Winter to spring transition and diurnal variation of VOCs in Finland at an urban background site and a rural site

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We measured volatile organic compound (VOC) volume mixing ratios (VMRs) using a quadrupole proton-transfer-reaction mass spectrometer, and investigated the differences between winter and spring VMRs and sources at an urban background site in Helsinki (2006) and a rural site in Hyytiälä (2007) utilizing a receptor model EPA Unmix. In Helsinki, VMRs of VOCs were typically higher, and their diurnal variations were more pronounced than at the rural site. At both sites, monoterpenes have anthropogenic influence in winter, while in spring biogenic influence is dominating. At the urban background site, the main aromatic hydrocarbon source was traffic, which also explained most of the oxidized VOCs during the urban winter. At other times and at the rural location most of oxidated VOCs originated mainly from distant sources. At the rural site, traffic and distant sources contributed equally to the aromatics in winter but in spring the distant source dominated.

Introduction

Volatile organic compounds (VOCs) in the atmosphere have both anthropogenic and biogenic sources. Vegetation is known to be the major source of biogenic organic gases, and to dominate the overall VOC emission into the atmosphere (Müller 1992, Guenther *et al*. 1995, Goldstein and Galbally 2007). Even in densely populated Europe, there are countries where biogenic emissions surpass the anthropogenic ones. In Finland, the biogenic emissions are estimated to be twice as high as the anthropogenic ones (Simpson *et al*. 1999, Lindfors *et al*. 2000). However, in more densely populated areas, such

as central Europe, the anthropogenic VOC emissions dominate over the biogenic ones (Simpson *et al*. 1999). Main sources of anthropogenic VOCs are extraction, refining and incomplete burning of fossil fuels, evaporation of solvents as well as heat and electrical power generators (Blake *et al*. 2009). In the sparsely populated northern Europe, winter emissions may be dominated by anthropogenic emissions as biogenic emissions during that time are small due to cold weather and dormant vegetation (Tarvainen *et al*. 2007). The dominant sources of VOCs depend on the area and season considered. In Finland, VOC concentrations during the growing season in rural and remote locations are domi-

nated by biogenic compounds, but in winter by anthropogenic compounds (Hakola *et al.* 2000). Studies in urban locations have identified multiple anthropogenic sources such as traffic, wood combustion, dry cleaning, diesel vapour, liquid diesel, city gas and gasoline evaporation (Hellén *et al.* 2006, 2012), as well as saw mills and other heavy industry. Out of these sources, traffic has the strongest diurnal variation. Long distance transport of VOCs in air masses from areas with more anthropogenic influence e.g. from densely populated areas in continental Europe is also observed in Finland (Ruuskanen *et al.* 2009). Anthropogenic sources in Helsinki also include shipping and harbor sources, and several power plants.

VOCs play an important role in atmospheric chemistry because they react in the air with oxidants such as O_3, NO_3 and OH radicals and produce new oxidation products, which take part in chemical reactions in the atmosphere (Atkinson and Arey 2003). VOCs are known to participate in tropospheric ozone formation and destruction processes (Chameides *et al.* 1992), and in aerosol particle growth (Tunved *et al.* 2006).

Many previous studies on atmospheric VOCs relied on on-site sampling and subsequent laboratory analyses (e.g. Hellén *et al.* 2002, Hakola *et al.* 2003). Thus, the data did not consist of continuous time series and, for example, diurnal behaviour of many compounds remained uncertain. Few studies utilizing continuous on-line VOC concentration measurements in northern Europe were conducted in rural or remote areas (Rinne *et al.* 2005, Lappalainen *et al.* 2009, Hakola *et al.* 2012). Many studies concentrated on the summer events, while winter and spring with a change in biogenic activity were not studied. Thus, the temporal behaviour of VOC VMRs at the northern-latitude urban background and rural areas is not yet well characterized particularly during the winter to spring transition. Temperature and radiation increase rapidly during the transition period from winter to the start of the growing season in spring. The spring awakening and the coincident increase in photochemical activity and biogenic emissions have been identified as an important feedback mechanism connecting the biosphere and the atmosphere (Dal Maso *et al.* 2009, Kulmala *et al.* 2004).

In this study, we measured VOC mixing ratios continuously with a quadrupole proton-transfer-reaction mass spectrometer (PTR-MS; Lindinger *et al.* 1998a, de Gouw and Warneke 2007). The ambient VOC VMRs were measured both at an urban background site and in a rural location in Finland for several months during winter and spring. Our aim was to study the differences in VMRs and diurnal cycles of the VOCs between these two sites. Our interest was also to reveal how the influences of different sources on ambient VMRs of VOCs differ in winter and spring between the two locations. Sources of VOC were studied with a receptor model together with changes in ambient inorganic trace gases (NO_x, O_3, CO) and aerosol particles.

Methods

In this study, an urban background measurement site SMEAR III in Helsinki (Järvi *et al.* 2009) was compared with a rural measurement site SMEAR II (Hari and Kulmala 2005) in Hyytiälä.

At the urban background site, the measurements were conducted from 1 January to 30 April 2006. For the analysis, the measurement period was divided into two seasons: the period from 9 January to 9 February 2006 was considered the urban background winter, while the period 1–30 April 2006 was considered the urban background spring. The measurements carried out between these two periods describe transition from winter to spring. During winter in Finland days are quite short. In Helsinki and Hyytiälä, there is approximately six hours of daylight in January. However, at the end of April the amount of the daylight increases to about 16 hours. At the urban background site, the volume mixing ratios (VMRs) of VOCs were measured every hour.

At the rural site, the measurements were conducted from 1 January to 30 April 2007. The period chosen for the rural winter was 1–31 January, and for rural spring 1–30 April. At the rural site, our sampling protocol changed between January and April. In January, the measurement sequence consisted of one-hour VMR measurements followed by and one-hour disjunct eddy covariance measurements (Rinne *et al.* 2007). In other words, VMR data were obtained every

second hour. In March 2007, a chamber with a Scots pine shoot was added to the measurement cycle. In April, VOC VMRs were measured every third hour because of addition of a third measurement period which also changed the timing of the measurements.

At both measurement sites, the following VOCs were measured with the PTR-MS: methanol (M33), acetaldehyde (M45), acetone (M59), isoprene, methylbutenol (MBO) fragments and furan (M69), methylvinylketone (MVK) or methacrolein (M71), methyl ethyl ketone (MEK) (M73), benzene (M79), methylbutenol (M87) toluene (M93), hexenal (M99), hexanal and *cis*-3-hexenol (M101) and monoterpenes (M137). The measurements at the two sites took place in consecutive years and annual differences in emission as well as weather and air mass transport conditions may affect the measured VOC VMRs. To minimize the effect of inter-annual variation, the periods describing winter and spring were selected so that they would describe the main characteristics of the two seasons and we assume that the monthly median VMRs of the two different years represent typical winter and spring. We calculated one-hour VOC VMRs averages for SMEAR II and III from about a hundred measurement cycles in which each VOC was integrated for two seconds consequently. All the data are presented in local winter time (UTC + 2 hours).

Description of the measurement sites

SMEAR III (Station for Measuring Ecosystem–Atmosphere Relations III; *see* Fig. 1) is an urban background measurement station in Helsinki, southern Finland (60°12′N, 24°58′E, 26 m a.s.l.). Helsinki metropolitan area includes Helsinki and its three neighbouring cities (Espoo, Vantaa and Kauniainen) with a total population of about one million. The SMEAR III station is located five kilometres northeast of downtown Helsinki. The surroundings are heterogeneous, comprising both vegetated areas and roads. The nearest major road is 150 m from the SMEAR III measurement tower and traffic rates are monitored at distance of 2.5 km by the Helsinki City Planning Department (Järvi *et al.* 2009). In
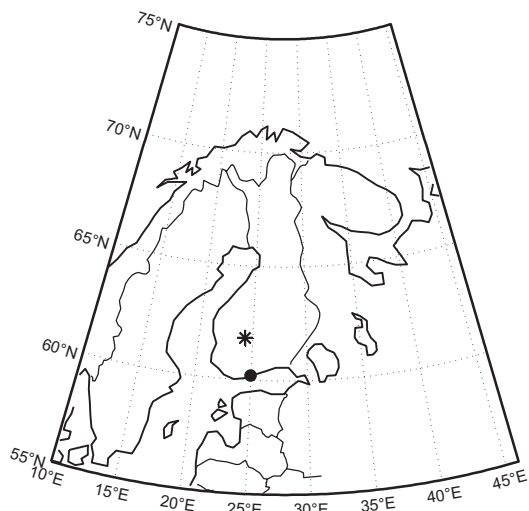

Fig. 1. Locations of the measurement sites: dot is the urban background site SMEAR III in Helsinki, and star is the rural site SMEAR II in Hyytiälä.

winter, the morning rush hour starts at 08:00 and ends at 09:00, and the afternoon rush hour starts at 16:00 and ends at 17:00. Due to daylight saving time, the respective rush-hour times in spring are 06:00–07:00 and 14:00–15:00 (Fig. 2). The SMEAR III site and the measurement techniques are described in detail in Vesala *et al.* (2008) and Järvi *et al.* (2009).

SMEAR II (Station for measuring Ecosystem–Atmosphere Relations II; *see* Fig. 1) is a rural station located in a forested area in Hyytiälä, southern Finland (61°51′N, 24°17′E, 180 m a.s.l.) 220 kilometres from Helsinki and 60 kilometres from Tampere. Tampere is the largest city near SMEAR II with the population of about 200 000. The canopy height around the measurement tower is about 16 metres. At SMEAR II, continuous long term measurements of trace gases, aerosol particles and micrometeorology are carried out (Vesala *et al.* 1998). The forest surrounding the station is dominated by Scots pine (*Pinus sylvestris*) sowed in 1964. There is also some Norway spruce (*Picea abies*), aspen (*Populus tremula*) and birch (*Betula* sp.) (Hari and Kulmala 2005). Norway spruce is a monoterpene and isoprene emitter. Terpenoid emissions from Scots pine largely consist of monoterpenes while isoprene and MBO emissions are of minor importance (Janson and de Serves 2001).
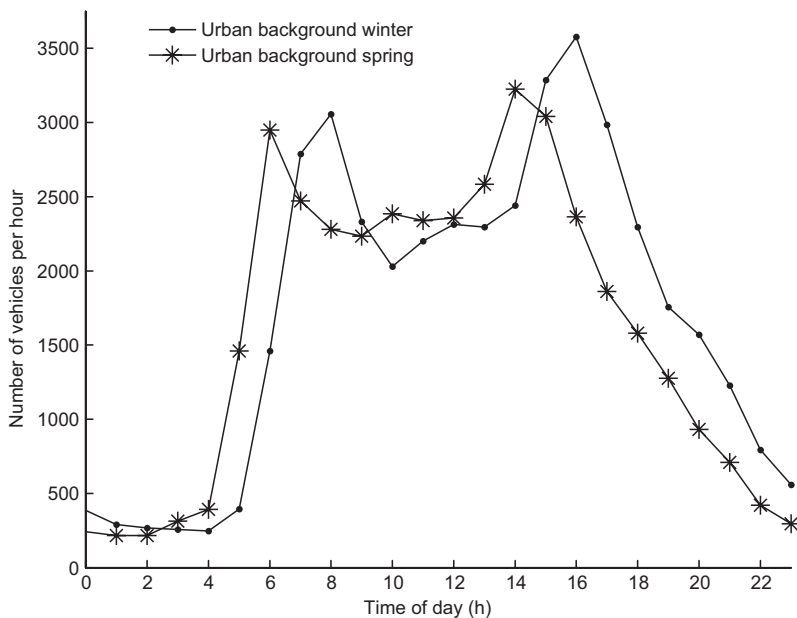
Fig. 2. Numbers of vehicles per hour near the urban background site SMEAR III in winter and spring.

Monoterpene emissions at SMEAR II have their maxima at afternoons and minima at nights (Ruuskanen *et al*. 2005, Rinne *et al*. 2007). Vegetation surrounding the SMEAR II forest is more uniform than around SMEAR III, where the vegetation is park-like with a very complex composition including planted trees as well as the University Botanical Garden and an allotment garden (Vesala *et al*. 2008). Trees in the vicinity of SMEAR III are mainly birch (*Bedula* sp.), Norway maple (*Acer platanoides*), aspen (*Populus tremula*), goat willow (*Salix caprea*) and bird cherry (*Prunus padus*).

Instrumentation and sampling setup

At both measurement sites, we measured VOCs with a quadrupole proton-transfer-reaction mass spectrometer (PTR-MS, Ionicon Analytik GmbH). In the PTR-MS, hydronium ion (H_3O^+) is used as a primary reactant ion. VOCs, which have a larger proton affinity than H_2O, will readily react with H_3O^+ (Lindinger *et al*. 1998a, 1998b) making this method suitable for the atmospheric VOC measurements. the PTR-MS uses a soft ionization method and many compounds do not fragment at all (Tani *et al*. 2003). The reagent ion is formed from water vapor by a hollow cathode discharge

in an ion source. VOCs subsequently react with the hydronium ions. The reactant and the product ions (M+1) are mass filtered with a quadrupole mass spectrometer and detected with a secondary electron multiplier (SEM). VOCs were identified based on their protonated masses, e.g. methanol at M33. An advantage of the PTR-MS is its ability to measure online and without pre-treatment of the samples. The PTR-MS has a high sensitivity (10–100 parts per trillion by volume [pptv]) for a suite of VOCs and a fast response time (0.1–10 s) (de Gouw *et al*. 2003, Warneke *et al*. 2003). During our measurements, we calibrated the PTR-MS weekly or every second week with a VOC calibration gas mixture (Apel-Riemer Environmental Inc.). The calibration procedure and the VMR calculation methodology are presented in detail by Taipale *et al*. (2008).

At SMEAR III, we measured ambient air VOC VMRs continuously at a height of the fourth floor of the University of Helsinki building next to a small street. The inlet consisted of 1.5-m PTFE tube with an inner diameter of 8 mm, and 0.5-m tube with an inner diameter of 1.6 mm going into the PTR-MS instrument. In the 1.5-m tube, an extra flow of 15 l min⁻¹ was used to avoid losses of the compounds on the walls of the inlet tube. The flow to the PTR-MS through the 0.5-m tube was 0.1 l min⁻¹. At SMEAR II, we measured

ambient air VOC VMRs at the height of 14 m inside the canopy from a scaffolding tower. The air was sampled continuously with a flow of 17.5 l min⁻¹ through a heated, 30-m-long PTFE tubing with an inner diameter of 8 mm. From the data gathered at SMEAR II, we removed those that arrived when wind was coming from the directions between 125° and 145° due to an occasional influence of a sawmill, located upwind. The sawmill has been identified as a major source of monoterpenes (Eerdekens *et al*. 2009, Williams *et al*. 2011, Liao *et al*. 2011).

The detection limit (DL) for each compound was calculated from the calibration measurement as described by Taipale *et al*. (2008). In this study, we calculated hourly averages of our measured raw data and calculated the DL as follows:

$$DL = \frac{2\sigma_0}{\sqrt{N}} \qquad (1)$$

where N is the number of data points during one hour and σ_0 is the standard deviation of the zero measurements. The DLs for both sites are listed in Appendix in Table A1.

Ancillary data

For both sites, we calculated friction velocities (u^*) from the Eddy Covariance (EC) measurements. Wind was measured with Metek USA-1 at SMEAR III at 31 m hight and at SMEAR II at 23.3 m height (Vesala *et al*. 1998, Vesala *et al*. 2008, Järvi *et al*. 2009).

At SMEAR II, mixing ratios of nitrogen oxides (NO_x) were measured using a chemiluminescence technique (Thermo Instruments, model TEI 42C TL), and O_3 by an ultraviolet light absorption technique (Thermo Instruments, TEI 49). Carbon monoxide (CO) was measured with an infrared light absorption analyzer (HORIBA APMA 360, Horiba, Japan). We measured the trace gas mixing ratios at 8.4 m height.

Aerosol particle concentrations were measured using a twin Differential Mobility Particle Sizer (DMPS, Aalto *et al*. 2001), which uses Hauke-type Differential Mobility Analyzers (Winklmayr *et al*. 1991), one with a length of 10.9 cm for particle size range 3–50 nm accom-

panied with a TSI model 3025 Condensation Particle Counter (CPC), and the other with a 28.0 cm DMA connected to a TSI model 3010 CPC. The system provides sub-micron aerosol number size distribution from 3 nm to 1000 nm with 10-min resolution.

Receptor model

We studied source compositions and contributions using a multivariate receptor model EPA Unmix 6.0 (Norris *et al*. 2007) developed by Ronald Henry from the University of Southern California. A basic problem of multivariate receptor models is how to determine the most optimal number of sources, source fingerprints and their contributions, from the ambient air VOC measurement data alone. Some additional constrains must be added to be able to obtain a unique solution. In Unmix, the composition and contribution of the sources must be nonnegative. In addition to this, Unmix searches for times, when the data indicates that the contribution of one of the sources is missing completely or its contribution is minor. Application of Unmix to the VOC data in combination with the data from chromatographic methods in Helsinki is described in Hellén *et al*. (2003).

According to the recommendations of the model, the coefficient of determination (r^2) of the regression between each of the species explained by the sources should be over 0.8 while the signal-to-noise ratio should be over 2. In this study, we applied Unmix for all the four measurement periods and all the results exceeded the recommended r^2 and signal-to-noise values deeming the receptor modeling results applicable and valid. As an input data, we used hourly averaged trace gas and particle data.

Results and discussion

Median volume mixing ratios and diurnal cycles of the VOCs

Generally, the medians of the volume mixing ratios (VMRs) of most of VOCs were higher at the urban background site in Helsinki than in the

rural Hyytiälä (Fig. 3A–D, Tables A2 and A3). Only monoterpenes (M137) and hexanal (M101) had lower median VMRs at the urban background site than at the rural site. At both sites, the medians of VMRs were mostly higher in spring than in winter. Exceptions were methanol at the urban site, and toluene and benzene at both sites. Isoprene, MVK and methacrolein as well as hexanal medians were almost constant during winter and spring at the rural site.

In the urban background Helsinki data, the median VMRs in January were lower than in February and March (Fig. 3A and B). A potential explanation is that during 2006 the Christmas holidays continued until 8 January, reducing the traffic intensity around the measurement site. After 8 January, VMRs were clearly higher than at the beginning of the month, and typical morning and afternoon rush-hour maxima in traffic-related VOCs from the nearby road were recorded. Therefore, we selected a period from 9 January to 9 February 2006 to represent a typical urban background winter period.

We calculated OH, O_3 and NO_3 oxidation rates, photo-oxidation rates and lifetimes for measured VOCs in order to define the primary oxidants for each VOC. The OH and NO_3 radical concentrations were taken from Hakola *et al*. (2003). The summertime OH from Hakola *et al*. (2003), fits well with measurements by Rinne *et al*. (2012). However, the summertime NO_3 radical concentration is at least two times higher than the measured by Rinne *et al*. (2012). Thus, we scaled the annual cycle of NO_3 as presented by Hakola *et al*. (2003) by dividing it by 2. We used the same OH and NO_3 values for the urban background and rural sites as the solar angle and cloudiness at the two sites are similar. Hellén *et al*. (2004) calculated photolysis rates for Hyytiälä in spring midday clear sky conditions. We approximated winter values of photolysis rates from spring values by scaling them with radiation. Thus we multiplied spring values by 0.31; (for reaction rate coefficients (k_{OH}, k_{O3}, k_{NO3}) and photolysis rate constants for winter and spring *see* Table A4, and for lifetimes for each measured VOCs *see* Tables A5–A8).

In this study, we discuss VOCs — methanol, benzene, toluene and monoterpenes — with various lifetimes and sources. Of these, monot-erpenes represent a typical reactive compound with mainly biogenic sources, toluene and benzene are compounds with mainly anthropogenic sources, and methanol has both biogenic and anthropogenic sources and a long lifetime.

Methanol

At the urban background station, the winter and spring median VMRs of methanol (M33) were 1.66 and 1.17 ppbv, respectively. At the rural site, the medians were an order of magnitude lower in winter, 0.19 ppbv, and increased in spring to 0.64 ppbv. The rural winter value was at the same level as Boudries *et al*. (2002) and Heikes *et al*. (2002) reported earlier from remote Arctic (0.20 ppbv) and Arctic (0.25 ppbv). Sellegri *et al*. (2005) also measured methanol VMRs at the rural Hyytiälä site during spring, and in their study the values varied from 0.23 to 0.43 ppbv which is similar to this study.

At the urban background site, methanol (M33) had the lowest VMRs at night and early morning and the highest during daytime (Fig. 4A). In both periods, VMRs were rising sharply during the morning rush hour, and again in the afternoon. These variations follow the corresponding variation in traffic rates. At the rural site, there was no diurnal variation in winter, and diurnal variation in spring was marginal (Fig. 5A). In contrast to the urban background site, methanol VMRs at the rural site were higher in spring than in winter.

The difference in the seasonal behaviour of methanol mixing ratio between the sites suggests that methanol sources affecting the atmospheric concentrations are different in these two locations. In the urban background area, with high VMRs in winter, methanol is likely to be strongly affected by local anthropogenic sources from nearby traffic. Especially in winter, this can be partly from cold starts of cars. Other local sources of methanol can be various industrial processes and solvents (Jacob *et al*. 2005). Also, the strong diurnal cycle of methanol in winter and spring suggests a local source (Fig. 4A). Diurnal cycle in winter is stronger than in spring. Even though daytime mixing time scales, z/u^* (where z is the measurement height, and u^* is
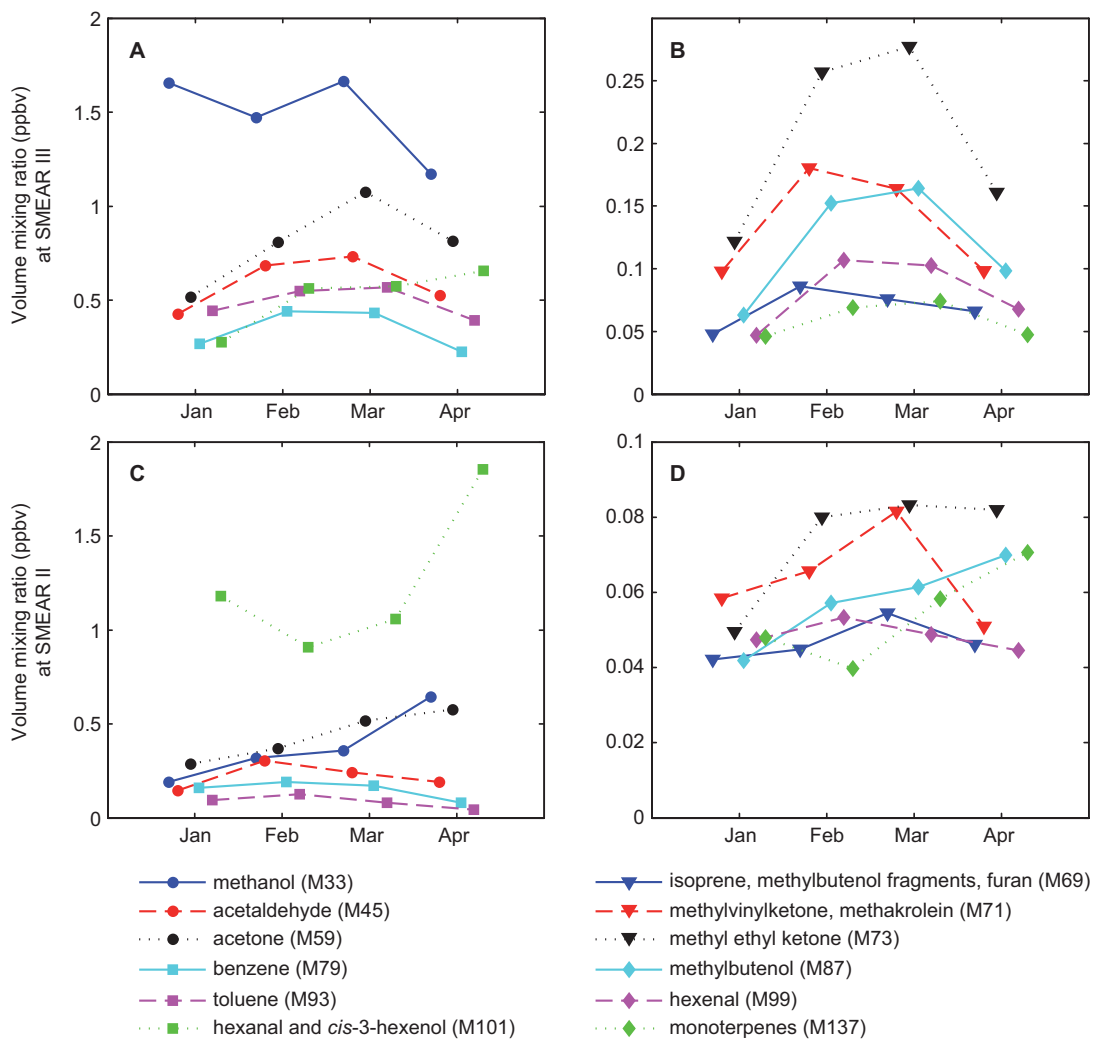
Fig. 3. Monthly medians of measured VOCs at (**A** and **B**) the urban background SMEAR III site, and (**C** and **D**) the rural SMEAR II site.

the friction velocity), are similar in winter and spring (Fig. 6A), it is likely that the boundary layer is shallower in winter leading to higher daytime VMRs. Also the methanol lifetime towards OH in winter (234 days) is much longer than in spring (16 days) (Table A5). At the rural site, on the other hand, the seasonal behaviour with mixing ratio increasing in spring and an absence of a strong diurnal cycle suggests a mostly regional photochemical and/or biogenic source starting to contribute in spring. This is expected due to the start of biogenic activity in nature in April in Finland (Hakola *et al.* 2003, Dal Maso *et al.* 2009).

Aromatic hydrocarbons

At the urban background site, the monthly median mixing ratio of benzene (M79) was 0.27 ppbv in winter and 0.23 ppbv in spring. The toluene (M93) VMR was 0.44 and 0.39 ppbv in winter and spring, respectively. As compared with the earlier results from Helsinki (Hellén *et al.* 2002, 2012), the winter values for benzene were lower whereas the spring values were slightly higher. For toluene, both values were somewhat higher in this study as compared with those reported by Hellén *et al.* (2012). At the rural site, the median VMRs of benzene and toluene were 0.16 ppbv
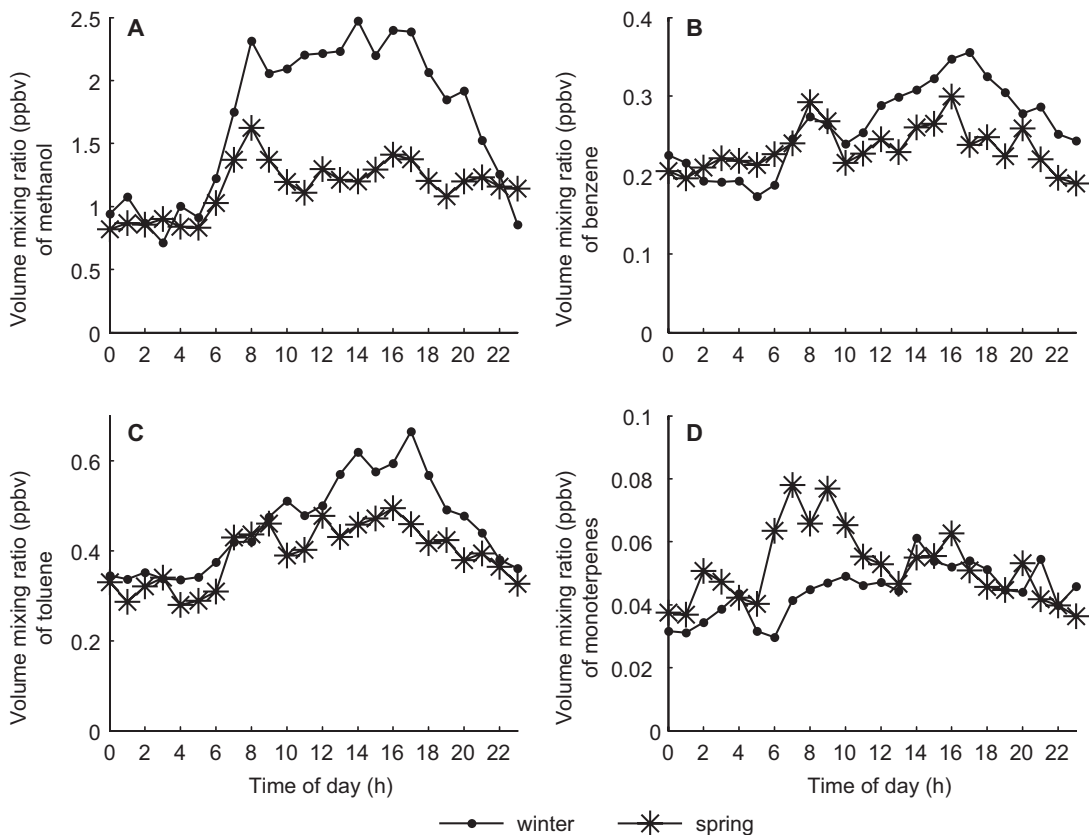
Fig. 4. Median diurnal cycles of selected VOCs at the urban background SMEAR III site. (**A**) methanol (M 33), (**B**) benzene (M 79), (**C**) toluene (M93) and, (**D**) monoterpenes (M137).

and 0.09 ppbv, respectively, in winter and 0.08 ppbv and 0.04 ppbv, respectively, in spring (Table A3). A similar seasonality and VMR levels were reported for Hyytiälä by Hakola *et al.* (2003) and for Helsinki by Hellén *et al.* (2002, 2012). Higher aromatic hydrocarbon levels are generally measured in winter due to longer atmospheric lifetimes and elevated emissions associated with cold starts of cars and wood combustion for residential heating while mixing remains suppressed via lower boundary layer (inversion). The atmospheric lifetimes of benzene and toluene were limited by reactions with the OH radicals (Table A4). In winter, the benzene lifetime due to oxidation with OH is 177 days, and in spring 12 days. For toluene, the lifetimes due to OH oxidation were 38 days in winter and 2.6 days in spring (Table A5). Mixing during winter days was nearly constant. In spring, mixing begun earlier than peaks in diurnal cycles of VOC VMRs were observed

(Fig. 6A). Thus peaks in benzene's and toluene's diurnal cycles seem to be associated with the diurnal cycle of traffic density.

At the urban background site, VOCs originating from traffic, such as benzene (M79) and toluene (M93), had distinct diurnal cycles in both winter and spring, with higher VMRs during rush hours (Fig. 4B and C). Benzene (M79) had a clear diel cycle in both seasons in Helsinki. Particularly, the winter afternoon peak was very clear (Fig. 4B). In spring, an afternoon peak was apparent while the VMR level was lower than in winter. For benzene, there were also morning peaks with similar amplitudes during urban background winter and spring. In the morning, the benzene VMR peak was sharper and higher as compared with the broader and lower peak in the afternoon. The benzene peak was likely from traffic on the road near the measurement station, and the peaks coincided with the highest intensities of traffic
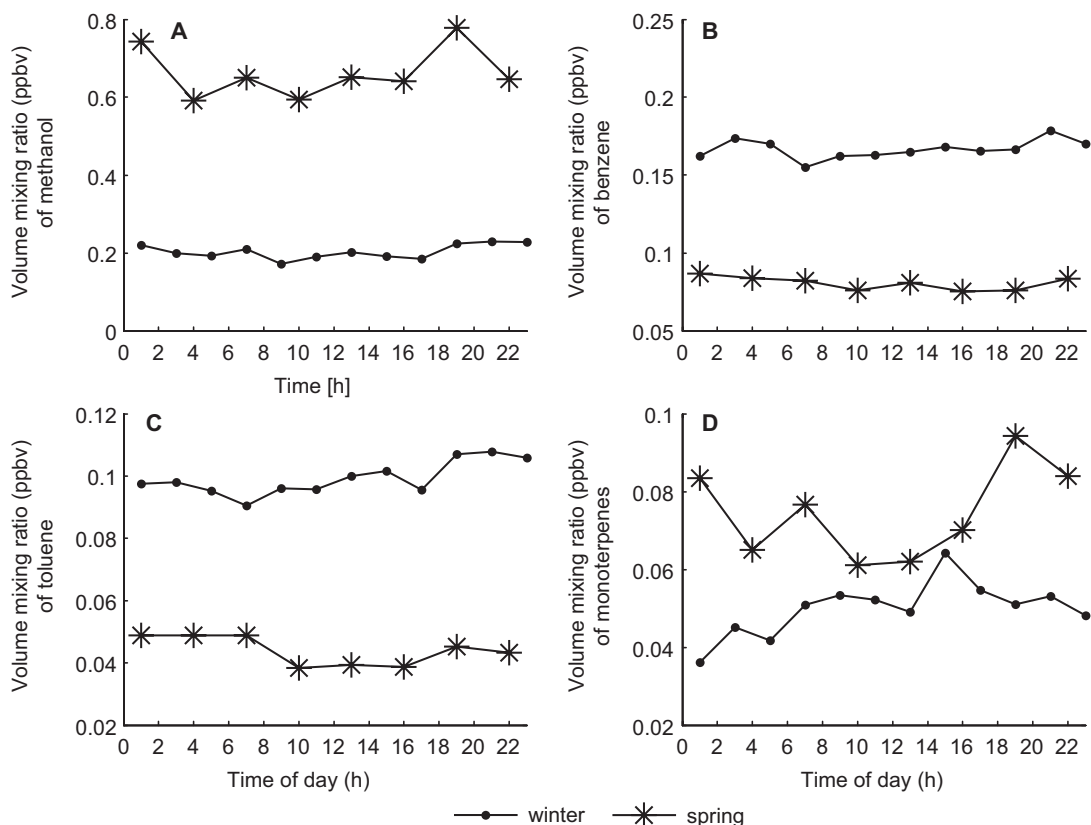
Fig. 5. Median diurnal cycles of selected VOCs at the rural SMEAR II site. (**A**) methanol (M 33), (**B**) benzene (M 79), (**C**) toluene (M93) and, (**D**) monoterpenes (M137).

(Fig. 2). For toluene (M93), afternoon peaks were observed, but the morning rush hour peak, similar to that found for benzene, was not clear in winter. The toluene VMR peak shapes were similar to those of benzene especially in spring, suggesting that they came from the same traffic source. During spring, photochemical reactions are more rapid during the day, and in the afternoon than in the morning. These reactions lower VMRs as the precursors react further. In spring, evening toluene's VMR was also a bit lower than in winter (Fig. 4C). At the rural site, VMRs of toluene and benzene remained constant during the day in both seasons (Fig. 5B and C). However at the rural site, toluene and benzene had clearly higher VMRs in winter than in spring which is probably due to higher photochemical oxidation and shorter lifetimes of these compounds during spring.

The main sources of toluene and benzene in Finland are traffic and wood combustion (Hellén

et al. 2006). The measured toluene-to-benzene ratios for wood combustion are usually lower than for traffic (Hedberg *et al*. 2002). The median ratios of toluene to benzene at the urban background site in winter and spring were 1.64 and 1.74, respectively (Fig. 7). The ratios were lower than the ratios reported earlier by Barrefors (1996) for Göteborg, Sweden and Kourtidis *et al*. (2002) for Thessaloniki, Greece. The difference in the ratios may be caused by higher numbers of vehicles and diversity in fuel composition used by the vehicle fleet in Göteborg and Thessaloniki as compared with those in Helsinki. Also, wood combustion may lower the ratio in Helsinki (Hellén *et al*. 2006) as domestic heating sources emit more benzene than toluene. Furthermore, the atmospheric lifetime of toluene is shorter than the lifetime of benzene (Seinfeld and Pandis 1998), and thus the toluene-to-benzene ratio decreases further away from the source areas. In
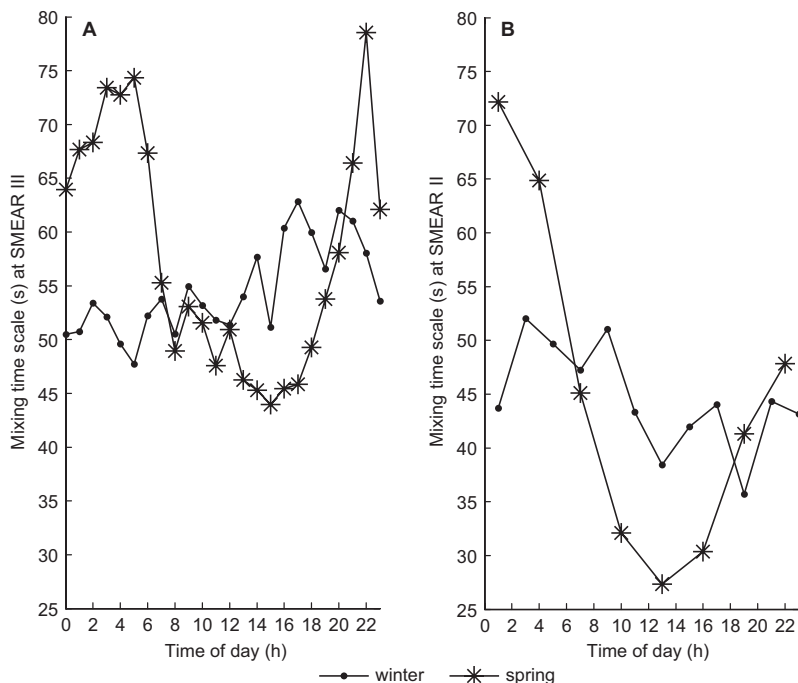
Fig. 6. Mixing time scales in winter and in spring at (**A**) the urban background SMEAR III site, and (**B**) the rural SMEAR II site.

the urban background areas, the toluene-to-benzene ratio increased when the emission was fresh in the morning, and decreased in the evening, when the emissions were lower and they were mixed with the background air (Kourtidis *et al.* 2002). This behaviour was visible in Helsinki both in winter and in spring.

The median ratios of toluene to benzene at the rural site in winter and spring were 0.60 and 0.55, respectively (Fig. 7). As expected, the ratios were lower than in Helsinki. They were also lower than the ratios of 1.04–1.06 reported by Gelencsér *et al.* (1997) for few remote sites in Hungary. There was no diurnal variation in the toluene-to-benzene ratio in Hyytiälä. A low variation together with the low toluene-to-benzene ratio tentatively indicates that local sources such as traffic were not as important in Hyytiälä as in Helsinki. Photochemical reactions played an important role also in rural spring, which is revealed by lower VMRs of aromatic compounds and toluene-to-benzene ratio.

Monoterpenes

In Helsinki, the median VMR of monoterpenes

was 0.05 ppbv both in winter and in spring. Filella *et al.* (2006) and Hellén *et al.* (2012) reported monoterpene measurements in urban areas. Filella *et al.* (2006) measured slightly higher values 0.10–0.18, but the values from Hellén *et al.* (2012), 0.05 ppbv in winter and 0.07 ppbv in spring, were similar to ours. In Hyytiälä, the median values for monoterpenes were 0.05 ppbv and 0.07 ppbv in winter and spring, respectively. Hakola *et al.* (2003) and Spanke *et al.* (2001) reported a similar value of 0.1 ppbv for Hyytiälä in winter and in spring.

At the urban background site, the diurnal cycle of monoterpenes had a maximum in the morning with a secondary maximum in the afternoon, and a minimum at night (Fig. 4D) both in winter and in spring, although there was less variation in winter. In Helsinki, there were similarities in the diurnal cycles of monoterpenes and benzene. Hellén *et al.* (2012) also observed a similar linkage between monoterpenes and aromatic hydrocarbons. In winter in Hyytiälä, there seemed to be an afternoon monoterpene peak, and they had the lowest values during nights. Diurnal profiles of monoterpenes at the urban background and the rural sites had a similar pattern in winter (Figs. 4D and 5D). At both sites,
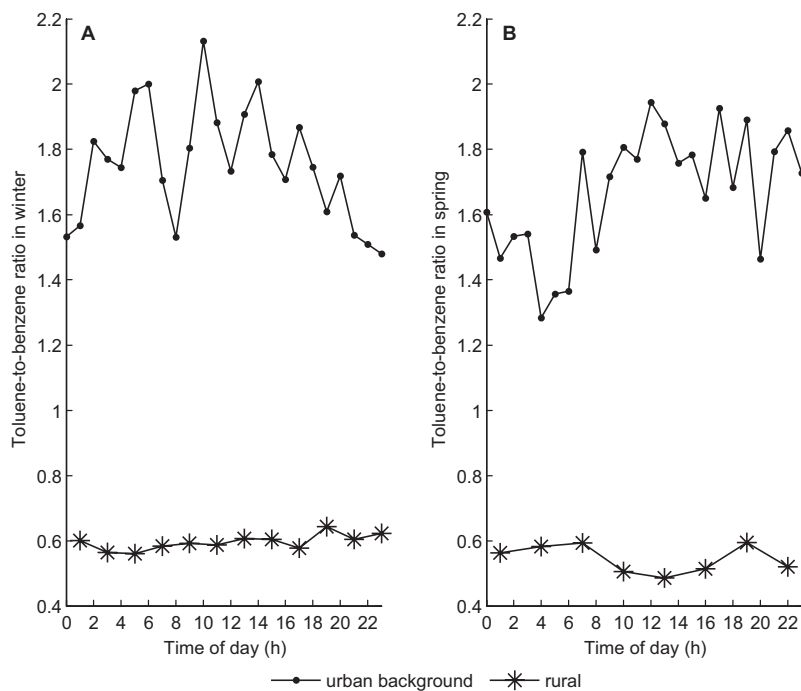
Fig. 7. Median diurnal cycle of toluene-to-benzene ratio at the urban background SMEAR III and the rural SMEAR II sites in (**A**) winter and (**B**) spring.

the mixing time scales were longer in midday in winter than in spring (Fig. 6). In addition, diurnal variation of mixing was missing in winter, and the increase of mixing after sunrise was clear in spring. In spring, in Hyytiälä monoterpenes had the highest VMRs in early morning and in the evening. In spring, the diurnal behaviour of monoterpenes' mixing ratio in Helsinki seems to be opposite to a typical diurnal cycle in rural remote areas with a coniferous forest cover (Hakola *et al.* 2000, Rinne *et al.* 2005). In spring in Hyytiälä during the day, photochemical reactions shortened the lifetime of monoterpenes and this affected the diurnal pattern of monoterpenes. Monoterpene lifetimes were limited by O_3 in winter to 1.7 (1.2) days at SMEAR III (SMEAR II), when reactions with OH would have resulted in lifetimes of 3 days at both sites. However in spring, monoterpene lifetimes were limited by OH (0.2 days) at both sites. Reactions with O_3 resulted in the lifetime of 0.8 day at SMEAR II and of 1 day at SMEAR III.

Identification of sources

The different sources given by Unmix were iden-

tified by source profiles and variations of source contributions. To avoid confusion with the sources as real world phenomenon, the sources as given by Unmix were labeled as UM-sources and are denoted with a capital first letter.

In Hyytiälä, the measured trace gases (NO_x, CO, O_3) and aerosol particle number concentrations were also included in the analysis. Depending on their size, the particles were divided into three groups. The particles smaller than 25 nm were called the nucleation mode while the Aitken mode particles were 25–100 nm in diameter. The accumulation mode represents the number concentration of 100–1000 nm particles. As particle concentration was given in cm^{-3}, while the trace gas data were in ppbv, the aerosol number concentrations were scaled by a factor of 100 to enable a feasible comparison with the trace gas mixing ratios.

UM-sources labeled as Traffic and Distant were always present at both sites. At the urban background site, two additional UM-sources were labeled as Methanol and Acetone in winter and Biogenic I and II in spring. In addition to the Distant and Traffic sources at the rural site, there were also Regional, Accumulation-mode-particle and Monoterpene sources. We identified and
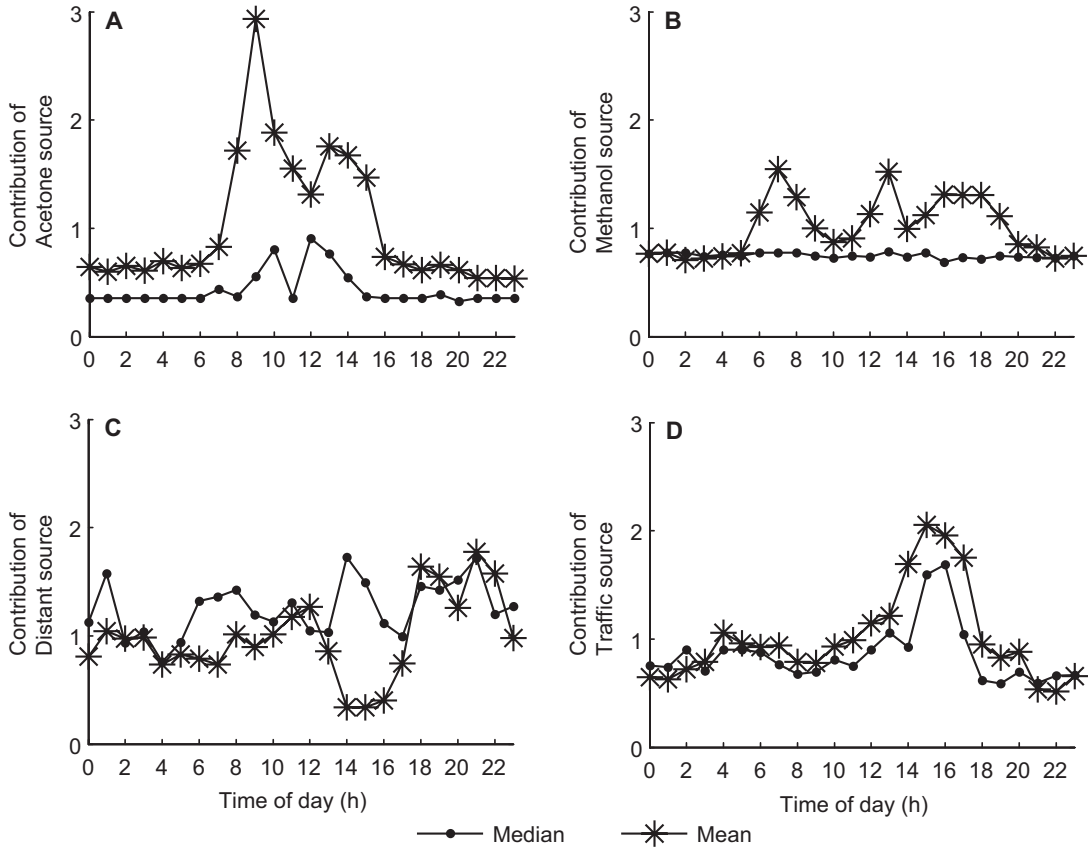
Fig. 8. Median and mean diurnal cycles of UM-source contributions in urban background winter. (**A**) Acetone source, (**B**) Methanol source, (**C**) Distant source, and (**D**) Traffic source.

labeled each UM-source based on its median, mean diurnal cycle (Figs. 8–11) and the composition of the source (Tables A9–A12).

At the urban background site, the Acetone UM-source had a diurnal cycle with the highest contribution in the middle of the day (Fig. 8A). This UM-source was mainly from acetone, and other VOCs had very minor contribution (< 10%) to it. Since acetone has several different sources in urban environments, it is hard to define a single source for it. Acetone is used as a solvent in many chemical products, for example paints, coatings and cleaners, and is also directly emitted from vehicle exhausts. It is also formed in oxidation reactions of other hydrocarbons (Jacob *et al*. 2002, Singh *et al*. 1994). Due to its relatively long lifetime, acetone can also be transported to Helsinki with long-range air masses.

Similarly to acetone, methanol had also a very large contribution to one single UM-source

at the urban background site. The Methanol UM-source had also small contribution of acetaldehyde, hexanal and monoterpenes. The Methanol UM-source did not show any median diurnal cycle, but if diurnal cycles were calculated for averages as in Fig. 8B, the UM-source had the highest contributions during the early morning, midday and late afternoon. As acetone, methanol has several sources, for example plant growth, vehicles, atmospheric oxidation of VOC, and industrial processes (Jacob *et al*. 2005). Thus attributing just one single source to methanol is difficult.

At both sites, one source, which consisted of oxygenated volatile organic compounds (OVOCs), was labeled as the Distant source. At the rural site, it also included some aromatic VOCs, O_3 and CO. At both sites, the Distant source showed a relatively stable contribution without any clear diurnal cycle (Figs. 8C, 9C,
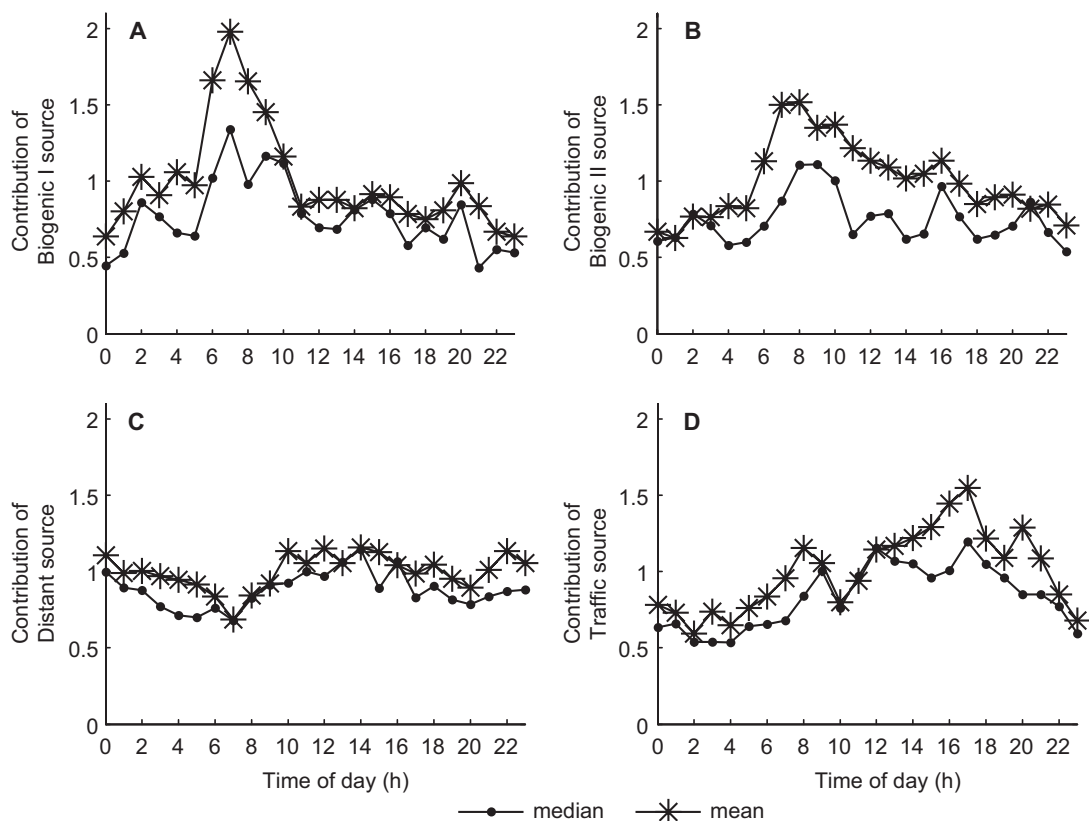
Fig. 9. Median and mean diurnal cycles of UM-source contributions in urban background spring (**A**) Biogenic I source, (**B**) Biogenic II source, (**C**) Distant source, and (**D**) Traffic source.

10D, 11D). The absence of diurnal variation can be a sign of long-distance transport of VOCs. Hellén *et al.* (2012) also identified a Distant source at the urban background station.

The UM-source which included aromatics, OVOCs and some terpenes at the urban background site and in addition NO_x and CO at the rural site was labeled as the Traffic source. In both seasons, about 90% of NO_x concentration was explained by this UM-source (Tables A11–12). The Traffic source showed the highest contributions during the afternoon rush hour. At both measurements sites, there was also more variation in the diurnal cycle of the Traffic source as compared with, for example, the diurnal behavior of the Distant source (Figs. 8C–D, 9C–D, 10D–E, 11D–E). This kind of diurnal variation indicates that there is a local source. In Hyytiälä, the diurnal difference was not so clear. In Helsinki, aromatics had a clearly higher contribution from the traffic source in winter than in spring. This

is expected since the background concentrations of these compounds are known to be higher in winter, when lifetimes of the compounds are longer (Hakola *et al.* 2006).

At the urban background site, two separate Biogenic UM-sources were found in spring instead of winter Acetone and Methanol UM-sources. Main compounds in the Biogenic I source profile were monoterpenes, and it also consisted of some OVOCs and aromatics. Methanol was the main compound of the Biogenic II profile. It also included MVK, hexenal and isoprene. All of these compounds are known to have biogenic sources in Finland (Janson and de Serves, 2001, Rinne *et al.* 2007, 2009). The diurnal cycle of the Biogenic I profile is similar to the diurnal cycle of monoterpenes in spring (Fig. 9A). It was also more pronounced than the diurnal pattern of Biogenic II which gives an evidence that Biogenic I emissions could be more local than those in the Biogenic II profile (Fig. 9B).
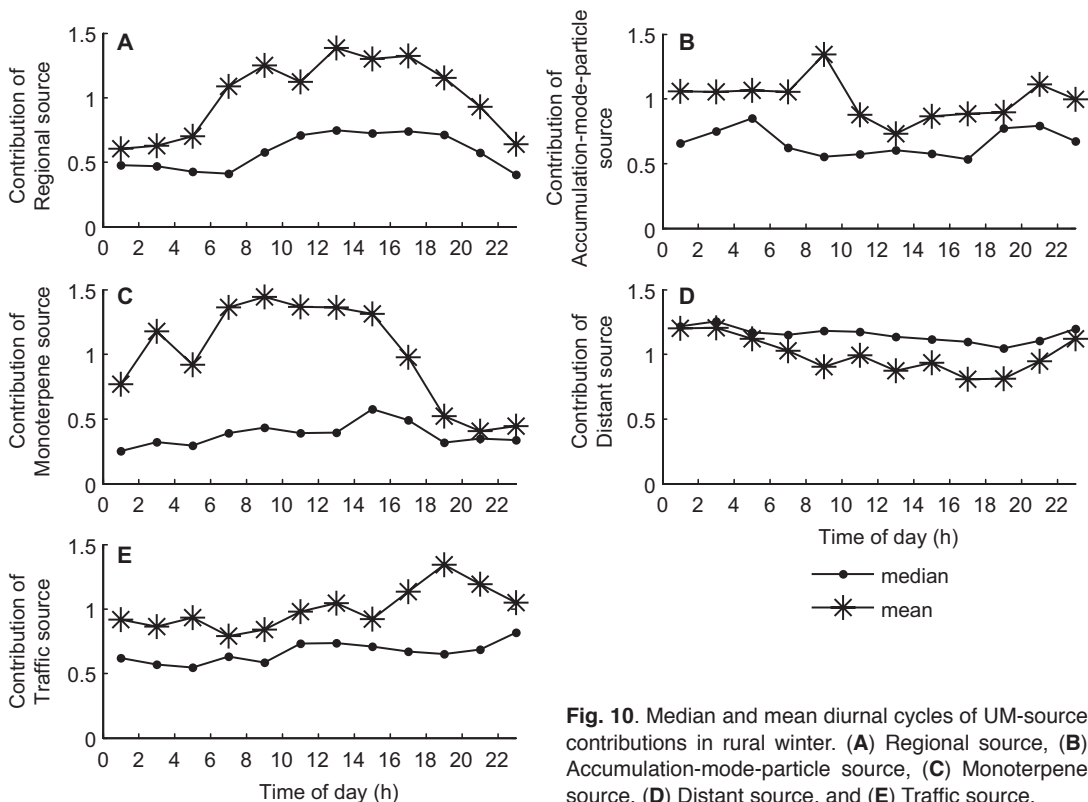
Fig. 10. Median and mean diurnal cycles of UM-source contributions in rural winter. (**A**) Regional source, (**B**) Accumulation-mode-particle source, (**C**) Monoterpene source, (**D**) Distant source, and (**E**) Traffic source.

At the rural site, the Regional UM-source included aromatics, OVOCs, nucleation mode particles and some CO indicating wood combustion processes, the source had a pronounced diurnal cycle indicating sources from neighboring regions. In winter, the highest contributions of the Regional source were during the day (Fig. 10A), whereas in spring the maximum was in the afternoon or evening (Fig. 11A). There are small villages near the measurement station, where wood is used for heating. Based on the wood combustion surveys in rural villages in Finland, fireplaces are most frequently used in the afternoon and evening (Tissari *et al*. 2007). The Regional source had a pronounced diurnal cycle indicating more local contributions as compared with those of the Distant source.

A UM-source including accumulation mode particles with some OVOCs, nucleation and Aitken-mode particles at the rural site was called the Accumulation-mode-particle source. In spring, there were only Aitken and accumulation-mode particles in this UM-source. Accumu-lation-mode particles are also transported over long distances and they had a UM-source of their own, possibly due to different sink processes i.e. more efficient wet and dry deposition than that of VOCs. The diurnal cycle of this UM-source varied only slightly which can also be an indicator of long-distance transport (Figs. 10B, 11B).

At the rural site in both seasons, one UM-source was called Monoterpene. There are no significant biogenic emissions in winter, but for example saw mills close to Hyytiälä are known to emit monoterpenes (Liao *et al*. 2011). As in rural winter, the rural spring Monoterpene UM-source included mainly monoterpenes but also some methanol and acetone. All these compounds are known to result form biogenic emissions in boreal forests (Janson and de Serves, 2001, Rinne *et al*. 2007, 2009). Diurnal cycle was also different than in winter (Figs. 10C, 11C). The contribution of this UM-source increased towards the end of the spring period, which is expected since it is the time when snow melts, and photosynthesis and growth processes
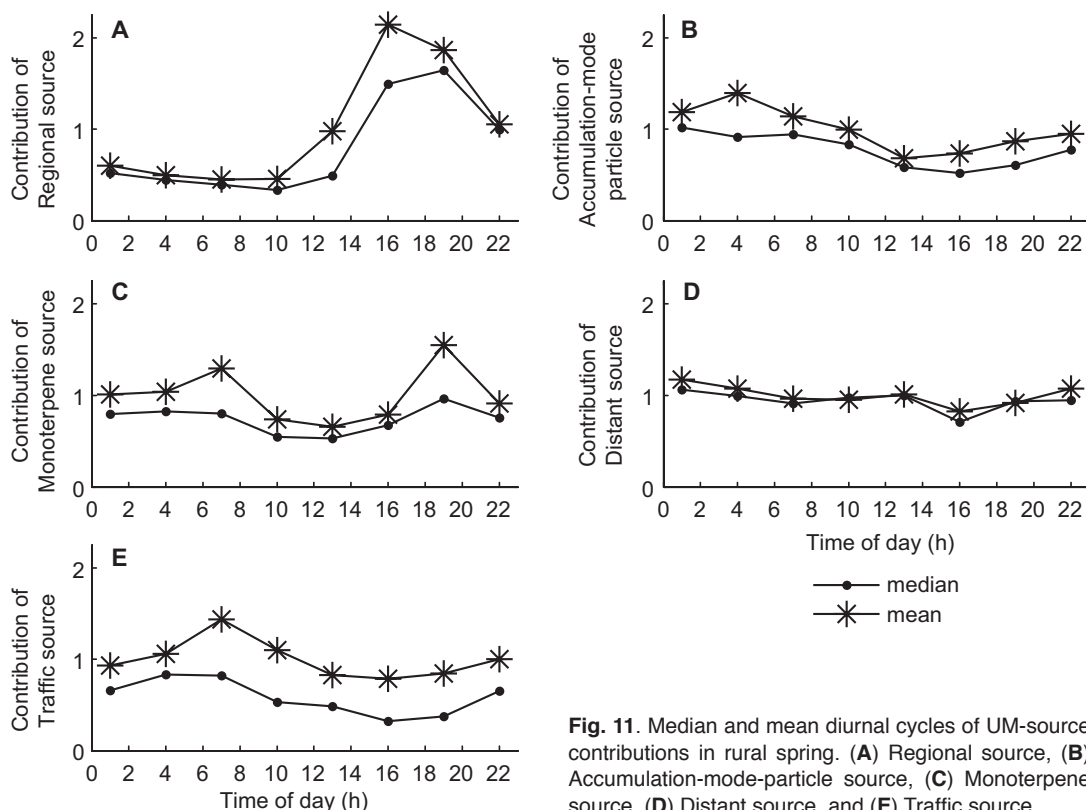
Fig. 11. Median and mean diurnal cycles of UM-source contributions in rural spring. (**A**) Regional source, (**B**) Accumulation-mode-particle source, (**C**) Monoterpene source, (**D**) Distant source, and (**E**) Traffic source.

begin and biogenic emissions from trees increase towards summer (Hakola *et al*. 2003).

Contribution of UM-source to trace gases

We pooled measured VOCs into four groups: (i) aromatics which included benzene and toluene; (ii) OVOCs which included acetone, acetaldehyde, MVK, MEK, MBO, hexanal and hexenal; (iii) terpenes which included monoterpenes and isoprene; and (iv) methanol which had its own group. The contributions of the different UM-sources to the measured compounds are presented in Fig. 12.

Sources of methanol

At the urban background site, methanol had its own UM-source in winter. In addition to the Methanol source, the Traffic and Distant sources explained a very small proportion (7% and 11%) of methanol in winter (Fig. 12A). In urban background spring, there was no separate Methanol UM-source, and VMR of methanol was explained mainly by the Biogenic II source (63%). Some of the observed methanol was also explained by the Traffic (17%) and Distant (14%) sources (Fig. 12B). At the rural site, the main source of methanol in winter was the Distant source (41%) but Traffic also had some contribution (28%) (Fig. 12C). In rural spring, the Distant source (66%) was clearly the main UM-source to methanol (Fig. 12D).

Sources of aromatics

At the urban background site, the main local UM-source of aromatics was Traffic (56%) (Fig. 12A) in winter. Also the Distant (28%) source had some contribution. Similarly to winter, in spring Traffic (42%) was the main UM-source to aromatics but the Biogenic I (19%) and II (15%) and Distant (24%) sources contributed as well

(Fig. 12B). In rural winter, the Traffic (34%) and Distant (40%) sources were almost evenly strong UM-sources to aromatics (Fig. 12C). However, in rural spring, the Distant source (52%) explained more aromatics than the Traffic source (30%) (Fig. 12D).

Sources of OVOC

In winter at the urban background site, OVOCs' main UM-source was Traffic (37%), except for acetone, which had its own UM-source. Additionally, the Distant (28%) and Acetone (27%) source had some contribution (Fig. 12A). Similarly to Methanol, Acetone did not have a separate UM-source in urban background spring, and thus the Distant source was the main contributor (48%) for acetone and other OVOCs. The Traffic (17%) and Biogenic sources (17% and 18%) had only minor contribution (Fig. 12B). Also at the rural site, the Distant source (49% in winter and 68% in spring) was the main UM-source to OVOCs in both seasons. The Traffic (19% in winter and 13% in spring) and Regional sources (26% in winter and 15% in spring) also contributed to some extent to OVOCs (Fig. 12C and D).

Sources of terpenes

The main UM-source for terpenes in urban background winter was Traffic (52%). The Distant source (29%) contributed marginally (Fig. 12A). Isoprene is known to be found in traffic emissions (Hellén *et al*. 2006, 2012). These results indicate that also monoterpenes may have some traffic-related sources. It is also possible that some other emissions (e.g. wood combustion) were not properly separated from the Traffic source by Unmix. However based on these results, monoterpenes are expected to have some anthropogenic sources. Hellén *et al*. (2012) reported same kind of behavior of terpenes in Helsinki. In urban background spring, the main UM-source for terpenes was the Biogenic I source (45%). The Traffic source (19%) had also some contribution in spring but it was minor as compared with its contribution to terpenes in urban background winter (Fig. 12B). Also

at the rural site, monoterpenes seem to have an anthropogenic origin in winter. The main monoterpene source in winter was the anthropogenic Monoterpene source (59%) (Fig. 12C). In rural spring, monoterpenes had a UM-source (46%) that differed from the winter UM-source (Fig. 12D), and it is expected to be of biogenic origin.

Conclusions

In this study, we explored winter to spring transition as well as differences and diurnal cycles of VMRs of selected VOCs measured with a proton-transfer-reaction mass spectrometer (PTR-MS) in the urban background and the rural settings. At the urban background Helsinki site, VMRs of VOCs had higher variations in their diurnal cycles than in the rural Hyytiälä. The monthly medians of most of VOCs were also higher in Helsinki than in Hyytiälä. Notable exceptions were monoterpenes and hexanal. In winter, a clear anthropogenic influence was found at both sites. Monoterpenes also seemed to have anthropogenic origin in winter. However in spring, biogenic activity was found to increase at both of the sites. Monoterpenes' diurnal cycle had different shape in winter and in spring, which indicates different origins of monoterpenes in winter and in spring. VMRs of other biogenic VOCs and oxidized VOCs increased at both sites in spring.

VMRs of toluene and benzene decreased in spring at both sites because of increased photochemical reactions. Toluene-to-benzene ratio indicated also that in the urban background Helsinki these compounds originated from local anthropogenic sources e.g. traffic and combustion. In Hyytiälä, toluene-to-benzene ratio's variation was lower than in Helsinki, which indicated that local combustion sources in Helsinki were more pronounced than in Hyytiälä.

Receptor modeling results indicate that in Helsinki traffic governs the major part of aromatics, terpenes and OVOCs in winter. Methanol had its own UM-source in winter. In spring, Traffic dominated the aromatics, the Distant source OVOCs, Biogenic I monoterpenes and Biogenic II methanol. The Distant source was present continuously in Helsinki during both seasons. At the rural site, the Traffic and Distant sources were
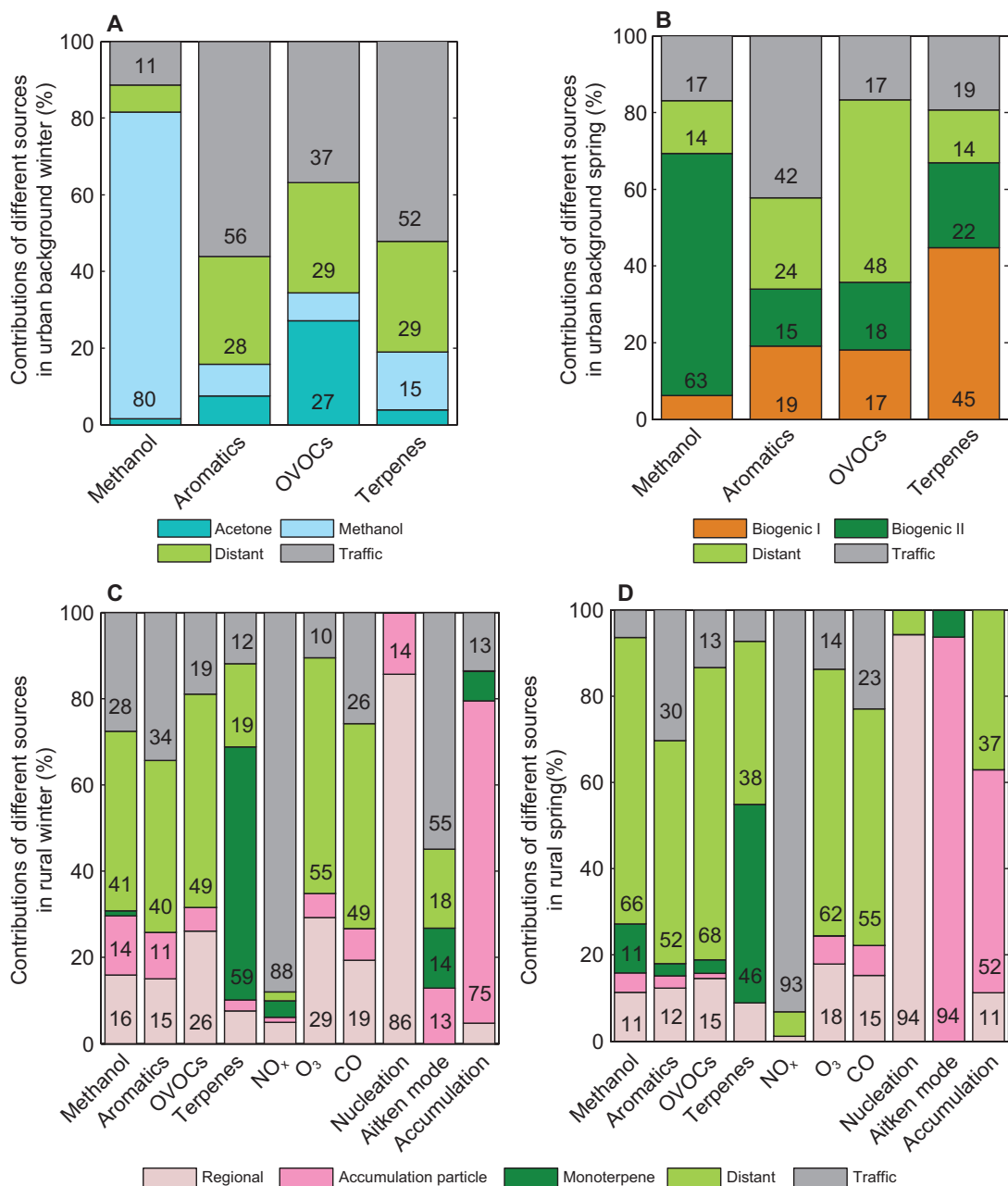
Fig. 12. Contributions of different UM-sources to measured species. (**A**) Urban background winter, (**B**) urban background spring, (**C**) rural winter, (**D**) rural spring. Aromatics included benzene and toluene; OVOCs: acetone, acetaldehyde, MVK, MEK, MBO, hexanal and hexenal; terpenes: isoprene and monoterpenes. Nucleation mode included particles smaller than 25 nm Aitken mode particles 25–100 nm and accumulation mode larger than 100 nm. If contribution of a group were lower than 10%, percentage has not been given in a bars.

almost even UM-sources to aromatics in winter. The Distant source was the main UM-source to methanol and OVOCs in both seasons, and it also governed aromatics in rural spring. Similarly to the urban background site, at the rural site winter monoterpenes were of anthropogenic origin, while in spring the biogenic sources governed a notably larger part of terpenes.

At both sites, the influence of anthropogenic sources was more significant in winter when the dilution effect due to mixing was smaller than in spring. In addition to the diurnal cycles of VOCs, the biogenic activity was evident also in the UM-source estimates in spring at both of the sites. Furthermore, the influences of regional VOC sources were continuously present in rural Hyytiälä.

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Appendix

Table A1. Detection limits (DL) of calibrated VOCs in the urban background SMEAR III and in the rural SMEAR II stations.

VOC (protonated mass, amu)	Median DL values (ppbv) at SMEAR III	Median DL values (ppbv) at SMEAR II
Methanol (M33)	0.60	0.66
Acetaldehyde (M45)	0.05	0.03
Acetone (M59)	0.02	0.02
Isoprene, MBO fragment (M69)	0.02	0.02
MVK, methacrolein (M71)	0.01	0.02
MEK (M73)	0.03	0.01
Benzene (M79)	0.01	0.01
Toluene (M93)	0.03	0.02
Hexanal (M101)	0.22	0.13
Monoterpenes (M137)	0.02	0.03

Table A2. Monthly median values, and 25% and 75% quartiles of measured VOC volume mixing ratios in ppbv in the urban background SMEAR III station.

Protonated mass and contributing compound(s)	January[1]			February[2]			March			April		
	25%	median	75%	25%	median	75%	25%	median	75%	25%	median	75%
Methanol (M 33)	1.00	1.66	2.43	1.02	1.47	2.05	1.23	1.66	2.03	0.72	1.17	1.89
Acetaldehyde (M 45)	0.27	0.43	0.65	0.47	0.68	0.90	0.55	0.73	0.92	0.37	0.53	0.81
Acetone (M59)	0.36	0.52	0.85	0.53	0.81	1.30	0.73	1.07	1.37	0.60	0.82	1.27
Isoprene, MBO fragment (M69)	0.03	0.05	0.07	0.05	0.09	0.12	0.06	0.08	0.10	0.04	0.07	0.10
MVK, methacrolein (M71)	0.05	0.10	0.17	0.12	0.18	0.27	0.13	0.16	0.23	0.06	0.10	0.16
MEK (M73)	0.08	0.12	0.22	0.15	0.26	0.38	0.18	0.28	0.33	0.12	0.16	0.24
Benzene (M93)	0.18	0.27	0.40	0.31	0.44	0.66	0.26	0.43	0.56	0.18	0.23	0.32
MBO (M87)	0.04	0.06	0.10	0.09	0.15	0.23	0.11	0.16	0.20	0.07	0.10	0.15
Toluene (M93)	0.34	0.44	0.62	0.38	0.55	0.81	0.44	0.57	0.77	0.30	0.39	0.54
Hexenal (M99)	0.03	0.05	0.07	0.06	0.11	0.15	0.07	0.10	0.13	0.04	0.07	0.14
Hexanal (M101)	0.21	0.28	0.36	0.37	0.56	0.74	0.50	0.57	0.67	0.43	0.66	0.95
Monoterpenes (M137)	0.03	0.05	0.08	0.04	0.07	0.13	0.04	0.07	0.11	0.03	0.05	0.08
Toluene-to-benzene ratio	1.31	1.64	1.96	1.00	1.29	1.59	1.25	1.40	1.63	1.36	1.74	2.13

1) 9 Jan.–9 Feb. 2006, 2) 10–28 Feb. 2006.

Table A3. Monthly median values, and 25% and 75% quartiles of measured VOC volume mixing ratios in ppbv in the rural SMEAR II station.

Protonated mass and contributing compound(s)	January			February			March			April		
	25%	median	75%	25%	median	75%	25%	median	75%	25%	median	75%
Methanol (M 33)	0.16	0.19	0.25	0.27	0.32	0.59	0.26	0.36	0.53	0.46	0.64	0.87
Acetaldehyde (M 45)	0.12	0.15	0.20	0.26	0.30	0.35	0.19	0.24	0.31	0.15	0.19	0.24
Acetone (M59)	0.25	0.29	0.34	0.31	0.37	0.42	0.39	0.52	0.65	0.48	0.58	0.73
Isoprene, MBO fragment (M69)	0.04	0.04	0.05	0.04	0.04	0.05	0.04	0.05	0.08	0.03	0.05	0.06
MVK, methacrolein (M71)	0.05	0.06	0.07	0.06	0.07	0.08	0.06	0.08	0.12	0.04	0.05	0.07
MEK (M73)	0.04	0.05	0.06	0.07	0.08	0.10	0.06	0.08	0.11	0.07	0.08	0.10
Benzene (M93)	0.14	0.16	0.18	0.18	0.19	0.21	0.13	0.17	0.20	0.07	0.08	0.09
MBO (M87)	0.03	0.04	0.05	0.05	0.06	0.06	0.05	0.06	0.09	0.06	0.07	0.08
Toluene (M93)	0.08	0.09	0.11	0.12	0.13	0.18	0.06	0.08	0.11	0.03	0.04	0.06
Hexenal (M99)	0.04	0.05	0.06	0.05	0.05	0.06	0.04	0.05	0.06	0.03	0.04	0.06
Hexanal (M101)	1.02	1.18	1.42	0.81	0.91	0.96	0.83	1.06	1.81	1.50	1.85	2.20
Monoterpenes (M137)	0.03	0.05	0.07	0.03	0.04	0.06	0.04	0.06	0.09	0.05	0.07	0.11
Toluene-to-benzene ratio	0.54	0.60	0.67	0.62	0.68	0.83	0.46	0.52	0.58	0.42	0.55	0.73

Table A4. Reaction rate coefficients (k_{OH}, k_{O3}, k_{NO3}) for measured VOCs and midday photolysis rates for spring (Hellén *et al.* 2004) and scaled photolysis rates for winter.

	k_{OH} (cm³ molecules⁻¹ s⁻¹)	k_{O3} (cm³ molecules⁻¹ s⁻¹)	k_{NO3} (cm³ molecules⁻¹ s⁻¹)	$k_{photolysis}$ spring (s⁻¹)	$k_{photolysis}$ winter (s⁻¹)
Methanol	$9.00 \times 10^{-13(a)}$		$2.42 \times 10^{-16(f)}$		
Acetaldehyde	$1.50 \times 10^{-12(a)}$		$2.72 \times 10^{-15(g)}$	$1.42 \times 10^{-6(h)}$	$4.40 \times 10^{-7(i)}$
Acetone	$1.80 \times 10^{-13(a)}$		$3.00 \times 10^{-17(g)}$	$2.10 \times 10^{-8(h)}$	$6.51 \times 10^{-8(i)}$
Isoprene	$1.00 \times 10^{-10(a)}$	$1.28 \times 10^{-17(d)}$	$6.78 \times 10^{-13(d)}$		
MVK	$3.00 \times 10^{-11(a)}$	$0.47 \times 10^{-17(b)}$		$9.40 \times 10^{-7(h)}$	$2.91 \times 10^{-7(i)}$
MEK	$1.20 \times 10^{-12(a)}$	$2.00 \times 10^{-17(e)}$		$3.97 \times 10^{-6(h)}$	$1.23 \times 10^{-6(i)}$
Benzene	$1.19 \times 10^{-12(a)}$	$1.70 \times 10^{-22(d)}$	$3.00 \times 10^{-17(e)}$		
MBO	$8.83 \times 10^{-12(b)}$	$7.39 \times 10^{-17(b)}$			
Toluene	$5.60 \times 10^{-12(a)}$	$4.10 \times 10^{-22(d)}$	$6.79 \times 10^{-17(e)}$		
Hexenal	$3.85 \times 10^{-11(b)}$	$9.1 \times 10^{-19(d)}$			
Hexanal	$2.82 \times 10^{-11(b)}$			$8.84 \times 10^{-6(h)}$	$2.74 \times 10^{-6(i)}$
Monoterpenes	$7.50 \times 10^{-11(c)}$	$1.4 \times 10^{-17(c)}$	$7.06 \times 10^{-12(c)}$		

Rate constants (k_{OH}, k_{O3} and k_{NO3}) used in calculations in Tables A5–A7: [a] iupac preferred, and [b] www.chemspider.com. Predicted data were generated using the US Environmental Protection Agency's EPI Suite. [c] Monoterpenes' rate constants k_{OH}, k_{O3} and k_{NO3} were calculated as weighted averages of individual monoterpenes typical in SMEAR II (Hakola *et al.* 2003), individual k-values Atkinson (1994); [d] Atkinson (1994); [e] http://kinetics.nist.gov/kinetics/index.jsp; [f] Atkinson *et al.* (1981); [g] Rinne *et al.* (2007); [h] Hellén *et al.* (2004); [i] winter photolysis rates scaled from spring photolysis rates by radiation.

Table A5. Lifetimes for measured VOCs during daytime at SMEAR III. Approximated concentrations for OH and ozone were in winter [OH] = 5.5×10^4 molecules cm⁻³ (Hakola *et al.* 2003) and [O₃] = 4.8×10^{11} molecules cm⁻³ and in spring [OH] = 8.0×10^5 molecules cm⁻³ (Hakola *et al.* 2003) and [O₃] = 5.7×10^{11} molecules cm⁻³ used in calculations.

	Winter				Spring			
	τ OH	τ O₃	photolysis	total	τ OH	τ O₃	photolysis	total
Methanol	234 d			234 d	16 d			16 d
Acetaldehyde	140 d		26 d	22 d	9.7 d		8 d	4.4 d
Acetone	3.2 y		177 d	154 d	80 d		55 d	32.7 d
Isoprene	2 d	1.9 d		1.00 d	0.1 d	1.2 d		0.1 d
MVK	7 d	0.7 d	39 d	0.60 d	0.5 d	0.4 d	12 d	0.20 d
MEK	175 d	2.9 d	9 d	0.10 d	12 d	0.07 d	3 d	0.07 d
Benzene	177 d	390 y		177 d	12 d	239 y		12 d
MBO	2 d	7.9 d		0.30 d	0.2 d	0.2 d		0.1 d
Toluene	38 d	171 y		38 d	2.6 d	99 y		2.6 d
Hexenal	5 d	26.7 d		4.50 d	0.4 d	16.3 d		0.4 d
Hexanal	7 d		4 d	2.70 d	0.5 d		1.3 d	0.4 d
Monoterpenes	3 d	1.7 d		1.00 d	0.2 d	1 d		0.2 d

Table A6. Lifetimes for measured VOCs during nighttime at SMEAR III. Approximated concentrations for ozone and NO_3 were in winter $[O_3] = 5.7 \times 10^{11}$ molecules cm^{-3} and scaled $[NO_3] = 1.2 \times 10^7$ molecules cm^{-3} (Hakola *et al.* 2003) and in spring $[O_3] = 7.4 \times 10^{11}$ molecules cm^{-3} and scaled $[NO_3] = 3.1 \times 10^7$ molecules cm^{-3} (Hakola *et al.* 2003) used in calculations.

	Winter			Spring		
	$\tau\ NO_3$	$\tau\ O_3$	total	$\tau\ NO_3$	$\tau\ O_3$	total
Methanol	1.1 y		1.1 y	154 d		154 d
Acetaldehyde	1.0 y		1.0 y	137 d		137 d
Acetone	88 y		88 y	34 y		34 y
Isoprene	1.4 d	1.5 d	0.7 d	0.6 d	1.1 d	0.4 d
MVK		0.6 d	0.6 d		0.4 d	0.4 d
MEK		0.1 d	0.1 d		0.07 d	0.07 d
Benzene	88 y	317 y	69 y	34 y	236 y	30 y
MBO		0.3 d	0.3 d		0.2 d	0.2 d
Toluene	39 y	132 y	30 y	15 y	98 y	13 y
Hexenal		21.7 d	21.7 d		16 d	16 d
Monoterpenes	0.1 d	1.4 d	0.1 d	0.05 d	0.2 d	0.04 d

Table A7. Lifetimes for measured VOCs during daytime at SMEAR II. Approximated concentrations for OH and ozone were in winter $[OH] = 5.5 \times 10^4$ molecules cm^{-3} (Hakola *et al.* 2003) and $[O_3] = 6.8 \times 10^{11}$ molecules cm^{-3} and in spring $[OH] = 8.0 \times 10^5$ molecules cm^{-3} (Hakola *et al.* 2003) and $[O_3] = 1 \times 10^{12}$ molecules cm^{-3} used in calculations.

	Winter				Spring			
	$\tau\ OH$	$\tau\ O_3$	photolysis	total	$\tau\ OH$	$\tau\ O_3$	photolysis	total
Methanol	234 d			234 d	16 d			16 d
Acetaldehyde	140 d		26 d	22 d	10 d		8 d	4 d
Acetone	3.2 y		177 d	154 d	80 d		55 d	33 d
Isoprene	2 d	1.3 d		0.8 d	0.1 d	0.9 d		0.1 d
MVK	7 d	0.5 d	39 d	0.4 d	0.5 d	0.3 d	12 d	0.2 d
MEK	175 d	0.1 d	9 d	0.08 d	12 d	0.1 d	3 d	0.1 d
Benzene	177 d	276 y		177 d	12 d	178 y		12 d
MBO	2 d	0.2 d		0.2 d	0.2 d	0.1 d		0.1 d
Toluene	38 d	115 y		38 d	3 d	74 y		3 d
Hexenal	6 d	18.8 d		4 d	0.4 d	12 d		0.4 d
Hexanal	8 d		4 d	3 d	0.5 d		1.3 d	0.4 d
Monoterpenes	3 d	1.2 d		0.9 d	0.2 d	0.8 d		0.2 d

Table A8. Lifetimes for measured VOCs during nighttime at SMEAR II. Approximated concentrations for ozone and NO_3 were in winter $[O_3] = 6.8 \times 10^{11}$ molecules cm^{-3} and scaled $[NO_3] = 1.2 \times 10^7$ molecules cm^{-3} (Hakola *et al.* 2003) and in spring $[O_3] = 9.5 \times 10^{11}$ molecules cm^{-3} and scaled $[NO_3] = 3.1 \times 10^7$ molecules cm^{-3} (Hakola *et al.* 2003) used in calculations.

	Winter			Spring		
	$\tau\ NO_3$	$\tau\ O_3$	total	$\tau\ NO_3$	$\tau\ O_3$	total
Methanol	1.1 y		1.1 y	154 d		154 d
Acetaldehyde	1 y		1 y	137 d		137 d
Acetone	88 y		88 y	34 y		34 y
Isoprene	1.4 d	1.3 d	0.7 d	0.6 d	0.9 d	0.3 d
MVK		0.5 d	0.5 d		0.3 d	0.3 d
MEK		0.1 d	0.1 d		0.06 d	0.06 d
Benzene	88 y	262 y	66 y	34 y	193 y	29 y
MBO		0.2 d	0.2 d		0.2 d	0.2 d
Toluene	39 y	108 y	29 y	15 y	79 y	13 y
Hexenal		18 d	18 d		13 d	13 d
Monoterpenes	0.1 d	1.2 d	0.1 d	0.05 d	0.08 d	0.05 d

Table A9. Contributions of different sources to measured concentrations of different components in urban background winter.

Species	Acetone (%)	Methanol (%)	Distant (%)	Traffic (%)
Methanol	2	80	7	11
Acetaldehyde	5	13	36	45
Acetone	60	1	19	20
Isoprene	3	7	33	57
MVK	5	3	22	70
Benzene	5	9	38	48
MBO	6	5	53	37
Toluene	9	8	22	61
Hexenal	6	6	44	44
Hexanal	6	15	34	45
Monoterpenes	5	22	26	48

Table A10. Contributions of different sources to measured concentrations of different components in urban background spring.

Species	Biogen I (%)	Biogen II (%)	Distant (%)	Traffic (%)
Methanol	6	63	14	17
Acetaldehyde	15	31	34	20
Acetone	23	3	59	14
Isoprene	21	30	15	33
MVK	17	41	0	42
MEK	18	17	50	16
Benzene	14	14	35	37
MBO	12	22	52	13
Toluene	22	15	18	45
Hexenal	0	57	36	7
Hexanal	18	13	53	16
Monoterpenes	72	12	12	3

Table A11. Contributions of different sources to measured concentrations of different components in rural winter.

Species	Regional (%)	Accumulation-mode-particle (%)	Monoterpene (%)	Distant (%)	Traffic (%)
Methanol	16	14	1	42	28
Acetaldehyde	25	5	0	41	30
Acetone	22	7	0	45	25
Isoprene	21	9	0	49	21
MVK	21	7	0	50	23
MEK	19	13	0	41	28
Benzene	16	10	0	41	33
MBO	24	8	0	43	24
Toluene	13	12	0	38	37
Hexenal	25	4	0	48	22
Hexanal	28	5	0	52	15
Monoterpenes	2	0	84	6	8
NO_x	5	1	4	2	88
O_3	29	6	0	55	10
CO	19	7	0	48	26
Nucleation mode	86	14	0	0	0
Aitken mode	0	13	14	18	55
Accumulation mode	5	75	7	0	14

Table A12. Contributions of different sources to measured concentrations of different components in rural spring.

Species	Regional (%)	Accumulation-mode-particle (%)	Monoterpene (%)	Distant (%)	Traffic (%)
Methanol	11	5	11	66	6
Acetaldehyde	11	0	9	63	17
Acetone	12	1	10	67	11
Isoprene	9	0	5	74	12
MEK	12	3	2	68	15
Benzene	14	4	0	56	27
MBO	13	0	2	69	16
Toluene	10	1	8	44	37
Hexenal	12	0	6	71	12
Hexanal	16	1	0	69	14
Monoterpenes	9	0	66	20	5
NO_x	1	0	0	6	93
O_3	18	7	0	62	14
CO	15	7	0	55	23
Nucleation mode	94	0	0	6	0
Aitken mode	0	94	6	0	0
Accumulation mode	11	52	0	37	0