times higher in all sectors than in summer. Both summertime and wintertime diurnal cycles of the anthropogenic source show a maximum at night, possibly due to lower night-time mixing in the boundary layer.

Histograms of the source contributions, together with their mean, median and maximum values both in summer and in winter, are presented in Figs. 10 and 11. Many of these distributions are skewed, having a tail of high contribution values. Thus the mean and median values of these source contributions may have large differences. The skewness of the source distributions also indicates that the simplest statistical parameters, such as mean and median, may not adequately describe the distribution of the sources or their contribution to the local atmospheric mixing ratios of these compounds. There were considerable differences between the source distributions from different wind direction sectors. Air masses arriving from the North sector had in general lower source contributions than air masses from the Urbanized continental and the Urban and sea sectors. Particularly in summer there was a tail of high contributions in the Urbanized continental and the Urban and sea sectors for anthropogenic (maximum values were 17.2/4.7) and biogenic/combustion sources (9.8/6.1), as compared to the North sector whose maximum contributions were 1.6 and 4.9 for the anthropogenic and biogenic/combustion sources, respectively. Hence air masses from the north were clearly less polluted with the trace gases studied as compared to the two other sectors. These results combined with the earlier observations in this paper support the conclusion that air masses related to the highest VMRs of long-lived VOCs observed at SMEAR II have their origin in Russia and the Eastern European countries, the Northern part of Continental Europe and Southern and Central Fennoscandia.

4 Conclusions

This study has focused on identifying the source areas of the long-lived VOCs (methanol, acetonitrile, acetaldehyde, acetone, benzene) measured at the SMEAR II site in southern Finland, and to investigate the relative influences of biogenic and anthropogenic compounds arriving in Southern Finland from areas outside the country. The analysis is based on a data set which consisted of several years (2006–2011) of VMR measurements of OVOCs, acetonitrile, aromatic VOCs and monoterpenes. Annual trends of VOC VMRs based on summer monthly medians were presented for the measurement period. The trend of VMRs for monoterpenes was slightly positive. All the other VOCs had a small negative trend in their VMRs. Trend calculations showed, however, that none of these trends could be considered as significant. The origin and sources of the VOCs observed were analyzed by trajectory model and a multivariate receptor model.

During the measurement period, forest fire episodes occurred in Eastern Europe and Russia. Elevated VMR levels for several VOCs and other trace gases were observed in air masses arriving from areas in which abundant fire counts were observed. This corroborates the applicability of the trajectory analysis as a method for identifying the source areas of these trace gases.

Three sources (labelled SO_2, biogenic/combustion and anthropogenic) were separated by receptor analysis both in winter and summer. The biogenic/combustion source dominated in summer and the anthropogenic source in winter. Both the trajectory and Unmix analyses showed that air masses coming from a northerly direction were less polluted with the trace gases studied than the air-masses arriving from easterly and westerly directions.

Ten different source area regions were selected for further analysis. All the source areas seemed to have enhanced emissions due to anthropogenic activity: most of the areas contained with abundant industry. There were some differences in the importance of these source areas between summer and winter. Western Russia, Northern

Poland, Kaliningrad and the Baltic regions and Karelia turned out to be the most significant source area for all the VOCs. Benzene came mainly from areas related to the petrochemical industry, such as the Kola Peninsula, while acetone and acetaldehyde were related to areas where solvents are used in industry e.g. the Skagerrak and North Germany. Forest fire areas stood out clearly as sources for all the VOCs studied and especially for acetonitrile. Even though boreal forests, with their high OVOC emissions, covered large areas in the region, these forest areas were not specifically indicated as source areas. However, they probably did contribute to the regional background levels. The level of SO_2 concentration showed a clear difference between Eastern and Western European source areas, which was not seen in water soluble VOCs and thus, contributed to reduction in emissions. Some biogenic influence appeared in the Baltic Sea region in summer. One potential VOC emitter there could be algae or cyanobacteria, which would be worth studying in the future.

Acknowledgements. This work was financially supported by the Academy of Finland Centre of Excellence program (projects 1118615 and 272041) and the Nordic Centre of Excellence CRAICC. The authors thank H. Hellén for helping in the photolysis rate calculations. NASA MODIS is acknowledged for providing data at data server.

References

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

Anttila, P., Makkonen, U., Hellén, H., Kyllönen, K., Leppänen, S., Saari, H., and Hakola, H.: Impact of the open biomass fires in spring and summer of 2006 on the chemical composition of background air in south-eastern Finland, Atmos. Environ., 42, 6472–6486, 2008.

Artic Centre, University of Lapland: Main industrial centers in North-West Russia, available at: http://arcticcentre.ulapland.fi/maps.asp, last access: 13 January 2014, 2005.

Atkinson, R.: Gas-phase tropospheric chemistry of organic compounds, J. Phys. Chem. Ref. Data Monogr., 2, 1–216, 1994.

Atkinson, R. and Arey, J.: Atmospheric degradation of volatile organic compounds, Chem. Rev., 103, 4605–4638, 2003.

Austvik, O. G.: The geopolitics of Barents Sea oil and gas: the mouse and the bear, International association of energy economics (IAEE), Cleaveland, USA, available at: http://www.iaee.org/documents/newsletterarticles/Gunnar.pdf (last access: 5 May 2014), 2007.

Bäck, J., Aalto, J., Henriksson, M., Hakola, H., He, Q., and Boy, M.: Chemodiversity of a Scots pine stand and implications for terpene air concentrations, Biogeosciences, 9, 689–702, doi:10.5194/bg-9-689-2012, 2012.

Baker, A. K., Beyersdorf, A. J., Doezema, L. A., Katzenstein, A., Meinardi, S., Simpson, I. J., Blake, D. R., and Sherwood Rowland, F.: Measurement of nonmethane hydrocarbons in 28 United States cities, Atmos. Environ., 42, 170–182, 2008.

Blake, R. S., Monks, P. S., and Ellis, A. M.: Proton-transfer reaction mass spectrometry, Chem. Rev., 109, 861–896, 2009.

Bothnian green logistics corridor: new boost for European industrial future, available at: http://www.bothniangreen.se/wp-content/uploads/2012/12/%E2%80%93-New-boost-for-European-industrial-future.pdf, last access: 25 April 2014, 2012.

Crutzen, P. and Andreae, M. O.: Biomass burning in the Tropics: impact of atmospheric chemistry and biogeochemical cycles, Science, 250, 1669–1678, 1990.

de Gouw, J. and Warneke, C.: Measurements of volatile organic compounds in the earth's atmosphere using proton-transfer-reaction mass spectrometry, Mass. Spectrom. Rev., 26, 223–257, 2007.

de Gouw, J., Warneke, C., Karl, T., Eerdekens, G., van der Veen, C., and Fall, R.: Sensitivity and specificity of atmospheric trace gas detection by proton-transfer-reaction mass spectrometry, Int. J. Mass. Spectrom., 223–224, 265–382, 2003.

de Gouw, J. A., Warneke, C., Stohl, A., Wollny, A. G., Brock, C. A., Cooper, O. R., Holloway, J. S., Trainer, M., Fehsenfeld, F. C., Atlas, E.L, Donnely, S. G., Stroud, V., and Lueb, A.: Volatile organic compounds composition of merged and aged forest fire plumes from Alaska and western Canada, J. Geophys. Res., 111, D10303, doi:10.1029/2005JD006175, 2006.

Draxler, R. R. and Hess, G. D.: An overview of the HYSPLIT_4 modelling system for trajectories, dispersion and deposition, Aust. Meteorol. Mag., 47, 295–308, 1998.

Eerdekens, G., Yassaa, N., Sinha, V., Aalto, P. P., Aufmhoff, H., Arnold, F., Fiedler, V., Kulmala, M., and Williams, J.: VOC measurements within a boreal forest during spring 2005: on the occurrence of elevated monoterpene concentrations during night time intense particle concentration events, Atmos. Chem. Phys., 9, 8331–8350, doi:10.5194/acp-9-8331-2009, 2009.

Ehn, M., Thornton, J. A., Kleist, E., Sipilä, M., Junninen, H., Pullinen, I., Springer, M., Rubach, F., Tillmann, R., Lee, B., Lopez-Hilfiker, F., Andres, S., Acir, I.-H., Rissanen, M., Jokinen, T., Schobesberger, S., Kangasluoma, J., Kontkanen, J., Nieminen, T., Kurtén, T., Nielsen, L. B., Jørgensen, S., Kjaergaard, H. G., Canagaratna, M., Dal Maso, M., Berndt, T., Petäjä, T. Wahner, A., Kerminen,V.-M., Kulmala, M., Worsnop, D. R., Wildt, J., and Mentel, T. F.: A large source of low-volatility secondary organic aerosols, Nature, 506, 476–479, 2014.

EIA: International Energy Outlook, Washington, USA, available at: http://www.eia.gov/forecasts/ieo/pdf/0484%282014%29.pdf (last access: 6 May 2014), 2014.

Fink, P.: Ecological functions of volatile organic compounds in aquatic systems, Mar Freshw. Behav. Phy., 40, 155–168, 2007.

FIRMS MODIS: fires/hotspots observations from archive, available at: https://earthdata.nasa.gov/data/near-real-time-data/firms/active-fire-data#tab-content-6 (last access: 24 April 2014), 2014.

GTAI: Germany's Seaports, Berlin, Germany, available at: http://www.gtai.de/GTAI/Content/EN/Invest/_SharedDocs/Downloads/GTAI/Brochures/Industries/germanys-seaports-connecting-europe-with-the-world-en.pdf (last access: 2 April 2014), 2011.

GTAI: Industry Overview, Berlin, Germany, available at: http://www.gtai.de/GTAI/Content/EN/Invest/_SharedDocs/Downloads/GTAI/Industry-overviews/industry-overview-machinery-equipment-en.pdf (last access: 2 April 2014), 2013.

Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., and Zimmerman, P.: A global model of natural volatile organic compound emissions, J. Geophys. Res., 100, 8873–8892, 1995.

Haapanala, S., Rinne, J., Hakola, H., Hellén, H., Laakso, L., Lihavainen, H., Janson, R., O'Dowd, C., and Kulmala, M.: Boundary layer concentrations and landscape scale emissions of volatile organic compounds in early spring, Atmos. Chem. Phys., 7, 1869–1878, doi:10.5194/acp-7-1869-2007, 2007.

Haapanala, S., Hakola, H., Hellén, H., Vestenius, M., Levula, J., and Rinne, J.: Is forest management a significant source of monoterpenes into the boreal atmosphere?, Biogeosciences, 9, 1291–1300, doi:10.5194/bg-9-1291-2012, 2012.

Hakola, H., Laurila, T., Rinne, J., and Puhto, K.: The ambient concentrations of biogenic hydrocarbons at a North-European site, Atmos. Environ., 34, 4971–4982, 2000.

Hakola, H., Tarvainen, V., Laurila, T., Hiltunen, V., Hellén, H., and Keronen, P.: Seasonal variation of VOC concentrations above a boreal coniferous forest, Atmos. Environ., 37, 1623–1634, 2003.

Hakola, H., Hellén, H., Tarvainen, V., Bäck, J., Patokoski, J., and Rinne, J.: Annual variations of atmospheric VOC concentrations in a boreal forest, Boreal Environ. Res., 14, 722–730, 2009.

Hakola, H., Hellén, H., Hemmilä, M., Rinne, J., and Kulmala, M.: In situ measurements of volatile organic compounds in a boreal forest, Atmos. Chem. Phys., 12, 11665–11678, doi:10.5194/acp-12-11665-2012, 2012.

Hansen, E. and Tønnessen, A.: Environment and living conditions on the Kola Peninsula, Fafo-report 260, Fafo Institute for Applied Social Science, Oslo, Norway, 1998.

Hari, P. and Kulmala, M.: Station for measuring ecosystem – atmosphere relations (SMEAR II), Boreal Environ. Res., 10, 315–322, 2005.

Hellén, H., Hakola, H., and Laurila, T.: Determination of source contributions of NMHCs in Helsinki (60° N, 25° E) using chemical mass balance (CMB) and the Unmix multivariate receptor models, Atmos. Environ., 37, 1413–1424, 2003.

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.

Hellén, H., Hakola, H., Pirjola, L., Laurila, T., and Pystynen, K.-H.: Ambient air concentrations, source profiles and source apportionment of 71 different C_2–C_{10} volatile organic compounds in urban and residential areas of Finland, Environ. Sci. Technol., 40, 103–108, 2006.

Holzinger, R., Warneke, C., Hansel, A., Jordan, A., Lindinger, W., Scharffe, D. H., Schade, G., and Crutzen, P. J.: Biomass burning as a source of formaldehyde, acetaldehyde, methanol, acetone, acetonitrile, and hydrogen cyanide, Geophys. Res. Lett., 26, 1161–1164, 1999.

Intership to industry: The Industrial Sector in Sweden, available at: http://internship2industry.eu/tools/IndustrialSectorSweden.pdf (last access: 5 May 2014), Gothenburg, Sweden, 2009.

Jacob, D. J., Field, B. D., Li, Q., Blake, D. R., de Gouw, J., Warneke, C., Hansel, A., Wisthaler, A., Singh, H. B., and Guenther, A.: Global budget of methanol: Constraints from atmospheric observations, J. Geophys. Res., 110, D08303, doi:10.1029/2004JD005172, 2005.

Kajos, M. K., Rantala, P., Hill, M., Hellén, H., Aalto, J., Patokoski, J., Taipale, R., Hoerger, C. C., Reimann, S., Ruuskanen, T. M., Rinne, J., and Petäjä, T.: Ambient measurements of aromatic and oxidized VOCs by PTR-MS and GC-MS: intercomparison between four instruments in a boreal forest in Finland, Atmos. Meas. Tech. Discuss., 8, 3753–3802, doi:10.5194/amtd-8-3753-2015, 2015.

Kansal, A.: Sources and reactivity of NMHCs and VOCs in the atmosphere: a review, J. Hazard. Mater., 166, 17–26, 2009.

Koppmann, R. and Wildt, J.: Oxygenated Volatile Organic Compounds, edited by: Koppmann, R., Blackwell Publishing Ltd., Oxford, UK, 2007.

Lappalainen, H. K., Sevanto, S., Bäck, J., Ruuskanen, T. M., Kolari, P., Taipale, R., Rinne, J., Kulmala, M., and Hari, P.: Day-time concentrations of biogenic volatile organic compounds in a boreal forest canopy and their relation to environmental and biological factors, Atmos. Chem. Phys., 9, 5447–5459, doi:10.5194/acp-9-5447-2009, 2009.

Leino, K., Riuttanen, L., Nieminen, T., Dal Maso, M., Väänänen, R., Pohja, T., Keronen, P., Järvi, L., Aalto, P. P., Virkkula, A., Kerminen, V.-M., Petäjä, T., and Kulmala, M.: Biomass-burning smoke episodes in Finland from eastern European wildfires, Boreal Environ. Res., 19, 265–292, 2014.

Liao, L., Dal Maso, M., Taipale, R., Rinne, J., Ehn, M., Junninen, H., Äijälä, M., Nieminen, T., Alekseychik, P., Hulkkonen, M., Worsnop, D. R., Kerminen, V.-M., and Kulmala, M.: Monoterpene pollution episodes in a forest environment: indication of anthropogenic origin and association with aerosol particles, Boreal Environ. Res., 16, 288–303, 2011.

Lindinger, W., Hansel, A., and Jordan, A.: On-line monitoring of volatile organic compounds at pptv levels by means of proton-transfer-reaction mass spectrometry (PTR-MS) medical applications, food control and environmental research, Int. J. Mass. Spectrom., 173, 191–241, 1998a.

Lindinger, W., Hansel, A., and Jordan, A.: Proton-transfer-reaction mass spectrometry (PTR-MS): on-line monitoring of volatile organic compounds at pptv levels, Chem. Soc. Rev., 27, 347–354, 1998b.

Norris, G., Vedentham, R., and Duvall, R.: EPA Unmix 6.0 Fundamentals & User Guide, U. S. Environmental Protection Agency, Office of Research and Development, Washington, DC 20460, 2007.

Patokoski, J., Ruuskanen, T. M., Hellén, H., Taipale, R., Grönholm, T., Kajos, M. K., Petäjä, T., Hakola, H., Kulmala, M., Rinne, J.: Winter to spring transition and diurnal variation of VOCs in Finland at an urban background site and a rural site, Bor. Environ. Res., 19, 79–103, 2014.

Reimann, S. and Lewis, A. C.: Anthropogenic VOCs, edited by: Koppmann, R., Blackwell Publishing Ltd., Oxford, UK, 2007.

Ria Novosti: Russian Industry Against the Backdrop of the Economic Crisis, available at: http://en.ria.ru/infographics/20100408/158486046.html (last access: 3 April 2014), Moscow, Russia, 2010.

Rinne, J., Ruuskanen, T. M., Reissell, A., Taipale, R., Hakola, H., and Kulmala, M.: On-line PTR-MS measurements of atmospheric concentrations of volatile organic compounds in a European boreal forest ecosystem, Boreal Environ. Res., 10, 425–436, 2005.

Rinne, J., Taipale, R., Markkanen, T., Ruuskanen, T. M., Hellén, H., Kajos, M. K., Vesala, T., and Kulmala, M.: Hydrocarbon fluxes above a Scots pine forest canopy: measurements and modeling, Atmos. Chem. Phys., 7, 3361–3372, doi:10.5194/acp-7-3361-2007, 2007.

Rinne, J., Markkanen, T., Ruuskanen, T. M., Petäjä, T., Keronen, P., Tang, M.J., Crowley, J. N., Rannik, Ü., and Vesala, T.: Effect of chemical degradation on fluxes of reactive compounds – a study with a stochastic Lagrangian transport model, Atmos. Chem. Phys., 12, 4843–4854, doi:10.5194/acp-12-4843-2012, 2012.

Riuttanen, L., Hulkkonen, M., Dal Maso, M., Junninen, H., and Kulmala, M.: 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, Atmos. Chem. Phys., 13, 2153–2164, doi:10.5194/acp-13-2153-2013, 2013.

Ruuskanen, T. M., Kolari, P., Bäck, J., Kulmala, M., Rinne, J., Hakola, H., Taipale, R., Raivonen, M., Altimir, N., and Hari, P.: On-line field measurements of monoterpene emissions from Scots pine by proton-transfer-reaction mass spectrometry, Boreal Environ. Res., 10, 553–567, 2005.

Ruuskanen, T. M., Taipale, R., Rinne, J., Kajos, M. K., Hakola, H., and Kulmala, M.: Quantitative long-term measurements of VOC concentrations by PTR-MS: annual cycle at a boreal forest site, Atmos. Chem. Phys. Discuss., 9, 81–134, doi:10.5194/acpd-9-81-2009, 2009.

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

Simpson, D., Winiwarter, W., Börjesson, G., Cinderby, S., Ferreiro, A., Guenther, A., Hewitt, C. N., Janson, R., Khalil, M. A. K., Owen, S., Pierce, T. E., Puxbaum, H., Shearer, M., Skiba, U., Steinbrecher, R., Tarrasón, L., and Öquist, M. G.: Inventorying emissions from nature in Europe, J. Geophys. Res., 104, 8113–8152, 1999.

Simpson, I. J., Akagi, S. K., Barletta, B., Blake, N. J., Choi, Y., Diskin, G. S., Fried, A., Fuelberg, H. E., Meinardi, S., Rowland, F. S., Vay, S. A., Weinheimer, A. J., Wennberg, P. O., Wiebring, P., Wisthaler, A., Yang, M., Yokelson, R. J., and Blake, D. R.: Boreal forest fire emissions in fresh Canadian smoke plumes: C_1-C_{10} volatile organic compounds (VOCs), CO_2, CO, NO_2, NO, HCN and CH_3CN, Atmos. Chem. Phys., 11, 6445–6463, doi:10.5194/acp-11-6445-2011, 2011.

Singh, H. B., Salas, L. J., Chatfield, R. B., Czech, E., Fried, A., Walega, J., Evans, M. J., Field, B. D., Jacob, D. J., Blake, D., Heikes, B., Talbot, R., Sachse, G., Crawford, J. H., Avery, M. A., Sandholm, S., and Fuelberg, H.: Analysis of the atmospheric distribution, sources, and sinks of oxygenated volatile organic chemicals based on measurements over the Pacific during TRACE-P, J. Geophys. Res., 109, D15S07, doi:10.1029/2003JD003883, 2004.

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

Stohl, A. and Seibert, P.: Accuracy of trajectories as determined from the conservation of meteorological tracers, Q. J. Roy. Meteor. Soc., 124, 1465–1484, 1998.

Stohl, A., Wotawa, G., Seibert, P., and Kromp-Kolb, H.: Interpolation errors in wind fields as a function of spatial and temporal resolution and their impact on different types of kinematic trajectories, J. Appl. Meteorol., 34, 2149–2165, 1995.

Taipale, R., Ruuskanen, T. M., Rinne, J., Kajos, M. K., Hakola, H., Pohja, T., and Kulmala, M.: Technical Note: Quantitative long-term measurements of VOC concentrations by PTR-MS – measurement, calibration, and volume mixing ratio calculation methods, Atmos. Chem. Phys., 8, 6681–6698, doi:10.5194/acp-8-6681-2008, 2008.

Tani, A., Hayward, S., and Hewitt, C. N.: Measurement of monoterpenes and related compounds by proton-transfer-reaction mass spectrometer (PTR-MS), Int. J. Mass. Spectrom., 223–224, 561–578, 2003.

The World Factbook: Russia, available at: https://www.cia.gov/library/publications/the-world-factbook/geos/rs.html (last access: 3 April 2014), 2014a.

The World Factbook: Poland, available at: https://www.cia.gov/library/publications/the-world-factbook/geos/pl.html (last access: 3 April 2014), 2014b.

The World Factbook: Industries, available at: https://www.cia.gov/library/publications/the-world-factbook/fields/2090.html#pl (last access: 3 April 2014), 2014c.

Tunved, P., Hansson, H.-C., Kerminen, V.-M., Ström, J., Dal Maso, M., Lihavainen, H., Viisanen, Y., Aalto, P. P., Komppula, M., and Kulmala, M.: High natural aerosol loading over boreal forests, Science, 312, 261–263, 2006.

Twardosz, R. and Kossowska-Cezak, U.: Exceptionally hot summers in Central and Eastern Europe (1951–2010), Theor. Appl. Climatol., 112, 617–628, 2013.

Vesala, T., Haataja, J., Aalto, P. P., Altimir, N., Buzorius, G., Hämeri, K., Ilvesniemi, H., Jokinen, V., Keronen, P., Lahti, T., Markkanen, T., Mäkelä, J. M., Nikinmaa, E., Palmroth, S., Pohja, T., Pumpanen, J., Rannik, U., Siivola, E., Ylitalo, H., Hari, P., and Kulmala, M.: Long-term field measurements of atmosphere–surface interaction in boreal forest combining forest ecology, micrometeorology, aerosol physics and atmospheric chemistry, Trends Heat Mass Moment. Transf., 4, 17–35, 1998.

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., Levula, J., Pohja, T., Aalto, P. P., Keronen, P., Schobesberger, S., Clements, C. B., Pirjola, L., Kieloaho, A.-J., Kulmala, L., Aaltonen, H., Patokoski, J., Pumpanen, J., Rinne, J., Ruuskanen, T., Pihlatie, M., Manninen, H. E., Aaltonen, V., Junninen, H., Petäjä, T., Backman, J., Dal Maso, M., Nieminen, T., Olsson, T., Grönholm, T., Aalto, J., Virtanen, T. H., Kajos, M., Kerminen, V.-M., Schultz, D. M., Kukkonen, J., Sofiev, M., De Leeuw, G., Bäck, J., Hari, P., and Kulmala, M.: Prescribed burning of logging slash in the boreal forest of Finland: emissions and effects on meteorological quantities and soil properties, Atmos. Chem. Phys., 14, 4473–4502, doi:10.5194/acp-14-4473-2014, 2014.

Williams, J., Crowley, J., Fischer, H., Harder, H., Martinez, M., Petäjä, T., Rinne, J., Bäck, J., Boy, M., Dal Maso, M., Hakala, J., Kajos, M., Keronen, P., Rantala, P., Aalto, J., Aaltonen, H., Paatero, J., Vesala, T., Hakola, H., Levula, J., Pohja, T., Herrmann, F., Auld, J., Mesarchaki, E., Song, W., Yassaa, N., Nölscher, A., Johnson, A. M., Custer, T., Sinha, V., Thieser, J., Pouvesle, N., Taraborreli, D., Tang, M. J., Bozem, H., Hosaynali-Beygi, Z., Axinte, R., Oswald, R., Novelli, A., Kubistin, D., Hens, K., Javed, U., Trawny, K., Breitenberger, C., Hidalgo, P. J., Ebben, C. J., Geiger, F. M., Corrigan, A. L., Russell, L. M., Ouwersloot, H. G., Vilà-Guerau de Arellano, J., Ganzeveld, L., Vogel, A., Beck, M., Bayerle, A., Kampf, C. J., Bertelmann, M., Köllner, F., Hoffmann, T., Valverde, J., González, D., Riekkola, M.-L., Kulmala, M., and Lelieveld, J.: The summertime Boreal forest field measurements intensive (HUMPPA-COPEC-2010): an overview of meteorological and chemical influences, Atmos. Chem. Phys., 11, 10599–10618, doi:10.5194/acp-11-10599-2011, 2011.

Table 1. Detection limits ($\mathrm{ppb_v}$) for one hour averages of the measured VOCs during the measurement periods. Percentages of values below detection limit are presented in brackets.

VOC	DL1 (12 Jun– 26 Sep 2006)	DL2 (29 Nov 2006– 10 Jul 2007)	DL3 (12 Jul 2007– 22 Jun 2009)	DL4 (28 May 2010– 29 Dec 2011)
methanol	0.07 (1 %)	0.06 (1 %)	0.07 (1 %)	0.1 (3 %)
acetonitrile			0.004 (1 %)	0.005 (4 %)
acetaldehyde	0.02 (2 %)	0.02 (1 %)	0.02 (1 %)	0.03 (1 %)
acetone	0.02 (1 %)	0.01 (1 %)	0.02 (1 %)	0.03 (1 %)
benzene	0.005 (3 %)	0.003 (1 %)	0.005 (3 %)	0.006 (2 %)
toluene	0.02 (73 %)	0.01 (1 %)	0.02 (22 %)	0.02 (4 %)
monoterpenes	0.01 (3 %)	0.01 (19 %)	0.01 (4 %)	0.02 (12 %)

Table 2. Concentrations of hydroxyl (OH), ozone (O_3), and nitrate radicals (NO_3) used in the lifetime calculations of the VOCs.

Oxidants	winter [molecules cm^{-3}]	summer [molecules cm^{-3}]
[OH] day	5.5×10^4 [a]	1.5×10^6 [a]
[O_3] day/night	$6.8 \times 10^{11}/5.7 \times 10^{11}$	$8.6 \times 10^{11}/7.1 \times 10^{11}$
[NO_3] night	1.2×10^7 [a]	4.2×10^7 [a]

[a] Hakola et al. (2003).

Table 3. Reaction rate coefficients (k_{OH}, k_{O_3}, k_{NO_3}) and photolysis rates for the measured VOCs.

	k_{OH} [cm^3 molecules^{-1} s^{-1}]	k_{O_3} [cm^3 molecules^{-1} s^{-1}]	k_{NO_3} [cm^3 molecules^{-1} s^{-1}]	$k_{photolysis}$ in winter [s^{-1}]	$k_{photolysis}$ in summer [s^{-1}]
methanol	9.00×10^{-13} [a]		2.42×10^{-16} [d]		
acetaldehyde	1.50×10^{-12} [a]		2.72×10^{-15} [e]	1.50×10^{-6} [f]	3.27×10^{-6} [f]
acetone	1.80×10^{-13} [a]		3.00×10^{-17}[e]	2.32×10^{-7} [f]	4.85×10^{-7} [f]
benzene	1.19×10^{-12} [a]	1.70×10^{-22} [c]	3.00×10^{-17} [d]		
toluene	5.60×10^{-12} [a]	4.10×10^{-22} [c]	6.79×10^{-17} [d]		
monoterpenes	7.50×10^{-11} [b]	1.4×10^{-17} [b]	7.06×10^{-12} [b]		

Rate constants (k_{OH}, k_{O_3} and k_{NO_3}) used in calculations in Table 4: (a) iupac preferred, (b) Monoterpenes' rate constants k_{OH}, k_{O_3} and k_{NO_3} were calculated as weighted averages of individual monoterpenes typical in SMEAR II (Hakola et al., 2003), individual k values (Atkinson, 1994), (c) Atkinson, 1994, (d) http://kinetics.nist.gov/kinetics/Search.jsp, last access: 17 January 2013, (e) Rinne et al. (2007), (f) Calculated similar to Hellén et al. (2004).

Table 4. Total atmospheric lifetimes (e-folding times) of the VOCs studied, daytime and night-time in summer and winter. Daytime values are the sums of lifetimes calculated towards O_3, OH and photolysis. Night-time values were calculated towards O_3 and NO_3.

VOC	total lifetimes on a winter day	total lifetimes on a winter night	total lifetimes on a summer day	total lifetimes on a summer night
methanol	234 d	1 y	9 d	113 d
acetaldehyde	7 d	1 y	2 d	101 d
acetone	48 d	88 y	15 d	25 y
benzene	177 d	69 y	6 d	27 y
toluene	38 d	29 y	1 d	11 y
monoterpenes	1 d	3 h	1 h	0.9 h

ACPD
15, 14593–14641, 2015

Table 5. Mean VMRs of studied trace gases (ppb_v) and SDs (std) before and during the forest fire episodes in 2006 and 2010. The VMRs of the compounds were calculated from VMR data which were selected using trajectories from the burning areas. Area 1 is [27–36° E, 58–62° N] in 2006 and area 2 is [28–34° E, 56–61° N] in 2010.

Compounds	in 2006 before episode	std	in 2006 during episode	std	in 2010 before episode	std	in 2010 during episode	std
methanol	4.94	0.78	3.21	1.21	3.74	0.75	3.69	2.10
acetonitrile					0.06	0.01	0.13	0.07
benzene	0.08	0.03	0.17	0.13	0.05	0.03	0.09	0.06
sulphur dioxide	0.23	0.14	0.16	0.15	0.20	0.12	0.35	0.42
carbon monoxide	128	5	154	49	111	9	152	45

Table 6. Long-term trends of VOC VMRs calculated from summer monthly medians. A linear regression line is fitted to the summer monthly medians (Fig. 1) during the years 2006–2011. June 2006 (for acetonitrile July 2007) was used as the reference year when calculating the relative trend. The confidence intervals of the calculated trends included zero, thus the trends are not statistically significant.

Compound	Change per year [%]
methanol	−4
acetonitrile	−2
acetaldehyde	−2
acetone	−2
benzene	−8
monoterpenes	8

Table A1. Main industries of source areas.

Source area	Main industries
1. Western Russia	Oil and gas trade, shipbuilding yards, machine building, heavy machinery, mining, ferrous and nonferrous metallurgy, chemical industry and energy and paper production[1]
2. Northern Poland, Kaliningrad and Baltic countries	Machinery and chemical industry: chemicals, petroleum and refining, shipbuilding and coal mining[2], forestry with wood and processed wood products, chemical, pharmaceuticals, plastic and rubber industry, metal and electronics industry[3]
3. Karelia and White Sea	Forest industry, ferrous and non-ferrous metallurgy, coastal areas of the White Sea: oil production and processing[4]
4. Kola Peninsula and Barents Sea	Mining, iron industry (iron-ore enterprises and separators), apatite production and other metal industry such as aluminum and nickel plants and smelters[5], petroleum industry[6]
5. Bay of Bothnia	Metallurgy and wood and timber industry[7]
6. Coast of Norwegian Sea and Northern Sweden	Machinery, metal industry and mining [7,8]
7. Stockholm area	Electronics and chemical industry, machinery[7]
8. Skagerrak	Machinery, metallurgy and chemical industry[7]
9. North Sea and coastal areas	Oil production[9]
10. Northern Germany	Chemicals, plastics, electronics and automotive industry[10], dockyards for shipbuilding, metal industry and machinery[11]

[1] Ria Novosti (2010); World Factbook (2014a); [2] World Factbook (2014b); [3] Industries (2014c); [4] Artic Centre (2005); [5] Hansen and Tønnessen (1998); [6] Austvik (2007); [7] Internship to industry (2009); [8] Bothnian green logistics corridor (2012); [9] EIA (2014); [10] GTAI (2013); [11] GTAI (2011).

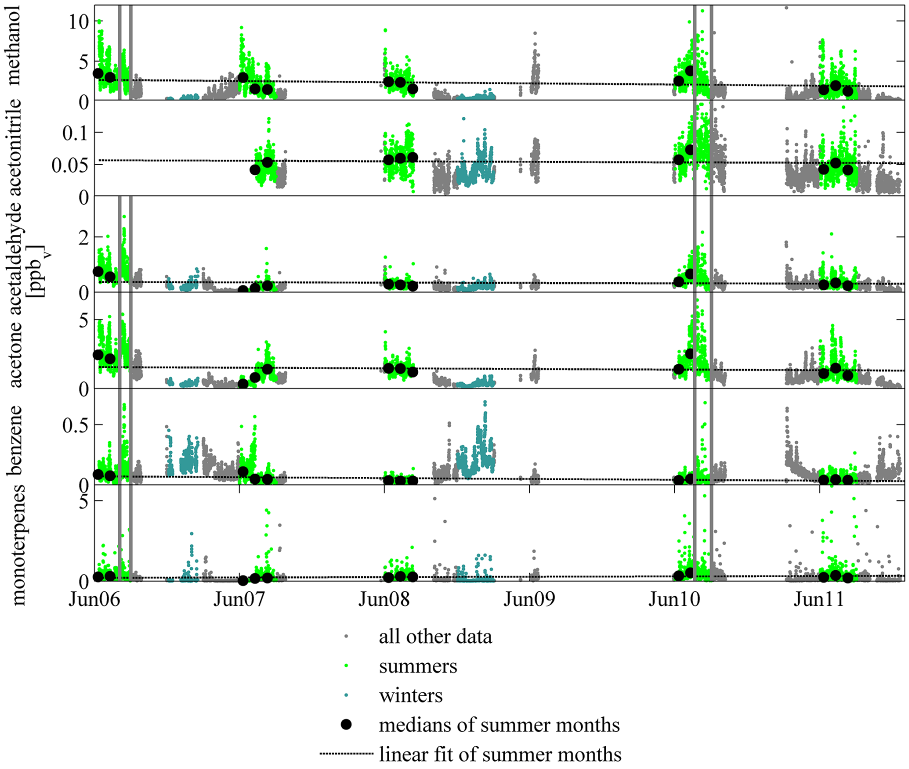

Figure 1. Time-series of the VMRs of the VOC studied during the measurement period. Summertime data used in source area analysis are marked in green and winter data in light blue. Data from other seasons are marked in grey. The monthly medians of the summer months are marked with black dots, and a linear fit based on summer-month medians is marked with a black dashed line. The forest fire periods in the summers of 2006 and 2010 are marked with grey vertical lines.

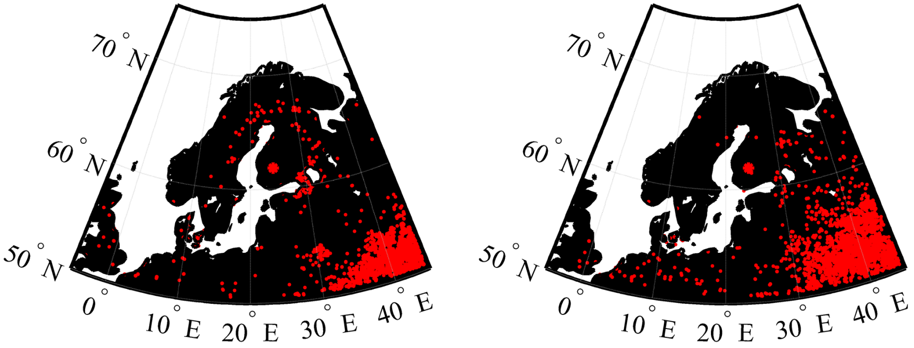

Figure 2. Map of forest fire locations during the forest fire episodes of the summers of 2006 (left) and 2010 (right). In 2006, the forest fire event occurred during 4–31 August and in 2010 during 20 July to 31 August. These maps depict the sum of all observed fire spots during the burning periods, each being shown by a dot. Data of forest fire locations are taken from the Fire Information Resource Managements System (FIRMS). The SMEAR II site is marked by a star in the map.

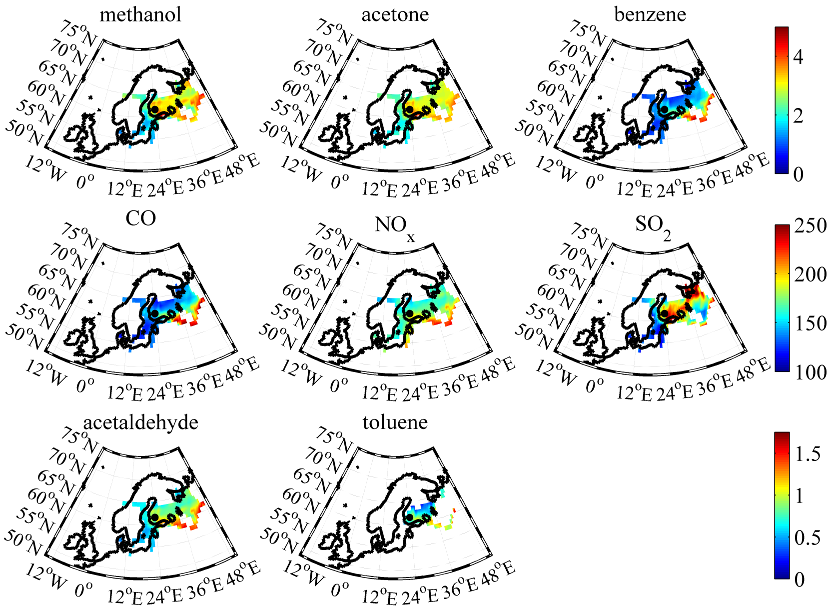

Figure 3. Mean trajectory fields for selected VOCs and trace gases (ppb$_v$) during the forest fires in summer 2006. VMR scales are presented on the right, with the scale for each compound being multiplied in the case of each compound by the indicated factor 10, 100 or 1000 if needed. Topmost row: methanol, acetone and benzene (multiplied by 10). Middle row: CO, NO$_x$ (multiplied by 10) and SO$_2$ (multiplied by 100). Bottom row: acetaldehyde and toluene (multiplied by 10). The SMEAR II site is marked by a dot in the map.

Title Page
Abstract
Introduction
Conclusions
References
Tables
Figures
◄
►
Back
Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◀◀ | ▶▶
◀ | ▶
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

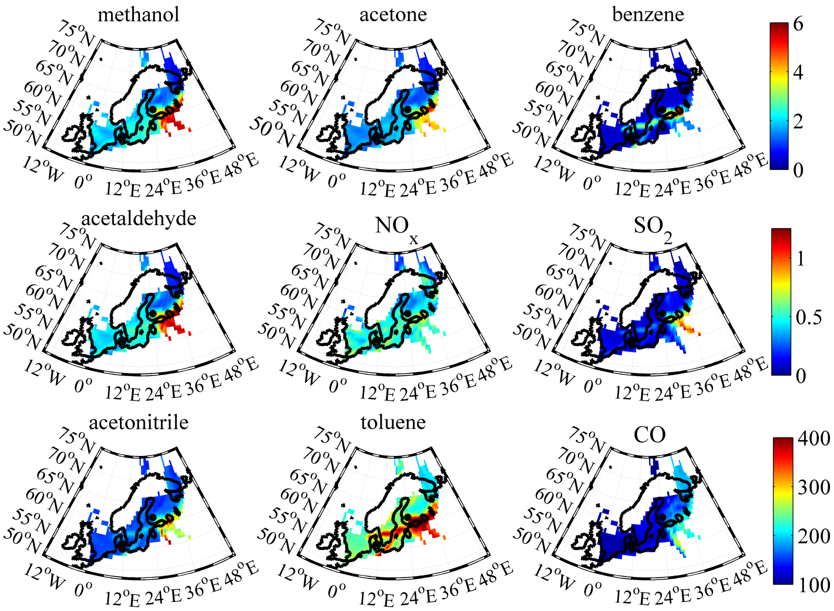

Figure 4. Mean trajectory fields for selected VOCs and trace gases (ppb$_v$) during the forest fires in summer 2010. VMR scales are presented on the right, with the scale for each compound being further multiplied in the case of each compound by the indicated factor 10, 100 or 1000 if needed. Topmost row: methanol, acetone and benzene (multiplied by 10). Middle row: acetaldehyde, NO$_x$ and SO$_2$. Bottom row: acetonitrile (multiplied by 1000), toluene (multiplied by 1000) and CO. The SMEAR II site is marked by a dot in the map.

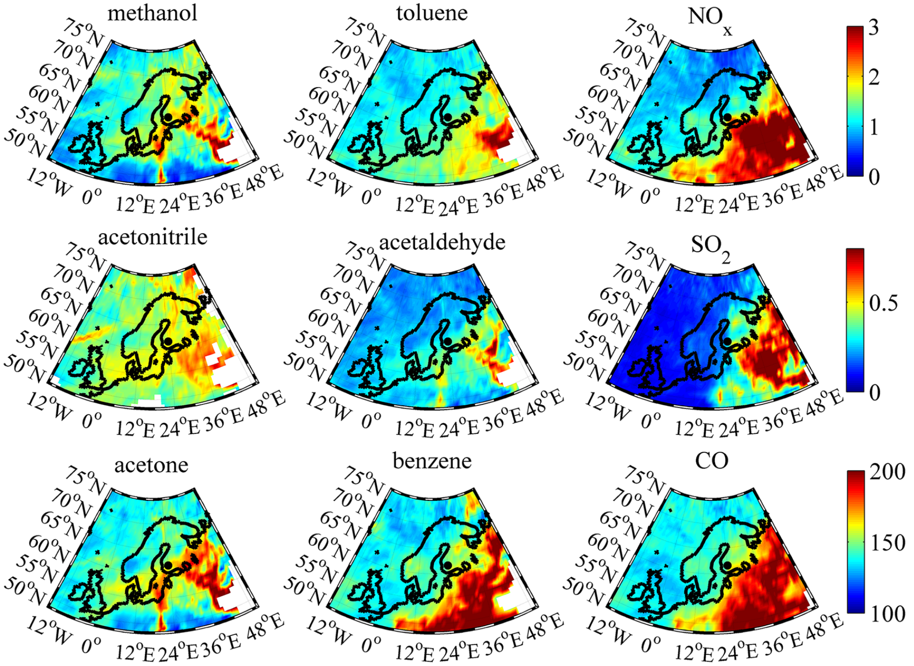

Figure 5. Mean trajectory fields (2006–2011) of selected VOCs and trace gases (ppb$_v$). VMR scales are presented on the right, with the scale for each compound being further multiplied in the case of each compound by the indicated factor 10, 100 or 1000 if needed. Topmost row: methanol, toluene (multiplied by 10) and NO$_x$. Middle row: acetonitrile (multiplied by 10), acetaldehyde, SO$_2$. Bottom row: acetone (multiplied by 100), benzene (multiplied by 1000) and CO. The SMEAR II site is marked by a dot in the maps.

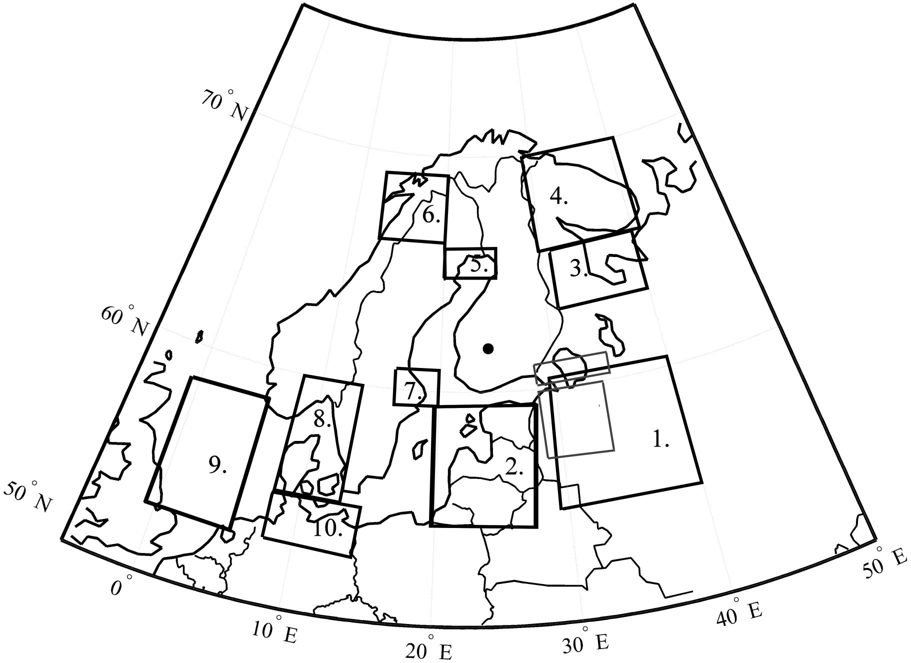

Figure 6. Main source areas of VOCs: (1) Western Russia, (2) Northern Poland, Kaliningrad and Baltic countries, (3) Karelia and the White Sea, (4) Kola Peninsula and Barents Sea, (5) Bay of Bothnia, (6) Coast of Norwegian Sea and Northern Sweden, (7) Stockholm area, (8) Skagerrak, (9) North Sea and coastal areas, (10) Northern Germany. Two forest fire source areas, limited in time, are marked by grey boxes. These are treated separately for the episodes (see Table 5) The SMEAR II site is marked by a dot in the map.

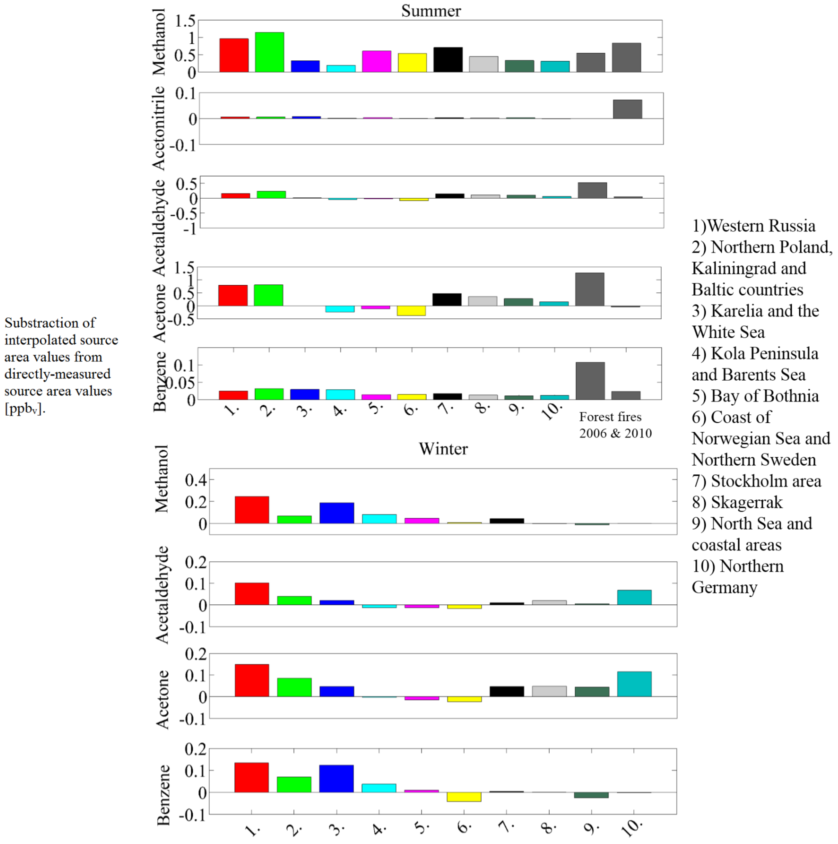

Figure 7. Hourly VMR values of source areas interpolated from monthly medians were subtracted from directly-measured hourly values of source areas during summer (upper panel) and during winter (lower panel) for methanol (m 33), (acetonitrile (m 42), in summer only), acetaldehyde (m 45), acetone (m 59) and benzene (m 79).

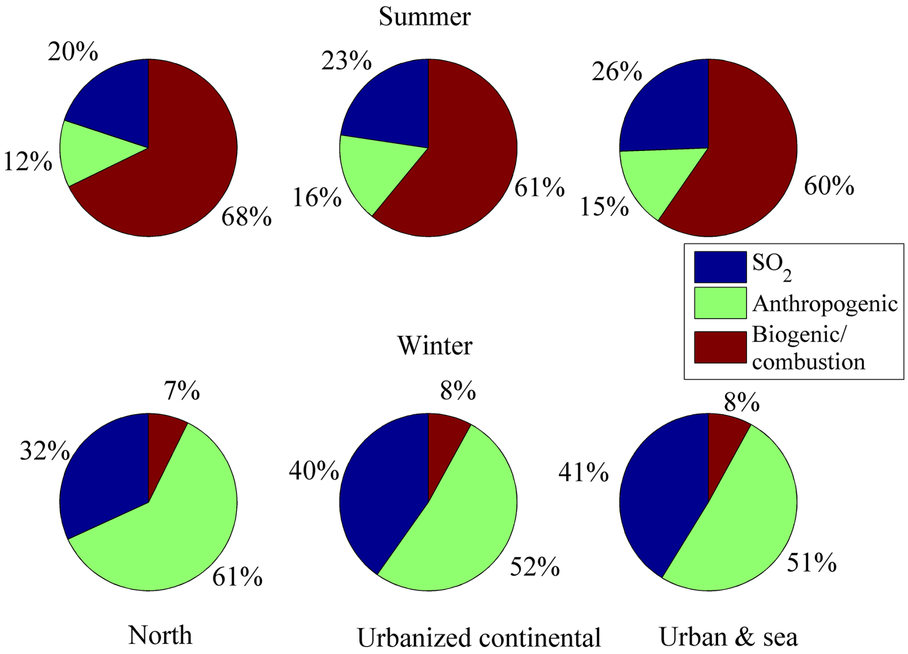

Figure 8. Pie charts of mean values of sources in each sector during summer (June–August) (topmost row) and during winter (December–February) (bottom row). The North sector includes data from direction 0–5 and 300–360°, Urbanized continental from 5–210° and Urban and sea sector from 210–300°.

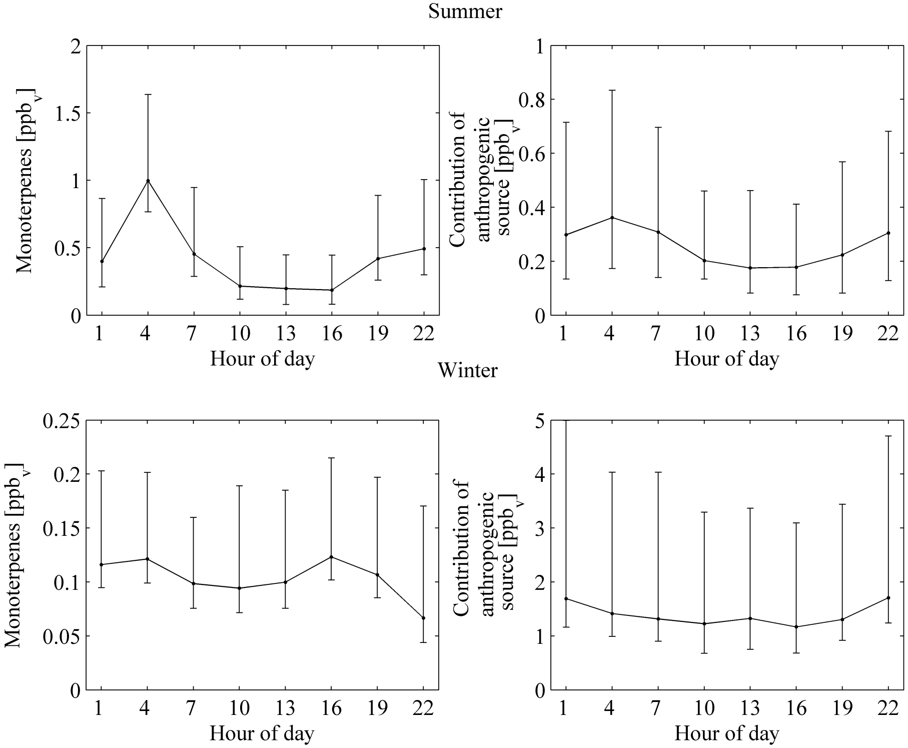

Figure 9. Diurnal cycles of monoterpenes (left) and the diurnal cycle of the anthropogenic source's contribution (right) in summer (top row) and in winter (bottom row) are presented as mean values and 20 to 80 percentiles. Data in all figures are from the urbanized continental sector.

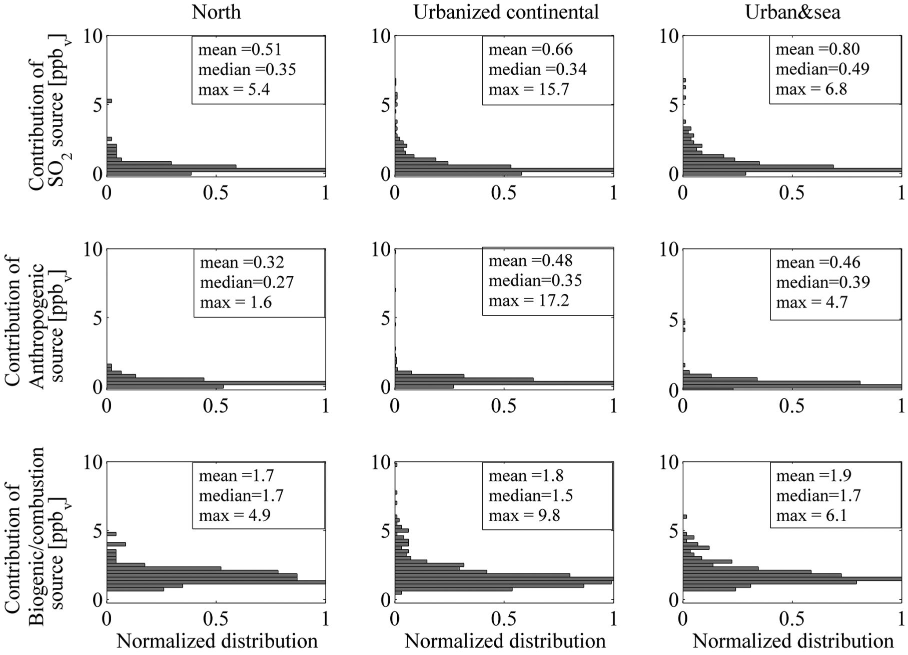

Figure 10. Normalized distributions of different sources in three sectors during the summer. The first column is the North sector ($N = 338$), the second column is the Urbanized continental sector ($N = 1817$) and the third column is the Urban and sea sector ($N = 952$). In the topmost row all panels are distributions of the SO_2 source, the middle row the anthropogenic source and the lowest row biogenic/combustion source. Each sector has been normalized with the maximum value of the observations. Mean, median and maximum values of source contributions are shown for each sector.

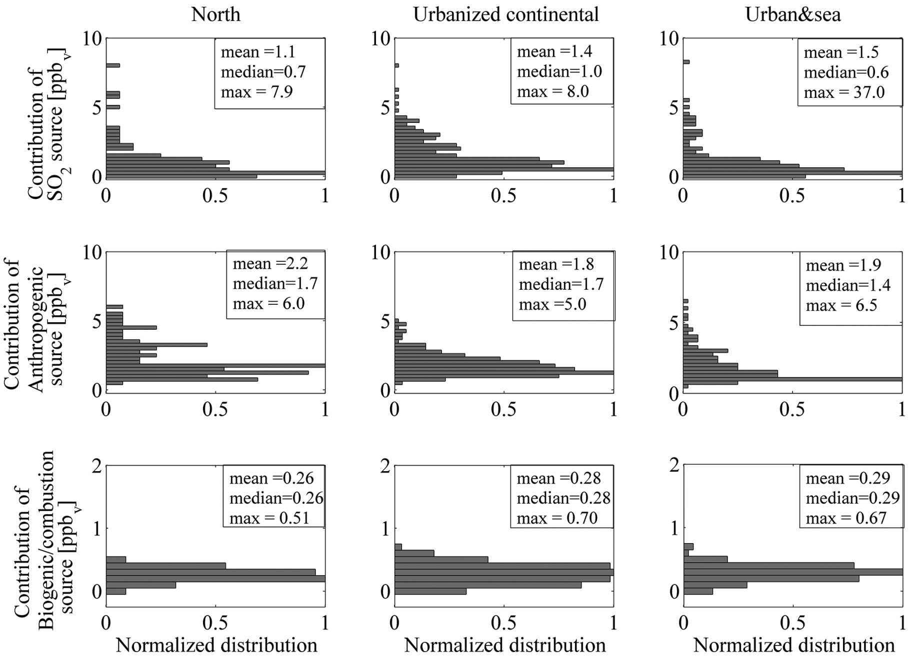

Figure 11. Normalized distributions of different sources in three sectors during the winters. The first column is the North sector ($N = 142$), the second column is the Urbanized continental sector ($N = 714$) and the third column is the Urban and sea sector ($N = 391$). In the topmost row all panels are distributions of the SO_2 source, the middle row the anthropogenic source and the lowest row the biogenic/combustion source. Each sector has been normalized with the maximum value of the observations. Mean, median and maximum values of source contributions are shown for each sector.

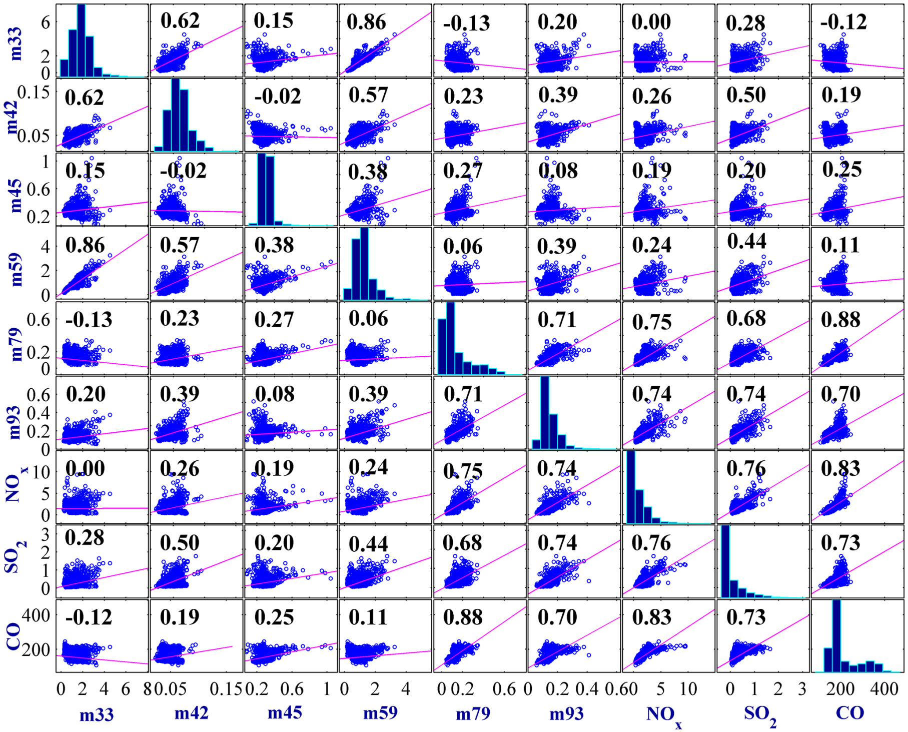

Figure A1. Correlation matrix for calculated trace gas (m 33 (methanol) m 42 (acetonitrile) m 45 (acetaldehyde) m 59 (acetone) m 79 (benzene) m 93 (toluene) NO_x (nitrogen oxides) CO (carbon monoxide) and SO_2 (sulfur dioxide)) correlations. Diagonal in the matrix is distribution of data.