Sources and concentrations of volatile organic compounds

ARTICLE

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Ambient Air Concentrations, Source Profiles, and Source Apportionment of 71 Different C2–C10 Volatile Organic Compounds in Urban and Residential Areas of Finland

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Ambient air concentrations and source contributions of 71 volatile organic compounds (VOCs) including C_2–C_{10} nonmethane hydrocarbons, halogenated hydrocarbons, and carbonyls were studied at urban and residential sites in Finland. On the basis of the emission profile and concentration measurements, the contributions of different sources were estimated using a chemical mass balance (CMB) receptor model. It was shown that it is possible to apply CMB in the case of a large number of different compounds with different properties. However, the performance of the model varies significantly for the different compounds. According to the CMB analysis, major sources for these VOCs at the urban site were traffic and distant sources. At the residential site, the contribution due to traffic was minor while distant sources, liquid gasoline, and wood combustion made higher contributions. However, different compound groups or compounds were found to have totally different sources. It was also shown that a biogenic compound, isoprene, also has significant anthropogenic sources and that at some locations wood combustion can be an important source for some VOCs usually considered as traffic-related compounds (e.g., benzene).

Introduction

Volatile organic compounds (VOCs) have a great influence on tropospheric chemistry; they affect ozone formation and they or their reaction products may take part in new particle formation (*1*). Knowing the concentrations and sources of different reactive volatile organic compounds is essential for the development of ozone control strategies and for studies of secondary organic aerosol formation. Some of the measured compounds are themselves toxic. In addition to this, halocarbons can cause ozone reduction in the stratosphere.

Traffic is known to be the major source of nonmethane hydrocarbons (NMHCs) in urban areas (*2*), but in residential areas the contribution of other sources may be more important. In the Nordic countries, wood is a domestic and renewable energy source, and the use of wood as a fuel source

has increased lately (*3*, *4*). However, recent estimates (*3*–*5*) have suggested that small-scale wood combustion can be a major source of some VOCs in the Nordic countries, where houses usually have fireplaces and saunas that can be heated with wood. Many of the VOCs emitted during wood combustion are very harmful or toxic (for example, benzene and formaldehyde). Although the importance of small-scale wood combustion as a VOC source has been recognized, its magnitude is hard to determine because of the complexity of the burning processes and habits of use.

The chemical mass balance (CMB) has been widely used for automated GC and canister samples (*2*, *6*–*8*), but applications for VOCs other than NMHCs are not so common. There are some studies in which both canister and adsorbent sampling have been used to widen the selection of NMHCs (*9*), and some investigations of halogenated hydrocarbons have also been made using adsorbent sampling (*10*). In Fujita et al. (*11*), carbonyls were studied together with the NMHCs, and carbonyls were found to be the main source of the unexplained mass in the CMB calculations.

In this study, concentration measurements using different techniques and source apportionment estimations by CMB modeling were conducted for 71 different VOCs including alkanes, alkenes, alkynes, aromatic hydrocarbons (HCs), biogenic HCs, halogenated HCs, gasoline additives, and carbonyl compounds at urban and residential sites. Source profiles were determined for these VOCs by conducting emission measurements and using emission data from the literature. Contributions due to wood combustion and other sources were estimated by CMB modeling, and source apportionments of urban and residential locations were compared. Usually in published CMB studies, only the results for total NMHC or VOC concentrations are given, and the sources of different compounds or compound groups are not discussed. Here, the results for the sources of the individual compounds are given for both measuring sites.

In an earlier study in Helsinki (*9*), the chemical mass balance was applied only for the NMHCs and not for the other VOCs, wood combustion was not considered, and only one urban background site was studied. In addition to this, individual hydrocarbons were not studied.

Material and Methods

Measurement Stations. Measurements were conducted at two different locations: at an urban background station in Helsinki and at a residential site in Järvenpää. Helsinki is situated on the shores of the Baltic Sea (60°11′N, 24°57′E). In 2004, the population of the Helsinki metropolitan area was 960 000 and its area was 760 km². The urban background station in Helsinki is situated in a sports field in the city center; its distance from the closest street is approximately 80 m.

Järvenpää (60°29′N, 25°4′E) is a small city 38 km north of Helsinki with a population of 37 000 and an area of 40 km². Measurements in Järvenpää were conducted on a residential site close to the city center.

Concentration Measurements. Twenty-four-hour concentration measurements were conducted in Helsinki in February, May, and September of 2004 on 16 different days and in Järvenpää in November and December of 2004 and in January of 2005 on 10 different days. During the measurement periods, the average daily temperature in Helsinki varied between −0.8 and 3.5 °C in February, 7.7 and 11.7 °C in May, and 9.1 and 16.9 °C in September; in Järvenpää, the temperature varied between −6.6 and 4 °C.

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Sampling of the light (C_2-C_7) hydrocarbons and some halogenated hydrocarbons (CFC-12, chloromethane, CFC-11, and CFC-113) was conducted using evacuated stainless steel canisters (6 L). The samples were analyzed using a gas chromatograph (HP-6890) with a flame ionization detector for the NMHCs and an electron capture detector for the halogenated hydrocarbons. Detection limits calculated for a signal-to-noise ratio of 3:1 varied between 10 and 115 ng/m^3.

For C_8-C_{10} alkanes, aromatic hydrocarbons, methyl-*tert*-butyl ether (MTBE), *tert*-amylmethyl ether (TAME), 1,2-dichloroethane, chloroform, 1,1,1-trichloroethane, tetrachloroethane (CCl$_4$), trichloroethene, tetrachloroethene, methacrolein, and monoterpenes, pumped adsorbent sampling with Tenax TA/Carbopack B adsorbent tubes was used. Samples were analyzed using a thermal desorption system (Perkin-Elmer ATD-400) with a gas chromatograph (HP-5890) and a mass spectrometer (HP-5972). Detection limits calculated from the standard deviation of blank samples (3 times the stdev) or at a signal-to-noise ratio of 3:1 varied between 6 and 258 ng/m^3. A more detailed description of the adsorbent sampling and the analysis method can be found in ref 12.

Carbonyl samples were collected by drawing air through C_{18}-cartridges (Sep-Pak, Waters) coated with DNPH (2,4-dinitrophenyl hydrazine). The samples were analyzed using a liquid chromatograph (LC) equipped with an ion trap mass spectrometer (Agilent 1100 Series LC/MSD trap). Detection limits calculated from the standard deviation of blank samples (3 times the stdev) or at a signal-to-noise ratio of 3:1 varied from 1 to 135 ng/m^3. A more detailed description of the method can be found in ref 13.

The uncertainty (U) was calculated from the ambient concentrations (c), detection limits (DL), and standard deviations (CV) of the duplicate samples using the same procedure as Fujita et al. (8) and Hellén et al. (9): $U = \sqrt{(2\times DL)^2 + (CV \times c)^2}$. The average uncertainties for the canister, adsorbent, and carbonyl samples were 108 ± 44 ng/m^3, 170 ± 185 ng/m^3, and 46 ± 42 ng/m^3, respectively.

Source Profile Measurements. The sources to be measured were chosen on the basis of published emission inventories (14, 15) and our own considerations. Samples were taken and analyzed using the same methods as for the ambient air samples, only with shorter sampling times.

The traffic profile was obtained from follow-up car/car-chasing measurements conducted in Helsinki in October 2004 (16). These measurements were made in the existing traffic and thus described real-world emissions of VOCs. The follow-up car was not used for the chasing of any particular cars but for driving in traffic in the city center and on main roads in Helsinki. Twenty-six traffic samples were taken, and the profile was defined from their averages. The gasoline or diesel fuel vapors emitted during driving are included in the traffic profile. Because of the short sampling times in these tests, carbonyls could not be measured. Their contribution was obtained mainly from dynamometric measurements conducted in Finland (17). The contributions of those carbonyl compounds that were not included in the dynamometric tests were added to the profile using tailpipe emission measurements conducted on a parking place immediately after starting the car. In the Helsinki area, the traffic consists of approximately 10% heavy-duty (diesel) vehicles and 90% light-duty, of which 80% are gasoline and 20% diesel vehicles (18).

Liquid gasoline and diesel fuel profiles were produced by analyzing the most common liquid gasoline (95-RON) and diesel fuels purchased from a local filling station. Gasoline and diesel fuel vapor samples were taken during the refueling of cars at a filling station. The levels of the various components in gasoline produced by different manufacturers can vary tremendously. However, on the basis of information from
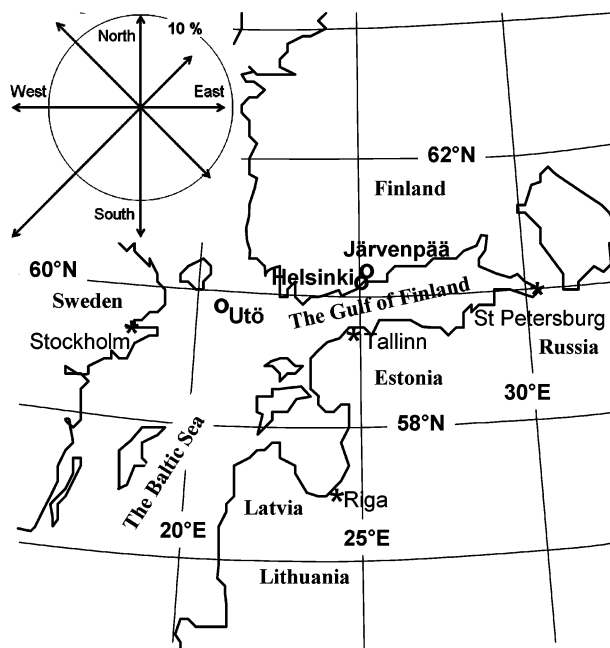

FIGURE 1. Location of the measurement sites Helsinki, Järvenpää, and Utö. The wind rose depicts wind direction frequencies at Utö in 2004.

the Finnish Oil and Gas Federation (19), ~80% of the gasoline sold in Finland is produced by a local oil refinery. This was the gasoline sampled in this study.

Emissions from small-scale wood combustion were measured from different sources: a kitchen oven, saunas, and fireplaces. The profile was defined as the average of the 11 measurements.

To estimate the contribution of air pollution advected into the study area by long-range transported air masses, measurements were conducted on the small remote island of Utö (area < 1 km^2, 59° 47′N, 21° 23′E, 7 m above sea level) in the Baltic Sea. Air arriving at Utö is long-range transported over the sea without the additional contribution of any major anthropogenic emissions during the transportation. During the transportation, atmospheric transformation changes the profile, and the contribution of compounds with longer lifetime (e.g., halogenated compounds and ethane) increases. Figure 1 shows the sampling sites and the wind rose for the Utö in 2004. Diurnal samples were taken in different seasons to get the proper distant source profiles for the different urban measurement periods. Often, distant sources or background concentrations are not taken into account in CMB studies, but in this case locally emitted concentrations are so low that the importance of the background concentration is significant, and leaving it out would deteriorate the performance of the model.

A commercial natural gas profile was obtained by sampling the leakage from a gas stove in Helsinki. A similar profile was obtained also in the earlier study in Helsinki (9), when a different gas stove was used. In Finland, the only commercial natural gas used is from Western Siberia (19).

A biogenic hydrocarbon profile from an earlier study (9) was used for monoterpenes and isoprene.

In the dry-cleaning profile, the only compound is tetrachloroethene, which is the solvent used in dry cleaning, according to information given by local dry-cleaning firms. No other major solvent emissions were reported by local companies.

Because standard deviations, which would represent the variation in the source composition, could not be defined, a default uncertainty of 15%, which is little higher than the analytical uncertainty, was used for the source profiles.

TABLE 1. Average Winter Concentrations of Different Compound Groups (ng m^{-3}) at an Urban Site in Helsinki and at a Residential Site in Järvenpää and the Shares of the Different Compound Groups in the Source Profiles of Different VOC Sources (as % of the total measured mass)

	Helsinki	Järvenpää	TRA[a]	EGA	EDI	LGA	LDI	WCO	BIO	CNG	DCL	DS W	DSS
alkanes	22 630	13 980	0.283	0.781	0.624	0.552	0.529	0.099	0.000	0.995	0.000	0.538	0.384
alkenes	3490	2270	0.121	0.036	0.022	0.025	0.000	0.319	0.000	0.002	0.000	0.025	0.057
alkynes	1630	1400	0.041	0.000	0.000	0.000	0.000	0.181	0.000	0.000	0.000	0.027	0.031
aromatic HCs	9310	4650	0.362	0.034	0.302	0.278	0.461	0.100	0.000	0.000	0.000	0.048	0.063
biogenic HCs	180	220	0.002	0.002	0.001	0.004	0.000	0.001	1.000	0.000	0.000	0.000	0.002
halogenated HCs	7430	6910	0.000	0.000	0.000	0.000	0.000	0.004	0.000	0.000	1.000	0.289	0.347
carbonyls	2900	2880	0.114	0.032	0.008	0.000	0.000	0.286	0.000	0.003	0.000	0.035	0.071
VOC sum	49 320	33 450	1	1	1	1	1	1	1	1	1	1	1

[a] TRA, traffic; EGA, gasoline evaporation; EDI, diesel fuel evaporation; LGA, liquid gasoline; LDI, liquid diesel fuel; WCO, wood combustion; BIO, biogenic sources; CNG, commercial natural gas; DCL, dry cleaning; DSW, distant sources winter; and DSS, distant sources in May and September.

Chemical Mass Balance Receptor Model. Using the Chemical Mass Balance Model Version 8 of the U.S. EPA/Desert Research Institute, the contributions of the different sources to the ambient air concentration of VOCs were estimated. A detailed description of the fundamentals of CMB modeling can be found, for example, in ref 20. In the application of the model, CMB8 applications and validation protocol for PM$_{2.5}$ and VOCs (21) were followed.

The source profiles and fitting species were selected by conducting sensitivity tests. The most reactive species were not used as fitting species (lifetime against OH-radical ≤ lifetime of 1,2,3 trimethylbenzene). An exception was made in the case of the biogenic compounds, which are all very reactive; some of them had to be used to describe the biogenic emissions. Some compounds with concentrations very close to the detection limit were not used even if their lifetime was longer than that of 1,2,3 trimethylbenzene, and ethyne and butane were excluded because of their occasionally poor resolution in the chromatogram. The fitting species used are marked with an asterisk (*) in Table S1 (see Supporting Information).

The CMB model calculates some statistical parameters that describe its performance; R-square (R^2), chi-square (χ^2), the percent mass (mass%), the ratio C/M, and the ratio R/U. These parameters are described, for example, in ref 21. The performance goals are $R^2 \geq 0.8$, $\chi^2 < 4$, mass% = 80−120, $0.5 \leq C/M \leq 2$, and $-2 \leq R/U \leq 2$. If R/U is below the value −2 or C/M is below 0.5, the concentrations are underestimated by the model, while if either the R/U or C/M value is over 2, the concentration is overestimated. The reason for an under- or overestimation can be errors in the source profile estimations or in the concentration measurements. A missing source can also cause underestimations, and the reactivity of the compounds can cause overestimations. In this study, the average values of R/U and C/M (av$_{R/U}$ or av$_{C/M}$) for each compound and the standard deviation (stdev) of these values were calculated; if the sum of the average and its standard deviation (av + stdev) exceeded either of these two performance goals, the daily values were checked and are discussed in the text.

Results and Discussion

The Ambient VOC Concentrations. Alkanes were the dominant functional group in both Helsinki and Järvenpää with 43% and 41% of the total concentration, respectively.

Concentrations of alkanes, alkenes, aromatic HCs, and gasoline additives were lower in Järvenpää than in Helsinki, while the concentrations of biogenic HCs, halogenated HCs, and carbonyls were quite similar at both locations (Table 1, see also Table S1 in Supporting Information). An exception was tetrachloroethene, whose concentration was almost 4 times higher in Helsinki than in Järvenpää. Such compounds with elevated concentrations are expected to have anthropogenic sources in Helsinki.

The VOC Source Profiles. The profiles differ significantly from each other causing no collinearity problems in the CMB calculations. Traffic emissions consist of various VOCs (Table 1); the main compound group is aromatic hydrocarbons followed by alkanes. Direct emissions of carbonyls are also noteworthy in the traffic emissions. In the gasoline vapor profile, light alkanes (C$_4$−C$_5$) provide the main contribution, especially butane, which comprises 42% of the total emission. Compared to the vapor profile, the contributions of less volatile aromatic hydrocarbons and gasoline additives are higher in liquid gasoline profile. Diesel fuel vapor is mainly composed of larger C$_7$−C$_{10}$ alkanes and aromatic hydrocarbons. A characteristic feature of the liquid diesel fuel is the large contribution of high C$_8$−C$_{10}$ alkanes.

In wood combustion emissions, alkenes and carbonyls make the highest contributions, but the shares of alkynes, aromatics, and alkanes are also significant. In each functional group, the lightest compounds (ethane, ethene, ethyne, benzene, chloromethane, and formaldehyde) provide the highest contributions. This was also shown in the wood emission studies of Hedberg et al. (4). As in this study, a halogenated compound, chloromethane, is commonly found in the emissions from wood combustion and biomass burning (e.g., 22, 23).

Commercial natural gas is almost totally composed of light alkanes, the main compound being ethane with a 57% contribution.

In the distant source profiles, compounds with longer atmospheric lifetimes, such as alkanes and halogenated hydrocarbons, dominate.

The Chemical Mass Balance Model Results. *The Model Performance.* Overall, the CMB results fulfilled the performance goals quite well (see Table S2, Supporting Information). R^2 was between 0.86 and 0.98, χ^2 was between 0.78 and 3.72, and the mass% was between 87 and 106.

More deviation was found for the individual compounds (see Table S3, Supporting Information). On the basis of the C/M and R/U values and their sums with their standard deviations (av$_{C/M}$ + stdev or av$_{R/U}$ + stdev), the model gave quite good results for the alkanes in both Helsinki and Järvenpää. Of the alkanes, butane was the most overestimated and 2-methylbutane was the most underestimated compound in Helsinki. Some deviation was expected for butane, since coelution with ethyne was sometimes a problem in the analytical system. In Järvenpää, 2-methylbutane was overestimated.

The average C/M was over 1 for most alkenes in Helsinki. This was expected, since the alkenes have double bonds in their structure that make them very reactive not only toward the hydroxyl radical but also toward ozone. They can therefore
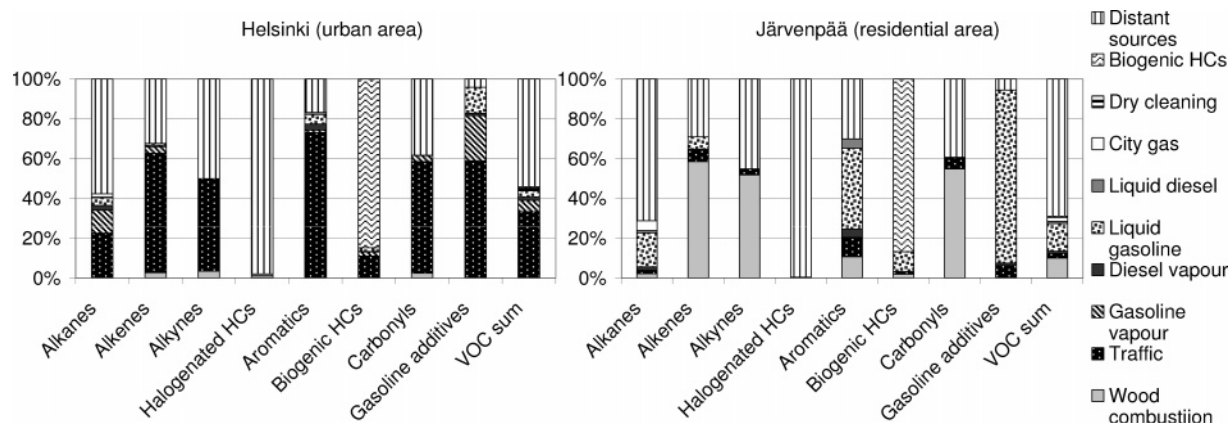
FIGURE 2. The contributions of different sources (as % of measured mass) to the concentrations of different compounds groups according to the CMB model.

react during the transport from the emission sources to the measuring site. The average C/M and R/U values for all alkenes fulfilled the performance goals, but for ethene, propene, and 1-butene, the sum of the average C/M or R/U values and their standard deviations ($av_{C/M}$ + stdev or $av_{R/U}$ + stdev) exceeded the goal values. The best results were obtained in February. In May, the reactivity is enhanced compared to the winter because of more sunlight and hence higher hydroxyl radical concentrations (1). In Järvenpää, concentrations of some of the alkenes were somewhat underestimated. However, their concentrations were so close to the detection limits that the sums of the R/U averages and the standard deviations ($av_{R/U}$ + stdev) were still within the performance goals. Despite a few deviations, the model performance was generally acceptable for alkenes in both Helsinki and Järvenpää.

In Helsinki in May and April, ethyne was all the time overestimated with the R/U values being 2.9–3.8. However, some deviation was expected because of the coelution problem with butane. For propyne, both measured and calculated concentrations were below the detection limit on most of the days.

For the aromatic hydrocarbons, the results were good, especially in Helsinki. In Järvenpää, the concentrations of most aromatic hydrocarbons were slightly underestimated. However, concentrations of the underestimated compounds were close to the detection limits and the deviation was therefore acceptable.

For the gasoline additives, MTBE and TAME, the results were acceptable in both Helsinki and Järvenpää.

C/M and R/U values indicated that there were some additional sources for chloroform in Helsinki and trichloroethene both in Helsinki and in Järvenpää. Otherwise, the model performance was good for the halogenated hydrocarbons.

Because biogenic compounds are very reactive and their concentrations are so close to the detection limits (most of the ambient concentration measurements were carried out during winter when biogenic emissions are very low), the model performance was not acceptable for most of these compounds. The only compound in this group for which the model gave acceptable results was isoprene.

A large part of the carbonyl concentrations was not explained by the sources used. The concentrations of some of the carbonyls (heptanal, pentanal, and nopinone) were not explained at all. An important source for carbonyl compounds, which was not taken into account in these calculations, is their formation in the atmospheric reactions of other VOCs (24). The model gave the best results in Helsinki in the cases of formaldehyde and acetaldehyde. For acetaldehyde, all C/M and R/U values were within the performance

goals in February and May. Formaldehyde values were slightly overestimated in February and underestimated in May and September. In May and September, the secondary production of these carbonyls is expected to be higher because of the shorter lifetimes of their precursors (1). The reason for the overestimated concentrations may be solubility. Formaldehyde is the most soluble carbonyl (25); the average precipitation amount on days when the formaldehyde concentrations were overestimated (ratio R/U > 2) was 2.2 mm, while on days when the ratio was acceptable (R/U < 2) it was 0.5 mm. In Järvenpää, acceptable results were only obtained for formaldehyde. For the other carbonyls, secondary or other sources played a major role, and the model performance was poor.

This shows that it is possible to apply the CMB in cases with a large number of different compounds with different properties. However, the performance of the model varies significantly for different compounds, and some of the results (for example, the carbonyls and terpenes) should be viewed with caution.

Total VOCs. Figure 2 shows the main VOC sources in Helsinki and Järvenpää. In both locations, distant sources were dominant, especially so in Järvenpää. In Helsinki, the traffic was a much more important source than at the residential site in Järvenpää, where the magnitude of wood combustion emissions exceeded those of traffic. Even at the urban site in Helsinki, contribution of distant sources is high compared to that of local sources. In many other studies (2, 6–8), local traffic has been the main contributor. However, in those studies, distant sources were not considered.

At the residential site in Järvenpää, the contribution of traffic was very low, only 2%, but the contribution of liquid gasoline was high (14%). This is probably partly explained by the filling station close by (<0.5 km). Traffic volumes in the residential area are indeed low, but even so the contribution of traffic is surprisingly small. The high contribution of distant sources and the low contribution of local sources may cause discrepancies in the local source apportionment.

In Järvenpää, wood combustion was responsible for a much higher contribution than in Helsinki. The reason for this is the higher volumes of small-scale wood combustion in residential areas, where fireplaces and saunas heated with wood are common. Small-scale wood combustion is not often included in CMB studies, and it may not be important in city centers. However, its contribution should be considered. In this study, the contribution of wood combustion to the VOC sum was 0.4% in Helsinki and 10% in Järvenpää. For some of the compounds, it was the main source. In an emission inventory for the Helsinki metropolitan area (3), the contribution of small-scale wood combustion to the total VOC

emissions was estimated to be 28%. In that emission inventory, distant sources are not considered. If only local sources are taken into account, the contribution of wood combustion according to our estimates was 0.8% in Helsinki and 32% in Järvenpää. In the Helsinki metropolitan area, there are large residential areas that are more similar to the residential site in Järvenpää than to the urban site close to the Helsinki city center.

Alkanes. The main source for alkanes in Helsinki and Järvenpää was distant sources (Figure 2). Of the local sources, traffic and gasoline vapor made the highest contributions in Helsinki, while the main local source in Järvenpää was liquid gasoline. Compared to the many other VOCs, alkanes have long lifetimes in the atmosphere (*24*), and therefore distant sources make a higher contribution to their concentrations than to that of the faster reacting VOCs.

For the lightest alkanes (C_2-C_3), other than distant sources made only a minor contribution in both Helsinki and Järvenpää (see Tables S4 and S5, Supporting Information), but for C_4-C_6 alkanes the contributions of traffic, liquid gasoline, and gasoline evaporation were high; for the largest alkanes ($>C_6$), the contribution of diesel fuel evaporation and liquid diesel fuel became important.

Alkenes. Traffic was the major source of most of the alkenes in Helsinki. Distant sources contributed 32%. In Järvenpää, wood combustion made a major contribution. Ethene is the most pronounced VOC in the wood-combustion profile (see Table S1, Supporting Information), and for ethene the contribution from wood combustion in Järvenpää was 69%. For 1,3-butadiene, wood combustion was also the main source with a 91% contribution, and for propene and 1-butene it was the main local source. For the other alkenes, liquid gasoline was the main local source in Järvenpää.

As shown here, not only traffic-related sources but also the wood combustion has a major influence on alkene concentrations, especially at the residential site. However, all ambient concentration measurements in Järvenpää were conducted during winter when most of the wood burning takes place. The contribution from traffic would probably be higher in summer.

Alkynes. The main alkyne (ethyne and propyne) source in both Helsinki and Järvenpää was distant sources. However, in Helsinki traffic also made a large contribution (Figure 2). In Järvenpää, wood combustion was the main local source, and the contribution due to traffic was only 2%. This shows that ethyne also has sources other than traffic-related sources, especially in areas other than urban areas.

Aromatic Hydrocarbons. For aromatic compounds in Helsinki, the most important source was traffic. The contribution of distant sources was much smaller than for alkanes and alkynes. This was expected, since the lifetimes of many aromatic hydrocarbons are shorter than those of the major alkanes and alkynes, and therefore aromatic hydrocarbons are not transported to such long distances.

Wood combustion has been estimated to be the major source of benzene in Finland (*5*), but at this urban location in Helsinki its contribution to the benzene concentration was <1% (see Table S4, Supporting Information). The most important source for benzene in Helsinki was distant sources with a 56% contribution, followed by traffic with 40%. For all other aromatic compounds, traffic was the main source. High contribution of distant sources to the benzene concentrations has also been noted earlier in a study comparing benzene concentrations at several urban and suburban stations in Helsinki to the concentrations at a regional and national background stations (*26*). Helsinki is not a very densely populated city (1260 inhabitant/km^2), and according to product data sheet of reformulated gasoline (RON-95) sold in Finland, benzene concentration in gasoline is low (typically 0.6%). Benzene content has been decreasing since the

beginning of the 1990s, when it was almost 10 times higher (~5%). Also, the number of catalyst cars has increased. Therefore, it is not surprising that the concentration of benzene in Helsinki is relatively low and that the contribution of distant sources is high.

For aromatic hydrocarbons in Järvenpää, the main source was liquid gasoline (Figure 2). However, for benzene and styrene, the contributions of liquid gasoline were low (see Table S5, Supporting Information). The main local source for these two compounds was wood combustion with 19% and 36%, respectively. This is not unexpected since benzene is the main aromatic hydrocarbon in wood combustion emission and also styrene is emitted by wood combustion (*4, 22*) (see Table S3, Supporting Information). In the emission inventories in Finland (*5*) and in Sweden (*27*), small-scale wood combustion has also been found to be the main source of benzene.

Gasoline Additives. For MTBE and TAME, the contribution of distant sources in Helsinki was small, and the highest source was traffic (Figure 2). The main source of TAME and MTBE in Järvenpää was liquid gasoline. Compared to the aromatic hydrocarbons, liquid gasoline and gasoline vapor were more important sources for these gasoline additives.

MTBE has been used as a tracer for automobile exhausts (*28*). In this study, traffic-related sources are able to explain the measured concentrations, and these results support the use of MTBE as a traffic tracer. However, gasoline vehicle exhausts are not the only source of gasoline additives, but gasoline vapor and liquid gasoline also contribute their share.

Halogenated Hydrocarbons. The concentrations of the halogenated hydrocarbons in the air of Helsinki were explained almost totally by the distant sources (Figure 2). The only additional source was dry cleaning. For tetrachloroethene, its contribution was high. There is a dry cleaner very close to the measuring site (~100 m), and therefore its impact is pronounced in these measurements.

Oceans are a source for some halogenated compounds (*29*), and the Arabian Sea was found to be a significant source for the halogenated compounds in the air of the city of Mumbai (*10*). Helsinki is located on the shores of the Baltic Sea. The distant source profile was measured on an island in the Baltic Sea, and possible emissions from the sea are therefore included in the profile. However, the Baltic Sea may not be such a significant source of these compounds because of its low salinity and cool water.

The concentrations of halogenated hydrocarbons in Järvenpää were explained by the distant sources with their almost 100% contribution. However, in addition to distant sources, wood combustion made a 2% contribution to chloromethane, and dry cleaning made a 16% contribution to tetrachloroethene

Biogenic Hydrocarbons. Isoprene was the only biogenic compound for which the model gave acceptable results. The major part of the isoprene concentrations was explained by the biogenic sources. However, traffic also made quite a high contribution (24%) in Helsinki, and in Järvenpää the contributions of liquid gasoline and wood combustion were 20% and 4%, respectively. This shows that there are also other important sources of isoprene other than biogenic emissions.

In urban areas, there might also be some other sources of biogenic VOCs, for example, biowaste and the processing of wood. Including their profiles could enhance the performance of the biogenic hydrocarbons in the model. However, because of the very low concentrations of biogenic hydrocarbons, no effort was put into quantifying these sources.

Carbonyls. Since the emissions and sources of the carbonyl compounds are uncertain, one aim of this study was to give some estimation of their direct anthropogenic sources; they were therefore not excluded, even if the model performance

was not acceptable. However, the results for the carbonyls should be viewed with caution.

The major sources of the carbonyls in Helsinki were traffic and distant sources (Figure 2). However, these sources could not explain a large part of the concentrations, and this indicates that secondary production in the atmosphere has an important role. Acetaldehyde had acceptable results in February and May in Helsinki. In those months, the main acetaldehyde source was traffic, with 86% and 73% contributions, respectively. For formaldehyde, which also had acceptable results, traffic contributed 70%. For the other carbonyls, secondary sources or some other sources played a major role.

In Järvenpää, small-scale wood combustion made a major contribution. Distant sources contributed 39% and traffic contributed only 5%. The main or at least the main local source for all carbonyls was wood combustion (Figure 2). As in the urban case, a large part of the concentrations was not explained by the model. However, the formaldehyde results were acceptable on most of the days. For formaldehyde, wood combustion contributed 64%. Distant sources and traffic were responsible for 33% and 3% contributions, respectively.

Acknowledgments

Supporting Information Available

Average winter concentrations of different compounds, statistical parameters, average source contributions of different VOCs. This material is available free of charge via the Internet at http://pubs.acs.org.

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