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SOURCES AND CONCENTRATIONS OF VOLATILE ORGANIC COMPOUNDS IN URBAN AIR

Heidi Hellén

ACADEMIC DISSERTATION

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Abstract

Volatile organic compounds (VOCs) have a great influence on tropospheric chemistry; they affect ozone formation and they or their reaction products are able to take part in secondary organic aerosol formation; some of the VOCs are themselves toxic. 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.

The objective of this work was to study volatile organic compounds in urban air, develop and validate determination methods for them, characterize their concentrations and estimate the contributions of different VOC sources.

Of the different compound groups detected in the urban air of Helsinki, alkanes were found to have the highest concentrations, but when the concentrations were scaled against the reactivity with hydroxyl radicals (OH), aromatic hydrocarbons and alkenes were found to have the greatest effect on local chemistry. Comparisons with rural sites showed that concentrations at Utö and Hyytiälä were generally lower than those in Helsinki, especially for the alkenes and aromatic hydrocarbons, but concentrations of halogenated hydrocarbons at Utö and carbonyls at Hyytiälä were at the same level as in Helsinki. Most halogenated hydrocarbons do not have any significant sources in Helsinki, and carbonyls are formed in the atmosphere in the reactions of other VOCs, and are therefore also produced in other than urban areas. At Hyytiälä carbonyls were found to have an important role in the local chemistry. The contribution of carbonyls as an OH sink was higher than that of the monoterpenes and aromatic hydrocarbons.

Based on the emission profile and concentration measurements, the contributions of different sources were estimated at urban (Helsinki) and residential (Järvenpää) sites 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. According to the CMB analysis, the major sources for these VOCs in Helsinki were traffic and distant sources. At the residential site in Järvenpää, the contribution due to traffic was minor, while distant sources, liquid gasoline and wood combustion made higher contributions. It was also shown that wood combustion can be an important source at some locations of VOCs usually considered as traffic-related compounds (e.g., benzene).

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Nimeke
Kaupunki-ilman haihtuvien orgaanisten yhdisteiden lähteet ja pitoisuudet

Tiivistelmä

Haihtuvat orgaaniset yhdisteet (VOC) vaikuttavat troposfäärin kemiaan ja osallistuvat otsonin sekä uusien hiukkasten muodostukseen. Lisäksi osa yhdisteistä on haitallisia tai myrkyllisiä. Reaktiivisten haihtuvien orgaanisten yhdisteiden lähteiden ja pitoisuuksien tietäminen onkin tärkeää mietittäessä mahdollisuuksia otsonipitoisuuksien vähentämiseksi ja tutkittaessa ilmakehän hiukkasten muodostumista ja kasvua.

Tämän työ tarkoitus oli tutkia kaupunki-ilman haihtuvia orgaanisia yhdisteitä, kehittää määritysmenetelmiä niiden mittaamiseksi ilmasta, määrittää pitoisuustasoja ja arvioida eri VOC-lähteiden merkitystä.

Eri yhdisteryhmistä alkaaneilla havaittiin olevan suurimmat pitoisuudet Helsingin ilmassa, mutta jos pitoisuuksia tarkasteltiin reaktiivisuuksien suhteen, aromaattisilla hiilivedyillä ja alkeeneilla havaittiin olevan suurin vaikutus paikalliseen ilmakemiaan. Aromaattisten hiilivetyjen ja alkeenien pitoisuuksien todettiin olevan Helsingissä korkeammat kuin tausta-alueilla Utössä ja Hyytiälässä, mutta halogenoitujen hiilivetyjen pitoisuudet Utössä ja karbonyylien pitoisuudet Hyytiälässä olivat samalla tasolla kuin Helsingissä. Useimmilla halogenoiduilla hiilivedyillä ei ole merkittäviä lähteitä Helsingissä. Karbonyylejä sen sijaan muodostuu ilmakehässä muiden orgaanisten yhdisteiden reaktiossa ja täten myös tausta-aluieilla. Hyytilässä karbonyyleillä havaittiin olevan merkittävä vaikutus paikalliseen ilmakemiaan. Karbonyylien todettiin olevan keväällä merkittävämpi hydroksyyliradikaalien nielu kuin monoterpeenit tai aromaattiset hiilivedyt.

Eri VOC-lähteiden merkitystä arvioitiin kaupunkialueella Helsingissä ja lähiöalueella Järvenpäässä kemiallisen massatasapaino (CMB) menetelmän avulla käyttäen lähtötietoina mitattuja päästölähdeprofiileja ja ilmapitoisuuksia. Päälähteet useimmille yhdisteille Helsingissä olivat liikenne ja kaukokulkeuma. Lähiöalueella Järvenpäässä liikenteen osuus oli pieni verrattuna kaukokulkeuman, bensiinin ja puunpolton osuuksiin. Tutkimuksen avulla pystyttiin toteamaan, että puunpoltto voi olla merkittävä lähde yhdisteille, joiden tavallisesti ajatellaan tulevan pääasiassa liikenteestä (esim. bentseeni).

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Heidi Hellén
Helsinki, May 2006

ABBREVIATIONS

APCI	atmospheric pressure chemical ionization
CFC	chlorofluorocarbon
CCl_4	tetrachloroethane
Cl	chlorine
$CH_3\cdot$	methyl radical
CH_4	methane
CMB	chemical mass balance
DNPH	dinitro phenyl hydrazine
ECD	electron capture detector
EU	European Union
FID	flame ionization detector
GC	gas chromatograph/chromatography
HAPs	harmful air pollutants
HCs	hydrocarbons
LC	liquid chromatograph/chromatography
MS	mass spectrometer/spectrometry
MTBE	methyl *tert*-butyl ether
NMHCs	non-methane hydrocarbons (i.e. alkanes, alkenes, alkynes, aromatic hydrocarbons and terpenes)
NO	nitrogen oxide
NO_2	nitrogen dioxide
NO_3	nitrate radical
NO_x	oxides of nitrogen ($NO+NO_2$)
O_3	ozone
$OH\cdot$	hydroxyl radical
PAN	peroxy acetyl nitrate
PE	propylene-equivalent
$R\cdot$	alkyl radical
$RCO\cdot$	acyl radical

RO·	alkoxy
RO_2·	alkyl peroxy
SOA	secondary organic aerosol
TAME	*tert*-amyl methyl ether
TMB	trimethylbenzene
UV	ultraviolet
VOC	volatile organic compound (i.e., NMHCs, halogenated hydrocarbons, aldehydes, ketones, and alcohols)
1,1,1-TCE	1,1,1-trichloroethane

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LIST OF ORIGINAL PAPERS

This thesis is based on the following five papers, hereafter referred to by their Roman numerals (I-V). Papers are reproduced with the kind permission of the journals concerned.

I: Hellén H., Hakola H., Laurila T., Hiltunen V. and Koskentalo T., 2002. Aromatic hydrocarbon and methyl tert-butyl ether measurements in ambient air of Helsinki (Finland) using diffusive samplers. The Science of the Total Environment, 298, 55-64.

II: Hellén H., Kukkonen J., Kauhaniemi M., Hakola H., Laurila T. and Pietarila H., 2005. Evaluation of atmospheric benzene concentrations in the Helsinki Metropolitan area in 2000-2003 using diffusive sampling and atmospheric dispersion modelling. Atmospheric Environment, 39, 4003-4014

III: Hellén H., Hakola H. and Laurila T., 2003. Determination of source contributions of NMHCs in Helsinki (60^{o}N, 25^{o}E) using chemical mass balance and the Unmix multivariate receptor models. Atmospheric Environment, 37, 1413-1424.

IV: Hellén H., Hakola H., Pirjola L., Laurila T. and Pystynen K.-H., 2006. Ambient air concentrations, source profiles and source apportionment of 71 different C2-C10 volatile organic compounds in urban and residential areas of Finland. Environmental Science and Technology, 40, 103-108.

V: Hellén H., Hakola H., Reissell A. and Ruuskanen T.M., 2004. Carbonyl compounds in boreal coniferous forest air in Hyytiälä, Southern Finland. Atmospheric Chemistry and Physics, 4, 1771-1780.

AUTHOR'S CONTRIBUTIONS

With great help from the other authors, the author of this thesis took the main responsibility for all parts of the studies presented, except for Paper II, in which J. Kukkonen, H. Pietarila and M. Kauhaniemi were responsible for the dispersion modelling.

1. INTRODUCTION

Volatile organic compounds (VOCs) are carbon-based compounds (with 2-10 carbon atoms) that have vapour pressures high enough to significantly vaporize and enter the atmosphere. Many different kinds of VOCs can be found in the air: alkanes, alkenes, alkynes, halogenated hydrocarbons, aromatic hydrocarbons, terpenes, aldehydes, ketones and alcohols. Some of these compounds are toxic or carcinogenic, and therefore there are limit values for their concentrations in the air (*U.S. EPA*, 2005a; *EU*, 2000).

VOCs affect atmospheric chemistry in many ways. In the atmosphere they are oxidized by hydroxyl radicals, ozone, nitrate radicals and halogens (Cl, Br, I) and in addition to this some of them can be photolysed. In the presence of nitrogen oxides they contribute to the ozone formation in the lower troposphere (reaction 1.1) (*Atkinson*, 2000). Ozone is toxic to humans and nature (*WHO*, 2003).

$$\text{VOC}+\text{NO}_x+\text{sunlight} \longrightarrow \text{O}_3 + \text{“other products”} \qquad (1.1)$$

“Other products” refers to gaseous peroxy acetyl nitrate (PAN), nitric acid and oxygenated hydrocarbons (e.g. carbonyls and organic acids). In the reactions of VOCs, water soluble hydroperoxides, carbonyls and acids are produced; VOCs therefore make a contribution to the organic content and acidity of precipitation (*Kawamura et al.*, 2001). One important aspect is that the reaction products of VOCs may also take part the in formation and growth of new particles, with possible climate and health consequences (*Griffin et al.*, 1999; *Hoffmann et al.*, 1997). Knowing the sources and concentrations of different VOCs is essential for the development of ozone control strategies and for studies of secondary organic aerosols.

Globally, are biogenic ones (e.g., trees and other vegetation) the main source of VOCs in the atmosphere (*Müller*, 1992). Estimated emission strengths for biogenic compounds are 500 Tg C/yr for isoprene, 128 Tg/yr for monoterpenes and 522 Tg/yr for other natural VOCs (*Guenther et al.,* 1995). Global anthropogenic VOC emissions are estimated to be only 142 Tg/yr (*Seinfeld and Pandis,* 1998). However, at urban locations biogenic sources make only a minor contribution, and anthropogenic VOC sources such as combustion processes, the use of fossil fuels, solvents and industrial production processes play the main role (*Friedrich and Obermeier,* 1999). Of the anthropogenic sources, traffic is the most important.

The objective of this work was to study volatile organic compounds in urban air, develop and validate measurement methods for them, characterize their concentrations and estimate the contributions of different VOC sources.

The more specific aims of the study were:

- to validate a diffusive sampling method for aromatic hydrocarbons and MTBE in urban air and estimate the diffusive uptake rates for them (paper I)
- to characterize concentrations of NMHCs (papers I-IV), halogenated HCs (paper IV) and carbonyls (papers IV and V) in urban air
- to compare the benzene results from the measurements and dispersion modelling (paper II)
- to determine profiles of the different VOC sources (papers III and IV)
- to study the source apportionments of NMHCs and aromatic hydrocarbons using receptor models (paper III)
- to compare the results of a chemical mass balance receptor model and a multivariate model UNMIX (paper III)
- to study source apportionments of individual VOCs using the chemical mass balance receptor model (paper IV)
- to develop a method for the sampling and analysis of C_2-C_{10} carbonyl compounds in ambient air (paper V)
- to study carbonyl compounds in the air of a forested site and compare concentrations with those of an urban site (paper V)

2. BACKGROUND

2.1. Emissions of VOCs

Globally, biogenic emissions of VOCs exceed those of anthropogenic origin (*Müller*, 1992). However, in urban areas the contribution of biogenic VOCs is much lower. Anthropogenic VOC sources include combustion processes, the use of fossil fuels, solvents, industrial production processes and biological processes (*Friedrich and Obermeier*, 1999). Whereas VOC emissions from combustion sources (e.g. traffic and wood combustion) mainly contain pure hydrocarbons, organic solvents and their vapours also consist of oxygenated HCs such as alcohols, carbonyls and esters.

Traffic and traffic-related sources are known to be a major source of non-methane hydrocarbons (NMHCs i.e., alkanes, alkenes, alkynes and aromatic HCs) in urban areas *(Friedrich and Obermeier, 1999; Watson et al., 2001*), but in residential or industrial areas other sources may also be important. In Nordic countries the use of wood as a fuel has increased lately (*Haaparanta et al.*, 2003; *Hedberg et al.*, 2002) and wood combustion is known to emit several different VOCs (i.e., NMHCs, halogenated hydrocarbons and oxygenated hydrocarbons) and other air pollutants *(McDonald et al.*, 2000). For the lightest alkanes, natural gas emissions may also be important (*Fujita*, 2001). Although ethene is a major constituent of the VOC emissions from traffic and from wood combustion (*Schauer et al.*, 2002 and *McDonald et al.*, 2000), it is also a plant hormone and is emitted by plants, soils and oceans (*Fall*, 1999). In addition to this, terpenes (isoprene and monoterpenes) have mainly biogenic sources.

Methyl *tert*-butyl ether (MTBE) and *tert*-amyl methyl ether (TAME) are used as gasoline additives in Finland. According to product specification sheet, content of ethers in gasoline typically sold in Finland is 11 %. Traffic is the main source of MTBE (*Chang et al.*, 2003), but also volatilization at gasoline station can make an important contribution to ambient concentrations, at least locally (*Vainiotalo et al.*, 1998).

Some halogenated HCs have both anthropogenic and biogenic sources. The main global anthropogenic sources of chloroform are pulp and paper manufacturing, other industrial sources and water treatment (*Aucott et al.*, 1999), while the main natural sources are the oceans, soil, termites and microalgae (*Laturnus et al.*, 2002). For chloromethane, industrial sources and biomass burning are the main anthropogenic sources, but large quantities are also emitted by the oceans and wetlands (*Butler*, 2000). Trichloroethene and tetrachloroethene are used as degreasing agents and tetrachloroethene is also used in dry-cleaning (*Rivett et al.* 2003). 1,1,1-trichloroethane is a solvent (*Rivett et al.* 2003) and chlorofluorocarbons (CFCs) have been used for example as aerosol propellants and refrigerants, but their use has been phased out as a result of the Montreal Protocol. Tetrachloromethane has been a chemical intermediate for the production of CFCs.

Carbonyls are also emitted from both anthropogenic and biogenic sources; in addition to this, they are formed in the atmosphere in the reactions of other organic compounds. Known primary anthropogenic sources are traffic and biomass burning (*Schauer et al.*, 2002 and *McDonald et al.*, 2000). However, the sources of carbonyls are not well characterized. In the global estimates by *Singh et al.* (2000), emissions from automobile exhausts and biomass burning comprised only 5% of the formaldehyde produced from methane oxidation. The main sources of propanal and acetaldehyde were found to be oceanic, and for them too the oxidation of hydrocarbons was found to be more significant than the primary anthropogenic sources. Vegetation is an important primary source of acetone and probably also of certain other carbonyls (*Singh et al.*, 2000; *Janson and De Serves*, 2001; *Bowman*, 2003).

2.2. Concentrations of VOCs

In some large cities, concentrations of VOCs can be very high compared with those in remote areas. In a recent study in Mumbay, India (*Srivastava et al.*, 2006), the annual average of benzene concentrations during rush hours in commercial areas and at traffic intersections were 127 $\mu g\ m^{-3}$ and 348 $\mu g\ m^{-3}$, respectively, and even in residential areas the average concentration was over 40 $\mu g\ m^{-3}$. In some European cities quite high concentrations have also been measured: for example, in a medium-sized Greek city, Ioannina, the annual average benzene concentrations measured at different locations in 2003/2004 were between 10 and 40 μg m^{-3} (*Pilidis et al.*, 2005). In measurements by *Hopkins et al.* (2002) taken on a ship in the Arctic area during August 1999, much lower benzene concentrations were found, averaging about 0.15 μg m^{-3}, while in the studies by *Kato et al.* (2001) in December 1999 of a remote island in the Pacific Ocean, the average concentration of benzene there was about 0.38 μg m^{-3}.

High differences in concentrations are also measured for most other VOCs. The lifetime of benzene is quite long and therefore it can be transported far from its emission sources. This is not the case for the more reactive compounds and, for example, the concentrations of most other aromatic hydrocarbons are below detection limits at a rural forested site in Central Finland even in winter, when the highest concentrations of NMHCs are measured *(Hakola et al.*, 2003).

In rural and remote areas NMHCs show a very clear seasonal cycle; in the Northern Hemisphere, the highest concentrations are measured in winter and the lowest in summer (*Hakola et al.,* 2006; *Gautrois et al.*, 2003). Winter maxima and summer minima of NMHCs are also observed in urban areas (e.g. *Morikawa et al*., 1998, *Sahu and Lal*, 2006 and paper II). For biogenic hydrocarbons and some carbonyls, the cycle is opposite: maximum concentrations are observed in summer, while minima occur in winter (*Hakola et al.*, 2003 and *Solberg et al*, 1996).

In Western Europe, emissions of VOCs have been decreasing since the early 1990's, and a decreasing trend in ambient concentrations has also been observed in Central Europe (*Solberg et al.,* 2002). However, in remote areas of Finland, for example, no clear decrease in concentrations has been found for most of the compounds; for some long-living compounds (ethane and propane) increasing trends have even been observed (*Hakola et al.,* 2006).

2.3. Reactions of VOCs in the troposphere

2.3.1. Reaction mechanisms of VOCs

Each volatile organic compound reacts in the air at a different rate and with different reaction mechanisms. These compounds react with OH radicals, ozone, NO_3 radicals or Cl atoms, or they photolyze. For most of the studied VOCs, the OH reactions are the most important in the daytime (*Atkinson*, 2000). NO_3 photolyses rapidly in the troposphere and therefore only exists in sufficient concentrations to play a role in night-time chemistry. Cl atoms can be important in the marine boundary layer. For some carbonyls, MTBE and TAME wet depositions may also be an important sink (*Kawamura et al.*, 2001, *Achten et al.*, 2001 and *Kolb and Püttmann,* 2006).

For the alkanes, the OH radical reactions are the main reaction in the troposphere, but reactions with NO_3 radicals and Cl atoms are also important (*Atkinson*, 2000). Alkanes do not undergo photolysis or react significantly with ozone. Alkane reactions proceed by hydrogen atom abstraction from the C-H bond forming alkyl radicals (reaction 2). These alkyl radicals (R·) react rapidly with O_2 to form alkyl peroxy radicals ($RO_2\cdot$) (reaction 3).

$$RH + OH\cdot \rightarrow R\cdot + H_2O \qquad (2)$$
$$R\cdot + O_2 + M \rightarrow RO_2\cdot + M \qquad (3)$$
$$RO_2\cdot + NO \rightarrow RO\cdot + NO_2 \qquad (4a)$$
$$\rightarrow RONO_2 \qquad (4b)$$

RO· reaction with O_2, isomerization or decomposition

The main reaction for the $RO_2\cdot$ radicals in polluted urban air is with NO, producing NO_2 and alkoxy radicals (RO·) (reaction 4a) (*Derwent*, 1999). For larger alkanes, the addition of NO to form an alkyl nitrate ($RONO_2$) may also be an important path (reaction 4b) (*Finlayson-Pitts and Pitts*, 2000). At very high NO_2 concentrations, reactions with NO_2 to form peroxynitrate (RO_2NO_2) may become important. Alkoxy (RO·) radicals have several possible atmospheric fates, depending on their structure. These include reactions with O_2 forming hydrogen peroxy radicals ($HO_2\cdot$), decomposition and isomerization. If isomerization is possible at room temperature, this process is the predominant one; otherwise, reaction with O_2 is significant. In those reactions carbonyls are formed, for example.

Alkenes are highly reactive towards $OH\cdot$, O_3 and $NO_3\cdot$. Reaction rates with O_3 are much smaller than with the OH radicals. However, concentrations of O_3 are much larger, and therefore the O_3 reactions are important removal processes, especially for the larger alkenes (e.g. biogenic hydrocarbons) (*Hakola et al.*, 2003; *Atkinson*, 2000). Reaction rates for NO_3 are also fast, and the NO_3 reaction is assumed to be a major fate for at least biogenic hydrocarbons during the night (*Hakola et al.* 2003). In the case of alkenes, $OH\cdot$ and $NO_3\cdot$ add to the double bonds and alkyl radicals are formed. The reactions of these alkyl radicals are analogous to the reactions of alkyl radicals formed in the alkane reactions. In the O_3 reaction, ozone adds to the carbon double bond, forming an energetically-excited primary ozonide (*Finlayson-Pitts and Pitts*, 2000). This will either decompose forming an ester (minor) or an unsaturated hydroperoxide (major). The latter is assumed to account for the $OH\cdot$ yield measured. In addition to this, the primary ozonide can be collisionally stabilized, forming the so-called stabilized Criegee intermediate, which further reacts with various different compounds, e.g. water vapour.

The only significant loss process for alkynes is a reaction with OH radicals. (*Finlayson-Pitts and Pitts*, 2000). The reaction is an addition to the triple bond forming the alkyl radical. The reactions of these alkyl radicals are analogous to the reactions of the alkyl radicals formed in the alkane reactions.

Under atmospheric conditions, aromatic hydrocarbons are oxidized by OH and $NO_3\cdot$radicals, with the OH radical reactions dominating as the tropospheric removal process (*Atkinson*, 2000). In aromatic reactions, the abstraction of H-atoms or the addition of an OH radical to the double bond may occur. The reactions of benzyl and alkyl-substituted benzyl radicals formed from the H-atom abstraction are analogous to those for the alkyl radicals discussed above. OH-aromatic adducts react with O_2 and NO_2.

The gasoline additives MTBE and TAME react with the OH radical, but also deposition with precipitation is significant loss process (*Kolb and Püttmann*, 2006)

The major tropospheric loss process for the halogenated hydrocarbons is by reaction with the OH radical (*Atkinson*, 2000). Halogenation generally decreases the reactivity towards the OH radicals, O_3 and NO_3 radicals compared to the corresponding alkanes and alkenes and therefore the reactions of most halogenated HCs are very slow in the troposphere.

Carbonyls (aldehydes and ketones) undergo photolysis and reactions with OH and NO_3 radicals (paper V). For unsaturated carbonyls O_3 reactions are also important. The reactions of OH· and NO_3· with aldehydes occur by abstraction of the H-atom from the –CHO group, forming acyl radicals (RCO·) (*Finlayson-Pitts and Pitts*, 2000). The RCO radical adds O_2 to form the acyl peroxy radical (RC(O)OO·). This radical reacts in turn with NO and NO_2 in an analogous way to alkyl peroxy radicals (*Atkinson*, 2000). From the reaction with NO_2, peroxy acyl nitrates are formed; for example, acetaldehyde is a classic precursor to peroxyacetyl nitrate (PAN). PAN thermally decomposes back to a peroxyacetyl radical and NO_2. The reactions of ketones are similar to those of alkanes, with abstraction by OH· and NO_3· occurring from the alkyl chain (*Finlayson-Pitts and Pitts*, 2000). In addition to the OH· reaction, photolysis is an important loss process for carbonyls in the troposphere (*Atkinson*, 2000 and paper V). In these photo-dissociation reactions both free radicals and stable products are formed; for example, in the photolysis of acetaldehyde (reaction 5) two sets of products, methyl (CH_3·) and acyl (HCO·) radicals (reaction 5a) or stable methane (CH_4) and carbon monoxide (CO) (reaction 5b), are formed (*Finlayson-Pitts and Pitts*, 2000):

$$CH_3CHO + h\nu \rightarrow CH_3\cdot + HCO\cdot \qquad (5a)$$

$$\rightarrow CH_4 + CO \qquad (5b)$$

2.3.2. Lifetimes of VOCs

The lifetime is the time for the concentration of an organic compound to fall to 1/e of its initial value (*Finlayson-Pitts and Pitts*, 2000). Natural lifetimes (τ) are defined as $\tau = 1/k_p[X]$, where k_p is the reaction rate of the compound and [X] is the concentration of the oxidant.

Based on the OH radical estimates by *Hakola et al.* (2003) for Central Finland, average daytime lifetimes involving the OH reaction vary for the studied VOCs from a few hours for monoterpenes to several hundred years for some halogenated HCs (Table 1). The lifetimes of VOCs for OH reactions are 20 times shorter in summer than in winter in Finland; for example, the lifetime of toluene in winter is 59 d, but in summer only 3 d.

Ozone reactions are only important for alkenes, biogenic hydrocarbons and some carbonyls with double bonds. Based on the estimates shown in Table 1, the ozone reaction is a more important loss process for most of the alkenes and biogenic hydrocarbons than hydroxyl radical reaction, at least in winter. The lifetimes of alkenes for ozone reactions vary from a few hours to 14 days.

2.3.3. Reaction products of VOCs

The reactions of VOCs can be complex and lots of different products are produced. For the studies of reaction products, models and smog chambers have been used. In the publication Master Chemical Mechanism, currently-available laboratory data (not field or photochemical reactor data) are collected and the reaction schemes of 135 VOCs can be followed (*Master Chemical Mechanism*, 2006). When considering all possible reactions of a VOC and its reaction products, schemes expand very rapidly. The full degradation scheme of butane, for example, consists of 510 reactions and 186 species, of which 20 are themselves primary emitted VOCs for which separate schemes are given.

Table 1. Average daytime lifetimes of VOCs in reaction with OH radicals (τOH) and O_3 (τO_3). Concentrations for OH radicals are daytime averages for winter (Dec-Feb) of $3.3*10^4$ molecule cm^{-3} and for summer (Jun-Aug) of $6.4*10^5$ molecule cm^{-3}; for O_3 the monthly average concentrations are for winter $5.6*10^{11}$ molecule cm^{-3} and for summer $8*10^{11}$ molecule cm^{-3} in Central Finland (adapted from *Hakola et al.* (2003)). Reaction rates at 298±2 K are from *Atkinson* (1994), except for carbonyls, for which the values from paper V are used and for the TAME reaction rate, which is from *Becker* (1996).

	τOH (win)	τOH (sum)	τO_3 (win)	τO_3 (sum)		τ OH (win)	τOH (sum)	τO_3 (win)	τO_3 (sum)
Alkanes					Biogenic HCs				
Ethane	1358 d	70 d	-	-	Isoprene	3,5 d	4,3 h	1.6 d	1.1 d
Propane	303 d	16 d	-	-	a-pinene	6,5 d	8,1 h	5.8 h	4.1 h
2-methylpropane	150 d	7,8 d	-	-	Camphene	6,6 d	8,2 h	23 d	16 d
Butane	138 d	7,2 d	-	-	b-pinene/myrcene	6,5 d	8,1 h	1.4 d	23 h
2-methylbutane	89 d	4,6 d	-	-	3-carene	4,0 d	4,9 h	13 h	9.4 h
Pentane	88 d	4,6 d	-	-	Gasoline additives				
Cyclohexane	47 d	2,4 d	-	-	MTBE*	119 d	6,1 d	-	-
2-methylpentane	62 d	3,2 d	-	-	TAME	55 d	2,9 d	-	-
3-methylpentane	61 d	3,2 d	-	-	Halogenated HCs				
Hexane*	62 d	3,2 d	-	-	CFC-12	-	-	-	-
Mecyclohexane	34 d	1,7 d	-	-	Chloromethane*	18 a	341 d	-	-
Octane	40 d	2,1 d	-	-	CFC-11	-	-	-	-
Nonane	34 d	1,8 d	-	-	CFC-113	-	-	-	-
Decane	30 d	1,6 d	-	-	Chloroform*	9,3 a	175 d	-	-
Alkenes					1,2-dichloroethane*	362 a	19 a	-	-
Ethene	41 d	2,1 d	14 d	9.7 d	1,1,1-TCE*	88 a	4,5 a	-	-
Propene	13 d	16 h	2.2 d	1.5 d	CCl4*	9,8 a	185 d	-	-
Trans-2-butene	5,5 d	6,8 h	2.6 h	1.9 h	Trichloroethene*	54 a	2,8 a	-	-
1-butene	11 d	14 h	2.4 d	1.6 d	Tetrachloroethene*	5,5 a	104 d	-	-
2-methylpropene	6,8 d	8,4 h	1.9 d	1.3 d	Carbonyls				
Cis-2-butene	6,2 d	7,7 h	4.1 h	2.9 h	Formaldehyde*	37 d	1,9 d	27000 a	19000 a
1,3-butadiene*	5,2 d	6,5 h	3.3 d	2.3 d	Acetaldehyde*	57 d	2,9 d	9.5 a	6.6 a
Trans-2-pentene	5,2 d	6,5 h	-	-	Acetone	1591 d	82 d	-	-
Cis-2-pentene	5,3 d	6,6 h	-	-	Propanal	35 d	1,8 d	-	-
Alkynes					Butanal	15 d	18 h	-	-
Ethyne	428 d	22 d	-	-	Pentanal	13 d	16 h	-	-
Propyne	59 d	3,1 d	-	-	Hexanal	12 d	15 h	-	-
Aromatic HCs					Heptanal	12 d	15 h	-	-
Benzene*	264 d	14 d	333 a	233 a	Octanal	12 d	15 h	-	-
Toluene*	59 d	3,0 d	138 a	97 a	Nonanal	9,7 d	12 h	-	-
Ethylbenzene	49 d	2,5 d	-	-	Decanal	11 d	14 h	-	-
p/m-xylene*	18 d	23 h	57 a	40 a	Methacrolein	13 d	16 h	16 d	11 d
Styrene*	6 d	7,5 h	-	-	Benzaldehyde	49 d	2,5 d	-	-
o-xylene*	25 d	1,3 d	33 a	23 a	m-tolualdehyde	-	-	-	-
Propylbenzene	58 d	3,0d	-	-	Nopinone	24 d	1,3 d	-	-
3-ethyltoluene	18 d	23 h	-	-					
4-ethyltoluene	29 d	1,5 d	-	-					
1,3,5-TMB	6,1 d	7,6 h	-	-					
2-ethyltoluene	28 d	1,5 d	-	-					
1,2,4-TMB	11 d	13 h	-	-					
1,2,3-TMB	11 d	13 h	-	-					

Mecyclohexane=methylcyclohexane, TMB=trimethylbenzene, MTBE=methyl-*tert*-butylether, TAME=*tert*-amylmethylether, 1,1,1-TCE= 1,1,1-trichloroethane, CCl_4=tetrachloroethane
*compounds marked with asterisks (*) are classified as hazardous air pollutant by U.S. EPA

Reaction products formed in chamber studies are mainly carbonyls, alcohols, organic nitrates and acids, found in both gas and aerosol phases (*Hamilton et al.*, 2005; *Forstner et al.*, 1997; *Yu et al.*, 1997). Multifunctional products are common. Concentrations in chambers are often 1000 times higher than in the real atmosphere, but some of the products identified in modelling or chamber studies have also been detected in the ambient atmosphere (*Hamilton et al.*, 2004; *Edney et al*, 2003).

The reactions of aromatic hydrocarbons are extremely complex; numerous reaction pathways have been identified, and a very large variety of different kinds of products has been found in chamber studies. Compounds include carbonyls, dicarbonyls, organic acids, aromatics, furans, furanones and pyranones (*Hamilton et al.*, 2005; *Yu et. al.*, 1997; *Forstner et al.,* 1997). Many of the products are capable of producing secondary organic aerosol (*Hamiltom et al.*, 2005; *Izumi and Fukuyama*, 1990; *Takekawa et al.*, 2003; *Odum et al.,* 1997; *Grosjean,* 1992).

Often some major products are found. For isoprene, methyl vinyl ketone, methacrolein and formaldehyde have been found to account for 60 % of the total OH reaction products (*Pinho et al., 2005*). Reactions of alkynes with OH radicals give as major products the corresponding dicarbonyls, i.e., ethyne gives glyoxal and propyne gives methylglyoxal (*Finlayson-Pitts and Pitts*, 2000), while the main product of the OH radical reaction of MTBE has been found to be *tert*-butylformate (TBF) (*Kolb and Püttmann*, 2006).

2.4. The role of VOCs in the troposphere

2.4.1. The role in ozone formation

In the troposphere, ozone is produced by photolysis of NO_2 (*Sillman*, 1999; *Atkinson*, 2000). Ozone then rapidly oxidises NO back to NO_2, as shown in reactions 6-8.

$$NO_2 + h\nu \rightarrow NO + O(^3P) \qquad (6)$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \qquad (7)$$

$$O_3 + NO \rightarrow NO_2 + O_2 \qquad (8)$$

However, in the atmosphere, in addition to ozone, there are other oxidants (hydroperoxy and alkylperoxy radicals) to convert NO to NO_2. These free radicals are formed in the reactions of VOCs (reactions 2-4). The relations between ozone, NO_x and VOCs are complex. In some conditions, ozone formation is controlled almost entirely by NO_x, while in other conditions ozone production increases with increasing VOC and does not increase with increasing NO_x. These relations are often described by ozone isopleths (e.g. Figure 1). These plots show ozone concentrations as a function of initial NO_x and VOC concentrations. Based on ozone isopleth plot in Figure 1 *(Seinfeld and Pandis*, 1998) ozone formation in average situation in Helsinki is controlled by NO_x. A more detailed description of ozone, NO_x and VOC relations can be found in *Sillman* (1999). For ozone control strategies, both emissions of VOCs and NO_x have to be considered.

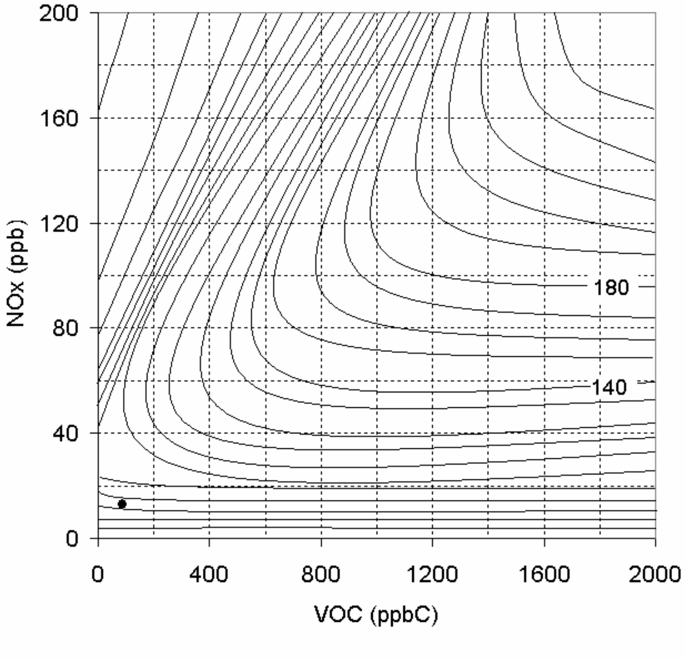

Figure 1. Ozone isopleth plot based on simulations of chemistry along air trajectories in Atlanta according to *Seinfeld and Pandis* (1998). Each isopleth is 10 ppb higher in O_3 as one moves upward and to the right. Black dot describes the average situation in Helsinki in summer. Concentrations of NOx (*Aarnio et al.*, 2005) and VOCs (paper IV) are summer averages at the urban background station of Kallio in Helsinki in 2004.

The rate of ozone production from a given VOC is a function of the compound's atmospheric concentration, its rate of reaction with OH (and NO_3 and O_3) and the number of ozone molecules produced each time the compound is oxidized (*Seinfeld and Pandis*, 1998). The propylene equivalent (PE) determines in an approximate manner the compound's relative role as an ozone precursor. The propylene equivalent is defined as (*Chameides et al.*, 1992):

$$PE(j) = Conc(j)\frac{k_{OH}(j)}{k_{OH}(propene)} \qquad (1.1)$$

where Conc(j) is the concentration of a compound j, $k_{OH}(j)$ is the reaction rate of compounds j with hydroxyl radicals and k_{OH}(propene) the reaction rate of propene with the hydroxyl radical.

Chameides et al. (1992) found that, based on their propylene equivalents, the most important groups for the ozone formation in the urban air of Atlanta were aromatic hydrocarbons and alkenes. To better describe the ozone-forming capability of individual organics, VOC "reactivity scales" have been developed (*Carter*, 1994). One approach is that of the Maximum Incremental Reactivity, which is defined as the amount of O_3 formed per amount of VOC added. Another commonly-used method is the calculation of photochemical ozone creation potentials, where the master chemical mechanism and air parcel trajectory models are used (*Derwent et al.*, 2001). In those studies, aromatic hydrocarbons and alkenes were found to be the main ozone precursors in urban air, but aldehydes also had quite high ozone formation potentials.

Peroxy acyl nitrates are formed from the reactions of VOCs; as already mentioned, acetaldehyde is a classic precursor to peroxyacetyl nitrate (PAN) (*Finlayson-Pitts and Pitts*, 2000). PANs are able to transport NO_x far away from the urban and industrial areas. This is important for tropospheric ozone production, as PANs transport NO_x to rural and remote regions, where ozone formation is NO_x-limited (*Sillman*, 1999)

2.4.2 VOCs as a free radical source

Some VOCs can also be a source of free radical. As a result of the photolysis reactions of carbonyls, free radicals are formed. *Possanzini et al.* (2002) showed in their studies, for example, that the photolysis of formaldehyde is the most intense source of hydroxyl radicals in Rome during all sunlight hours of both summer and winter days. In addition to this, in alkene reactions with O_3, free radicals are formed from the Criegee intermediates (*Finlayson-Pitts and Pitts,* 2000), and this can be an important source of OH radicals during the night.

2.4.3 Secondary organic aerosol formation

In the reactions of VOCs less volatile products are formed that can participate in secondary organic aerosol (SOA) formation. It has been estimated that the major SOA precursors are biogenic VOCs, but anthropogenic contribution to SOA formation can be important in polluted regions (*Kanakidou et al.*, 2005). SOA may account for a significant fraction of the total organic carbon in urban particulate matter (*Pandis et al.*, 1992). These less volatile reaction products, that may form SOA, include aliphatic acids, aromatic acids, nitro aromatics, carbonyls, esters, phenols, aliphatic nitrates and amides (*Grosjean*, 1992).

The biogenic hydrocarbons, monoterpenes and sesquiterpenes, are believed to have an important role in SOA formation in rural and remote areas (*Griffin et al.*, 1999; *Hoffmann et al.*, 1997; *Bonn and Moortgat*, 2003), but in urban areas aromatic hydrocarbons play a significant or even dominant role (*Pandis et al.*, 1992). There are number of studies of the formation of aerosols from the photo-oxidation of aromatics (e.g. *Izumi and Fukuyama*, 1990; *Takekawa et al.*, 2003; *Odum et al.,* 1997; *Grosjean D.*, 1992 and *Pandis et al.*, 1992;). Toluene and xylenes are estimated to be the main aromatic SOA precursors (*Odum et al.,* 1997; *Grosjean D.*, 1992 and *Pandis et al.,* 1992), but there is some recent evidence that even benzene may act as a precursor (*Martin-Reviejo and Wirtz*, 2005). In addition to aromatics, large (>6 carbon atoms) alkanes, cycloalkanes and cycloalkenes are considered to be SOA precursors (*Pandis et al.*, 1992 and *Grosjean*, 1992). The heterogeneous reactions of carbonyls on aerosol surfaces are also estimated to have great importance for SOA formation (*Jang et al.*, 2002 *and Kalberer et al.*, 2004).

2.4.4. VOCs and climate change

Non-methane volatile organic compounds influence climate change mainly through their production of organic aerosols and their involvement in the production of O_3 (*IPCC*, 2001). Other VOCs than halogenated hydrocarbons have only a small direct impact on radiative forcing. The halogenated HCs with the largest potential to influence climate are CFC-11 ($CFCl_3$), CFC-12 (CF_2Cl_2), and CFC-113 ($CF_2ClCFCl_2$). The radiative forcing due to these three halocarbons is approximately 13 % of the total radiative forcing due to carbon dioxide, methane and nitrous oxide.

2.5. Health effects of VOCs

There are many different compounds present in the air that can be harmful to humans or the environment. The European Union (EU) has set limit values for the some of the most harmful air pollutants, which can have health effects even at very low concentrations. Of the VOCs, there is a limit value of 5 $\mu g\ m^{-3}$ for the annual average benzene concentration in the air (*EU*, 2000). Benzene is a known genotoxic carcinogen.

The U.S. Environmental Protection Agency (*U.S. EPA*, 2005a) has listed 188 compounds as hazardous air pollutants (HAPs), which have to be controlled. They define hazardous air pollutants as those pollutants that cause or may cause cancer or other serious impacts upon health, such as reproductive effects or birth defects, or adverse environmental and ecological effects. In Table 1, compounds listed as HAPs are marked with asterisks (*). As can be seen, there are only a few HAPs among the alkanes, alkenes and alkynes, but of the aromatic and halogenated hydrocarbons many are harmful. Of the carbonyls only formaldehyde and acetaldehyde are listed as HAPs. For many of the HAPs, however, harmful concentrations are much higher than those found generally in urban air; close to the source, though, concentrations can be high.

In addition to this, ozone is a toxic to humans and the environment, and VOCs contribute to the enhanced production of ozone, as described above. Even though actual emissions of ozone precursors have decreased in Europe (*Jonson et al.*, 2006), ozone concentrations have increased in Finland in the years 1990-2000 (*Laurila et al.,* 2004). The Ozone Directive (*EU*, 2002) by the EU obligates member states in future to monitor 31 volatile organic compounds that are considered as ozone precursors.

It is also possible that the reaction products of some VOCs are more harmful than the VOCs themselves (*Yu and Jeffries*, 1997), and in addition to this, VOCs' reaction products are able to produce SOA and fine particles, which are known to have serious health effects (*WHO*, 2003).

3. EXPERIMENTAL

3.1. Measurement sites

Measurements of VOCs have been conducted in the cities of Helsinki and Järvenpää in southern Finland, in a forest research station at Hyytiälä in central Finland, on an island (Utö) in the Baltic Sea, at the Global Atmospheric Watch (GAW) station of Pallas in Northern Finland and at the end of a cape (Emäsalo) close to Helsinki. The locations of the different measurement sites are shown in Figure 2.

The aromatic hydrocarbons and MTBE used in these studies have been measured at 7 different locations in Helsinki in 2000, 2002 and 2003. The stations used represented urban traffic (Töölö), suburban traffic (Leppävaaara, Ruskeasanta and Tikkurila), an industrial environment (Herttoniemi) and an urban background (Kallio). Regional background concentrations were also monitored in a rural environment at Luukki, located approximately 20 km north-west of the centre of Helsinki. The locations and detailed descriptions of these stations are presented in paper II.

The urban background station of Kallio was used as a main station for the measurements in receptor modelling studies in 2001 and 2004. In 2004, measurements were also conducted at a residential site in the city of Järvenpää. Distant-source profile measurements for these studies were conducted at the end of a cape (Emäsalo) located 30 km to the east of Helsinki in 2001 and on an island (Utö) in the Baltic Sea in 2004. Measurements of the ambient concentrations of carbonyl compounds were also conducted at the SMEAR II station (Station For Measuring Forest Ecosystem-Atmosphere Relations, 61°51'N, 24°17'E, 181 m a.s.l.) located at Hyytiälä in Central Finland.

Figure 2. Location of the measurement sites of Helsinki, Järvenpää, Utö, Emäsalo, Hyytiälä and Pallas.

3.2. Sampling and analysis of volatile organic compounds

Because hundreds of different VOCs with different volatility and polarity exist in the air at different concentration levels, various different sampling and analysis methods are needed. Most of the concentrations are at very low levels (ng/m^3 – µg/m^3) and pre-concentration is necessary. Some of the VOCs are very reactive and, for example, ozone removal during sampling is crucial. Water and carbon dioxide can also cause problems when gas chromatographic methods or cold traps are used, and therefore various removal techniques are used. For some of the VOCs, ozone and water removal traps can also cause problems (*Pollmann et al.*, 2006 and *Zielinska et al.*, 1996). Figure 3 shows the overall schematics of the sampling and analyzing methods used in this study.

Because the analyzing systems for VOCs are not easily used in field conditions, sampling is mostly conducted using offline methods. Sampling times vary from a few seconds in canister sampling to several weeks in diffusive adsorbent sampling. The sampling time depends on method used, the detection limit, the flow rate and the concentration of the compound. Details of the sampling methods used in this study are listed in Table 2.

Table 2. Descriptions of the sampling methods used and references to the papers.

Compounds	Method	Notes	Flow rate	Sampling time	Paper
Aromatic HCs, MTBE	Diffusive adsorbents sampling	Carbopack-B tubes	0.44-0.64 cm^{3}min^{-1}	2 weeks	I, II
Aromatic HCs, C_6-C_{10} alkanes, MTBE, TAME, monoterpenes, halogenated HCs	Pumped adsorbent sampling	Tenax TA – Carbopack-B tubes	50-90 ml min-1	1-4 hours	I,II,II,IV
Light (C_2-C_6) HCs, halogenated HCs	Canister sampling	0.85 l and 6 l canisters		< ½min or 24 h	II,III,IV
Light (C_2-C_6) HCs	Tedlar bags	Emission studies		<½min	III
C_1-C_{12} carbonyls	DNPH-sampling	DNPH-cartridges	~900ml min^{-1}	24 h	V
Aromatic HCs	Online	Collection to a cold trap	52 ml min^{-1}	1 hour	I

Most of the chromatographic methods used in the analysis of volatile organic compounds are based on gas chromatography (*Hellén*, 2001). When analyzing these very volatile compounds, long columns with thick films (1-10 μm) are needed. For the most volatile compounds (C_2-C_4), porous-layer open-tubular (PLOT) columns are usually used. For C_6-C_{10} hydrocarbons, the most common columns are wall-coated open-tubular (WCOT) columns with non-polar stationary phases (e.g. dimethylpolysiloxane). For carbonyls, liquid chromatography with derivatization is also used. Details of the analysing methods used in this study are listed in Table 3.

Table 3. Descriptions of the analysing methods used and references to the papers.

Compounds	Method	Column	Column specifications	Notes	Paper
C_6-C_{10} HCs, MTBE, TAME, halogenated HCs	GC-MS	HP-1/HP-5 (Agilent technologies)	Length: 60 m Inner diameter: 0.25 mm, Film thickness: 1μm	Adsorbent tubes+thermal desorption (ATD-400), online sampling	I-IV
C_2-C_6 HCs + CH_3Cl	GC-FID	Al_2O_3/KCl PLOT (Chrompack)	Length: 50 m Inner diameter: 0.32 mm, Film thickness: 5 μm	Canisters, liquid nitrogen cold traps	III,IV
Halogenated HCs	GC-ECD	Al_2O_3/KCl PLOT (Chrompack)	Length: 50 m Inner diameter: 0.32 mm, Film thickness: 5 μm	Canisters , liquid nitrogen cold traps	IV
Formaldehyde, acetaldehyde	LC-UV	XORBAX Eclipse XDB-C8 (Agilent technologies)	Length: 150 mm Inner diameter: 4.6 mm Particle size: 5 μm	DNPH-cartridges, solvent desorption	IV,V
C_1-C_{12} carbonyls	LC-MS	XORBAX Eclipse XDB-C8 (Agilent technologies)	Length: 150 mm Inner diameter: 4.6 mm Particle size: 5 μm	DNPH-cartridges, solvent desorption	IV,V

Recently, fast online methods for VOC determinations have been developed. Proton transfer reaction mass spectrometry (PTR-MS) with a high time resolution, for example, has been able to provide a lot of new and valuable information for VOC studies (e.g. *Karl et al.*, 2002 and 2003, *Salisbury et al.*, 2003 and *Lee et al.*, 2005). In these methods, however, separation of different compounds having the same masses is not possible, and for the identification of the compounds an additional chromatographic method is usually needed. In addition to this, the detection limits for some compounds are higher than in chromatographic methods.

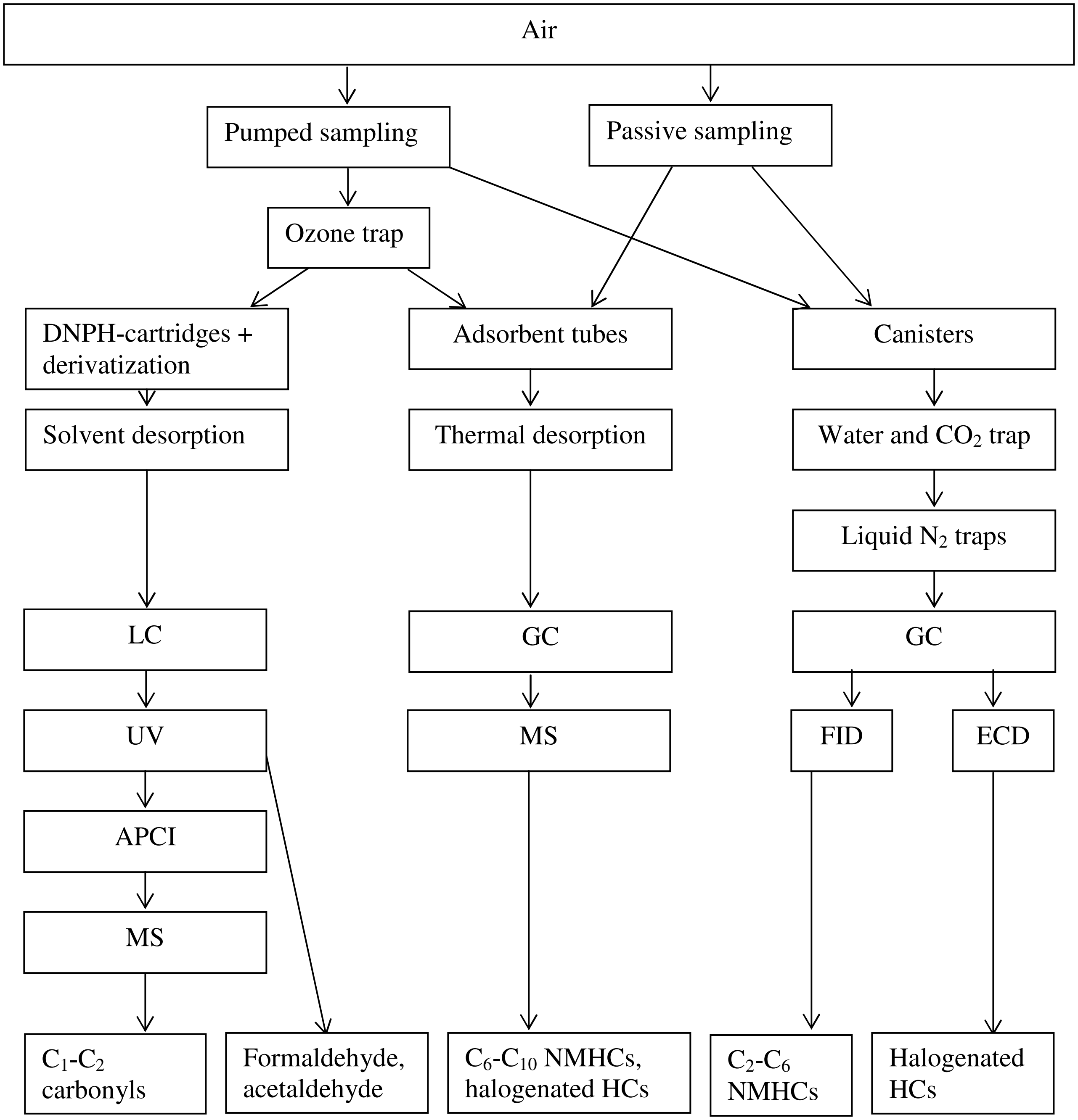

Figure 3. Analytical procedures used in this study for determination of VOC concentrations in ambient air.

3.2.1. Sampling and analysis of C_2-C_7 hydrocarbons

(Method 1)

Sampling of light (C_2-C_7) hydrocarbons was conducted using evacuated stainless steel canisters (0.85 l and 6 l). The inner surfaces of the canisters were passivated with a layer of chrome-nickel oxide. The canisters were either pressurised with sampling air at the site using Teflon membrane pumps, or afterwards at the laboratory with helium or nitrogen. Pressurising in the laboratory was used for passive canister sampling, in which a flow restrictor, that allowed air flow into the canister by flow rate of a few ml min^{-1}, was placed at the inlet of the canister and the sampling time was increased from less than a minute to 24 hours. Canisters were suitable only for the most volatile hydrocarbons, because other compounds are adsorbed onto the canister inner surfaces and are not stable (*Zielinska et al.,* 1996).

Samples were analyzed in the laboratory within a few weeks of sampling. *Brymer et al.* (1996) studied 194 volatile organic compounds and found that most of them are stable in canisters for at least 30 days. Before the analyses, samples (c.a. 500 ml) were concentrated in two liquid nitrogen traps. Drying and the removal of CO_2 was achieved by passing the air through a stainless-steel tube filled with K_2CO_3 and NaOH. The samples were analysed using a gas chromatograph (HP-6890) with a flame ionization detector and an Al_2O_3/KCl PLOT column. The calibration was performed with a UK National Physical Laboratory gaseous standard analyzed along with the regular samples.

Detection limits for the light hydrocarbons varied between 30 and 110 ng m^{-3} (Table 4). Uncertainties (U) derived from the ambient concentrations (c), detection limits (DL) and standard deviations (CV) between duplicate samples, determined using the procedure described in *Fujita et al.* (1994) and in papers III and IV, $U = \sqrt{(2 \times DL)^2 + (CV \times c)^2}$, were between 70 and 230 ng m^{-3} (Table 4).

Table 4. Sampling and analysis methods used (M), detection limit (DL) and estimated uncertainty (U) for different compounds. The detection limits and uncertainties are calculated for the sampling systems used in paper IV.

	M	DL (ng m^{-3})	U (ng m^{-3})
Alkanes			
Ethane	1	30	80
Propane	1	40	100
2-methylpropane	1	50	110
Butane	1	40	120
2-methylbutane	1	40	80
Pentane	1	100	210
Cyclohexane	1	40	80
2-methylpentane	1	70	130
3-methylpentane	1	70	140
Hexane	1	70	140
Methylcyclohexane	3	40	80
Octane	3	50	100
Nonane	3	60	130
Decane	3	110	220
Alkenes			
Ethene	1	30	70
Propene	1	50	100
Trans-2-butene	1	40	80
1-butene	1	50	90
2-methylpropene	1	50	100
Cis-2-butene	1	40	90
1,3-butadiene	1	40	100
Trans-2-pentene	1	40	90
Cis-2-pentene	1	50	100
Alkynes			
Ethyne	1	50	100
Propyne	1	120	230
Aromatic HCs			
Benzene	1,3	220	460
Toluene	3	210	430
Ethylbenzene	3	40	70
p/m-xylene	3	260	520
Styrene	3	80	160
o-xylene	3	100	190
Propylbenzene	3	20	40
3-ethyltoluene	3	70	140
4-ethyltoluene	3	40	80
1,3,5-TMB	3	50	90
2-ethyltoluene	3	40	80
1,2,4-TMB	3	140	270
1,2,3-TMB	3	50	90
Biogenic HCs			
Isoprene	1,3	90	190
a-pinene	3	30	280
Camphene	3	10	50
b-pinene/myrcene	3	20	40
3-carene	3	20	120
Gasoline additives			
MTBE	3	50	90
TAME	3	40	70
Halogenated HCs			
CFC-12	2	20	70
Chloromethane	2	20	90
CFC-11	2	10	40
CFC-113	2	30	60
Chloroform	2	10	20
1,2-dichloroethane	3	10	30
1,1,1-TCE	3	10	30
CCl4	2,3	40	100
Trichloroethene	3	20	40
Tetrachloroethene	2,3	20	40
Carbonyls			
Formaldehyde	4,5	10	80
Acetaldehyde	4,5	40	100
Acetone	4	60	120
Propanal	4	10	20
Butanal	4	5	10
Pentanal	4	20	30
Hexanal	4	5	10
Heptanal	4	10	30
Octanal	4	20	40
Nonanal	4	60	120
Decanal	4	10	40
Benzaldehyde	4	20	40
m-tolualdehyde	4	5	10
Nopinone	4	5	10

1. Canister sampling – liquid nitrogen traps – GC-FID
2. Canister sampling – liquid nitrogen traps – GC-ECD
3. Adsorbent sampling – thermal desorption – GC-MS
4. DNPH-sampling – solvent desorption – LC-MS
5. DNPH-sampling – solvent desorption – LC-UV

TMB=trimethylbenzene, MTBE=methyl-*tert*-butylether, TAME=*tert*-amylmethylether, 1,1,1-TCE= 1,1,1-trichloroethane, CCl_4=tetrachloroethane

3.2.2. Sampling and analysis of C_8-C_{10} alkanes, aromatic hydrocarbons, gasoline additives and biogenic hydrocarbons

(Method 3)

For C_8-C_{10} alkanes, aromatic hydrocarbons, gasoline additives and terpenes, pumped or diffusive adsorbent sampling was used. In pumped adsorbent sampling, air was drawn through Tenax TA/Carbopack B -adsorbent tubes using Alpha-2 pumps (Ametek) or critical orifices with membrane pumps. Two different adsorbents were used to widen the selection of the compounds retained in the tubes. The flow rates varied between 50 and 90 ml min^{-1} and the sampling time was from 1 to 4 hours for ambient samples. MnO_2-coated copper nets were used for ozone removal at the inlets to the sampling systems. This was essential when ozone-reactive biogenic hydrocarbons (terpenes) were measured. The adsorbents used are hydrophobic and therefore additional water removal systems were not used.

Diffusive sampling was used for 2-week sampling of aromatic HCs and MTBE with Carbopack B –tubes (papers I and II). Diffusive sampling tubes are exposed to the sampling air and compounds diffuse to the adsorbent. Uptake rates for aromatic hydrocarbons in a two-week sampling period with Carbopack-B adsorbent vary between 0.23 and 0.68 $cm^3 min^{-1}$. Sampling methods are described in more detail in paper I.

For sample preparation and analysis of adsorbent samples, an automated thermal desorption system (ATD-400) with a gas chromatograph (HP-5890) equipped with an HP-1 or HP-5 column and a mass spectrometer (HP-5972) was used. Both the scanning mode and the more sensitive selected ion monitoring were used for the mass spectrometer. Five-point calibration was conducted using liquid standards in a methanol solution. Standard solutions were injected onto adsorbent tubes and flushed with helium for five minutes in order to remove methanol. Adsorbent samples were already concentrated during sampling and additional concentration was achieved by the ATD-400 using a cold trap.

ATD-400 thermal desorption unit were also used for online sampling of aromatic hydrocarbons (paper I). In the online mode, samples were directed through a heated sampling line directly into the cold trap of the ATD-400. For water removal, the sample was passed through a Nafion dryer. The flow rate used was 52 ml/min and the sampling time 48 minutes.

Detection limits for pumped samples varied from 10 ng m^{-3} for camphene to 260 ng m^{-3} for p/m-xylene (Table 4). For diffusive samples, detection limits varied between 20 and 150 ng m^{-3} (paper I). For most of the compounds, uncertainties were below 25 % (paper I).

3.2.3. Sampling and analysis of halogenated compounds

(Methods 2 and 3)
Sampling of halogenated hydrocarbons was conducted using either the same canisters as for the light hydrocarbons, or adsorbent tubes as for the larger hydrocarbons. The most volatile halogenated compounds were not retained on the adsorbent tubes; only canister sampling could be used for them.

Halogenated hydrocarbon samples from canisters were concentrated and analysed using the same system as for the light HCs. When halogenated compounds were analysed, the sample was divided after chromatographic separation into two different detectors: the flame ionization detector (FID) and the electron capture detector (ECD). Halogenated compounds were detected using the ECD, except for chloromethane, which was detected by both the detectors. Calibration was performed with a gaseous standard purchased from the National Oceanic and Atmospheric Research Administration.

Adsorbent samples for the halogenated HCs were collected and analysed using the same procedure as for the other adsorbent samples. Calibration was performed with liquid standards in methanol solution. Detection limits for halogenated hydrocarbons varied between 10 and 40 ng m^{-3}; uncertainties were below 100 ng m^{-3}.

3.2.4. Sampling and analysis of carbonyl compounds

(Methods 5 and 6)

Carbonyl samples were collected by drawing air through C_{18}-cartridges (Sep-Pak, Waters) coated with DNPH (2,4-dinitrophenyl hydrazine) that acted as a derivatization reagent for carbonyls. An ozone scrubber (copper tubing coated with potassium iodide) was placed ahead of the sampling cartridges. The flow rate was between 900 and 1000 ml min^{-1}; the sampling time was 24 hours for the ambient samples and a few minutes for the emission samples. During sampling, the carbonyl compounds were derivatized on cartridges to (2,4-dinitrophenyl)hydrazones and subsequently eluted in the laboratory with 3 ml of acetonitrile. The eluate was analysed using a liquid chromatograph equipped with an XDB C-8 column and a mass spectrometer (Agilent 1100 Series LC/MSD trap) with negative atmospheric pressure chemical ionization (APCI). Water and acetonitrile were used as eluents.

DNPH-derivates of undecanal, heptanal, nonanal, trans-2-hexenal, laurinaldehyde, decanal, 2-methyl-2-hepten-6-one, nopinone, octanal and limona ketone were prepared according to the instructions of the EMEP manual for sampling and analysis (*EMEP*, 1996). For hexanal, formaldehyde, methyl ethyl ketone, butanal, pentanal, propanal, acetaldehyde, acetone, acrolein, benzaldehyde, 2-butenal, m-tolualdehyde and methacrolein, a liquid DNPH-carbonyl standard in acetonitrile purchased from Supelco was used. Detection limits of the compounds in ambient air samples varied from 5 to 60 ng m^{-3} and uncertainties between 10 and 120 ng m^{-3}.

An ultraviolet (UV) detector was used for the formaldehyde and acetaldehyde. Other compounds could not be detected by the UV detector, because of co-elution of the peaks. In the mass spectrometer, co-elution is not a problem if the masses of the co-eluting compounds are different. The sample passed through the UV detector before entering the mass spectrometer. Because the UV detector signal is more stable, the stability of the calibration in the mass spectrometer could be followed by comparing the results from these two detectors.

3.3. Source profile measurements

The sources to be measured were chosen based on published emission inventories (*Lyly et al.*, 2000; *Finnish Environment Institute*, 2001) and our own considerations. According to the report of the City of Helsinki Environment Centre, the major sources of VOCs in Helsinki are vehicle emissions, paints and solvents, household products and industry (*Lyly et al.*, 2000). The principal component analysis made by *Edwards et al.* (2001) suggests that emissions from distant sources, traffic, trees and seasonal oxidation products are the major sources of C_6-C_{10} VOCs in the air of Helsinki.

Source profile samples were taken and analyzed using the same methods as for the ambient air samples, only with shorter sampling times. For some profiles existing literature data was used.

3.4. Receptor modelling

Different sources emit VOCs with their own characteristic compositions. This gives one the opportunity of using receptor models, which enable backward estimations of how much each source contributed to the final, observed concentration in the ambient air. Different receptor models are used in the source apportionment studies of VOCs; Positive matrix factorization (*Kim et al.*, 2005), UNMIX (*Choi and Ehrman*, 2004), Principal component analysis (*Wang et al.*, 2000) and Chemical mass balance (*Watson et al.*, 2001). Combinations of these have also been tested (*Mukerjee et al., 2004*; *Jorquera and Rappenglück*, 2004; *Latella et al.*, 2005). In this study, the Chemical Mass Balance Model Version 8 (CMB8) of the US EPA/Desert Research Institute and the factor analysis method UNMIX 2.4, developed by Ronald Henry, have been used.

These receptor models are based on the following equation:

$$C_{ij} = \sum_{k=1}^{N} f_{ik} S_{kj} \qquad i = 1,...,m, \quad j = 1,...,n. \qquad (2.1)$$

Where C_{ij} is the observed concentration of species i in sample j, S_{kj} is the total mass of material from source k in sample j and f_{ik} is the mass fraction of species i in source k (k=1…N). N is the number of sources. This assumes that there are no loss processes for the elements between source and receptor.

3.4.1. Chemical mass balance

In chemical mass balance (CMB), the source profiles and the ambient concentrations with uncertainties serve as input data. The model is based on the effective variance least squares solution. A more detailed description of the fundamentals of CMB modelling can be found, for example, in 'Receptor modelling for air quality management' (*Hopke*, 1991). In the application of the model, CMB8 applications and the validation protocol for $PM_{2.5}$ and VOCs was followed (*Watson et al.*, 1998).

Certain assumptions are made in CMB models (*Watson et al.,* 1998): (1) the source compositions are assumed to be constant over the ambient air and source sampling period, (2) the included species are not reactive, (3) all major sources are identified, (4) the source profiles are linearly independent, (5) the number of sources is smaller than the number of species, and (6) the measurement errors are random, uncorrelated and normally distributed. These assumptions are not totally observed in practice, but the model can tolerate some deviation from these restrictions.

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 (*Watson et al.*, 1998). R-square measures the variance in the receptor concentrations, that can be explained by the calculated species concentrations. Chi-square is used to consider the uncertainty of the calculated species concentration. It is the weighted sum of the squares of the differences between the calculated and measured species concentrations. The percent mass is the percentage ratio of the sum of the calculated source contributions to the total mass, C/M is the ratio of calculated to measured values for individual compounds and R/U is the ratio of the signed difference between the calculated and measured concentration (i.e. residual (R)) divided by the uncertainty (U) of that residual (i.e. the square root of the sum of the squares of the uncertainty in the calculated and measured concentrations). 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 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, while the reactivity of the compounds can cause overestimations.

The selection of source profiles and the fitting species for the CMB calculations can be done by conducting sensitivity tests. In these tests the model is run with different selections, and the statistical parameters given by the model are compared. The selection that gives the values closest to the performance goals is chosen. 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.

The source profiles have to be linearly independent. Because of the collinearity, different exhaust profiles for cold starts or for catalyst-equipped and non-catalyst cars could not be used.

3.4.2. Multivariate receptor model UNMIX

UNMIX is a multivariate receptor model developed by Ronald Henry from the University of Southern California. A description of the fundamentals of UNMIX can be found in *Henry* (1997, 2001, and 2002). The number of sources, the source compositions and the contributions are estimated from the variations in the ambient air measurement data, and therefore a large data set is needed as input data. In UNMIX, the source compositions and the contributions must be non-negative. Furthermore, UNMIX uses data to find data points (edges) where one of the sources is missing or small. If there are such points, the sources can be identified. Also physical constraints (tracer compound) supplied by the user can be used. When interpreting the UNMIX results, identification of the sources can be problematic.

UNMIX also calculates some statistical parameters to describe the performance of the model. According to the recommendations, R-square (R^2), which describes how much of the variance of each species can be explained by the sources, should be over 0.80 and the signal-to-noise ratio over 2 (*Henry*, 2001).

In this study, UNMIX 2.4 was applied to the determination of the composition and the contribution of different emission sources for compounds collected on adsorbents. The results were used to confirm that the major sources were included in the CMB calculations. Using the combinations of different methods can be a powerful tool.

4. RESULTS

4.1. The VOC source profiles

Profiles of traffic, gasoline and diesel fuel evaporation, liquid gasoline and diesel fuel, wood combustion, biogenic emissions, commercial natural gas, dry cleaning and distant sources were determined for the studies in papers III and IV. All the profiles used differed significantly from each other, causing no co-linearity problems in the CMB calculations.

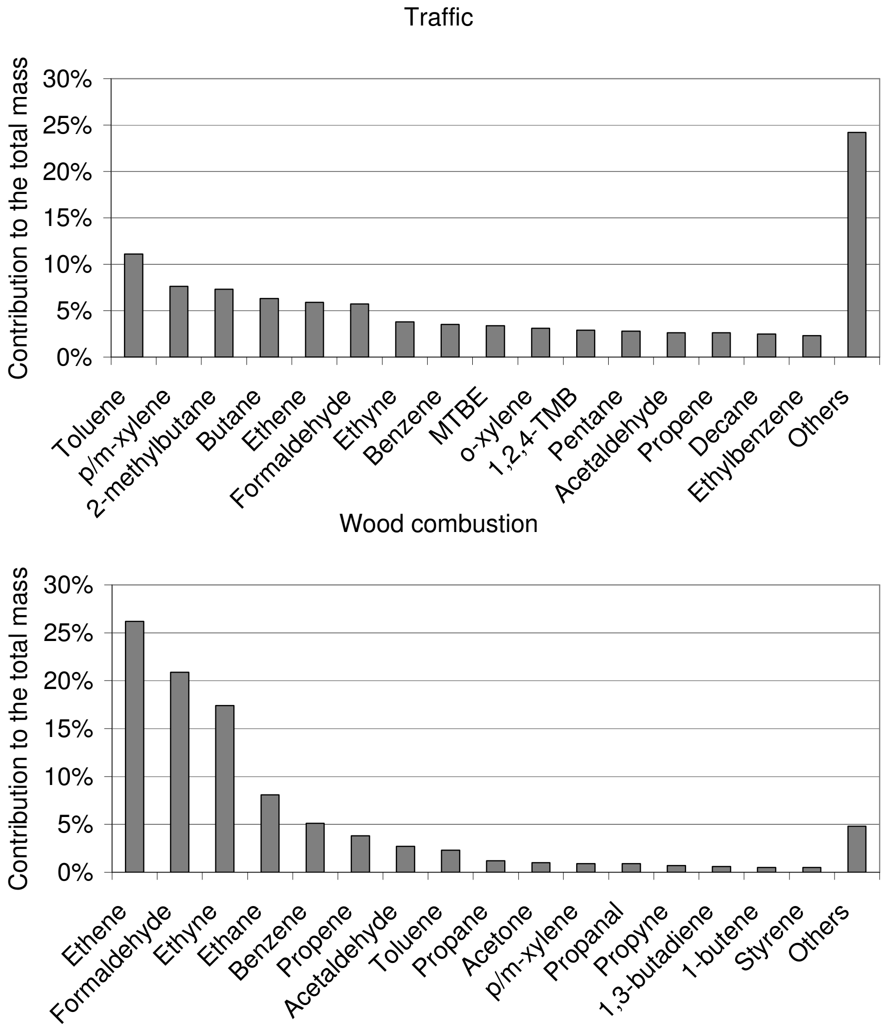

Figure 4. Source profiles of traffic and wood combustion.

Traffic emissions consist of various VOCs; the main compound group is aromatic hydrocarbons followed by alkanes (Figure 4). Direct emissions of carbonyls are also noteworthy in the traffic emissions. In the gasoline vapour profile, light alkanes (C_4-C_5) provide the main contribution, especially butane, which comprises 42% of the total emission. Compared to the vapour profile, the contributions of less volatile aromatic hydrocarbons and gasoline additives are higher in the liquid gasoline profile. Diesel fuel vapour is mainly composed of the 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 (Figure 4). 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.* (2002). As in this study, a halogenated compound, chloromethane, is commonly found in the emissions from wood combustion and biomass burning (e.g. *McDonald et al., 2000; Reinhard and Wang, 1995*). 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.

4.2. Sources and concentrations of different compound classes

4.2.1. The VOC sum

The sources and concentration of the VOC sum have been studied in papers III and IV. Based on chemical mass balance calculations for the NMHCs measured in Helsinki in 2001, the main source groups were gasoline exhausts (33%) and distant sources (37%) (paper III). All traffic-related sources (gasoline exhausts, liquid gasoline and gasoline vapour) were found to together make a contribution of over 50 %. At weekends, the contributions of gasoline exhausts and vapor decreased and the contribution of distant sources increased.

In paper IV it was shown that in the two cases of an urban area in Helsinki and in a residential area in Järvenpää, the VOCs have quite different local sources. According to the CMB analysis, major local source for these VOCs at the urban site was traffic. At the residential site, the contribution due to traffic was minor, while liquid gasoline and wood combustion made higher contributions. However, even at the urban site in Helsinki, the contribution of distant sources is high compared to that of local sources.

4.2.2. Alkanes

Alkanes are a group with the highest concentration of all the measured VOCs (Table 5, Figure 5). They have been studied in papers III and IV. The lifetimes of the lightest alkanes are relatively long (Table 1) and therefore they accumulate in the atmosphere, especially in winter, and their concentrations at other than urban stations are also quite high (Figure 6). Of the alkanes, butane and 2-methylbutane were found to have the highest concentrations in Helsinki in winter, but at the residential and rural sites, the concentration of ethane, which has the longest lifetime, is highest (Figure 6).

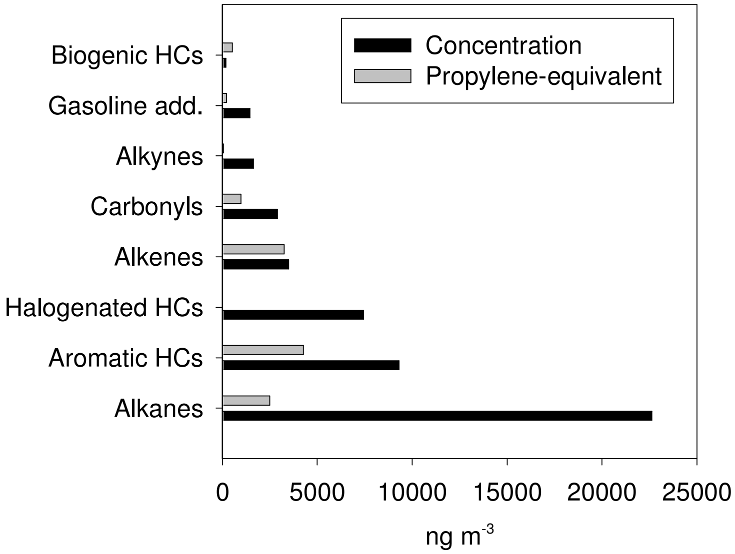

Figure 5. Concentrations and OH-reactivity-scaled concentrations (propylene equivalents) of different compound groups at the urban background station of Kallio in Helsinki in February 2004.

From the diurnal variation (Figure 7) of the higher alkanes (methylcyclohexane, octane, nonane and decane) in Helsinki, it is seen that higher concentrations are measured in daytime. Concentrations start rising in the morning during the rush hours, are a little lower in the middle of the day, rise again during the rush hours in the evening and are lowest in the early morning hours, when all the activity is at its lowest.

Table 5. Measured ambient air concentrations (Helsinki) and OH-reactivity-scaled concentrations (Hel$_{OH}$) as propylene-equivalents described in section 2.4.1. and in paper V at the urban background site in Helsinki in February 2004.

	Helsinki (ng m^{-3})	Hel$_{OH}$ (ng m^{-3})		Helsinki (ng m^{-3})	Hel$_{OH}$ (ng m^{-3})
Alkanes	22630	2500	Biogenic HCs	180	530
Ethane	3930	40	Isoprene	90	350
Propane	3130	130	a-pinene	80	160
2-methylpropane	2170	190	Camphene	10	20
Butane	4220	400	b-pinene/myrcene	<DL	-
2-methylbutane	4460	650	3-carene	<DL	-
Pentane	1770	260	Gasoline additives	1460	230
Cyclohexane	380	100	MTBE	900	100
2-methylpentane	630	130	TAME	560	130
3-methylpentane	400	90	Halogenated HCs	7430	6
Hexane	470	100	CFC-12	2900	-
Methylcyclohexane	220	80	Chloromethane	1140	2
Octane	220	70	CFC-11	1610	-
Nonane	290	110	CFC-113	770	-
Decane	340	150	Chloroform	70	0
Alkenes	3490	3260	1,2-dichloroethane	40	0
Ethene	1890	600	1,1,1-TCE	130	0
Propene	600	600	CCl4	530	2
Trans-2-butene	150	360	Trichloroethene	50	0
1-butene	150	170	Tetrachloroethene	200	1
2-methylpropene	330	620	Carbonyls	2900	970
Cis-2-butene	80	180	Formaldehyde	750	260
1,3-butadiene	150	390	Acetaldehyde	540	120
Trans-2-pentene	90	230	Acetone	820	10
Cis-2-pentene	50	120	Propanal	40	20
Alkynes	1630	50	Butanal	40	30
Ethyne	1630	50	Pentanal	<DL	-
Propyne	<DL	-	Hexanal	30	40
Aromatic HCs	9310	4270	Heptanal	20	20
Benzene	1810	90	Octanal	40	50
Toluene	2810	620	Nonanal	110	150
Ethylbenzene	560	150	Decanal	140	180
p/m-xylene	1670	1210	Methacrolein	<DL	-
Styrene	100	230	3-buten-2-one	340	-
o-xylene	660	340	Benzaldehyde	<DL	-
Propylbenzene	140	30	m-tolualdehyde	10	-
3-ethyltoluene	340	250	Nopinone	5	10
4-ethyltoluene	170	80			
1,3,5-TMB	160	340			
2-ethyltoluene	150	70			
1,2,4-TMB	580	680			
1,2,3-TMB	160	190	VOC sum	49320	23650

TMB=trimethylbenzene, MTBE=methyl-*tert*-butylether, TAME=*tert*-amylmethylether, 1,1,1-TCE= 1,1,1-trichloroethane, CCl$_4$=tetrachloroethene

In source profile studies, alkanes were found to exist in traffic, gasoline and diesel fuel evaporation, liquid gasoline and diesel fuel, wood combustion, commercial natural gas and distant source emissions (Papers III and IV). Their mass was >50% of the total VOC mass in all other than traffic and wood combustion emissions.

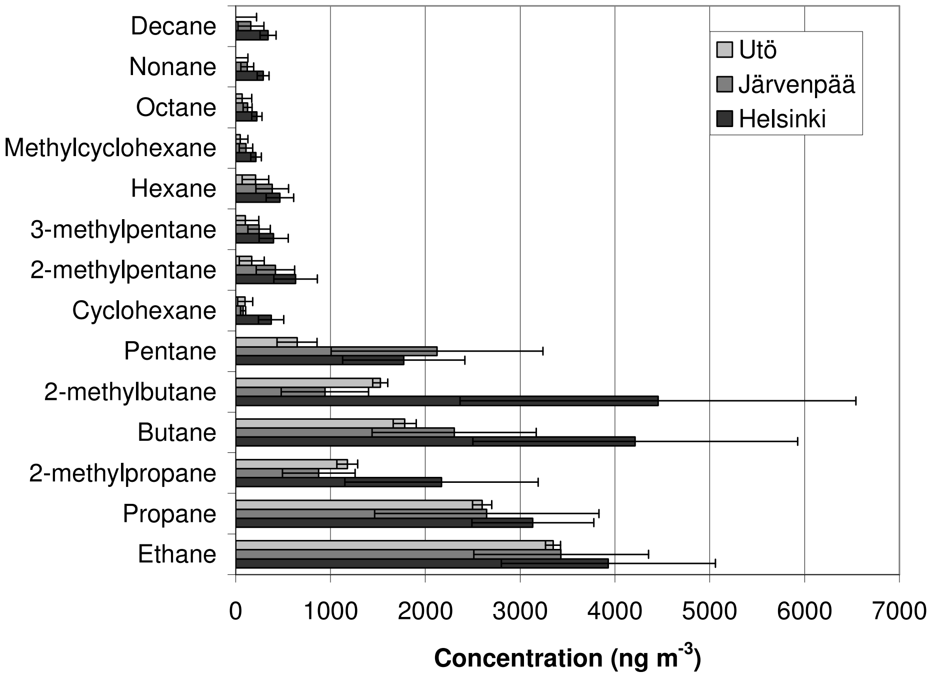

Figure 6. Concentrations of alkanes at the urban background station in Helsinki in February 2004, at the residential site in Järvenpää in December 2004 and January 2005 and at the background station of Utö at the beginning of March 2004. (Error bars for Helsinki and Järvenpää represent the standard deviation of daily averages. For Utö there were only two daily average values with a very low deviation, and therefore the uncertainty of the determination method was used as error bars for this station).

The main local source for alkanes in Helsinki was found to be traffic, but the contribution of distant sources was high (58%). For the lightest alkanes (ethane and propane), the contribution of distant sources was over 90 %. In a study by *Hakola et al.* (2006) of measurements of light hydrocarbons in background air in Finland, it was shown that the main source areas for these compounds in Finland are Southern and Eastern Europe, while air masses coming from the North Sea and the Arctic are cleaner. They also found that concentrations of ethane and propane have increased during the ten years of measurement starting in 1994. They concluded that this could indicate a growth of VOC emissions in areas outside Europe.

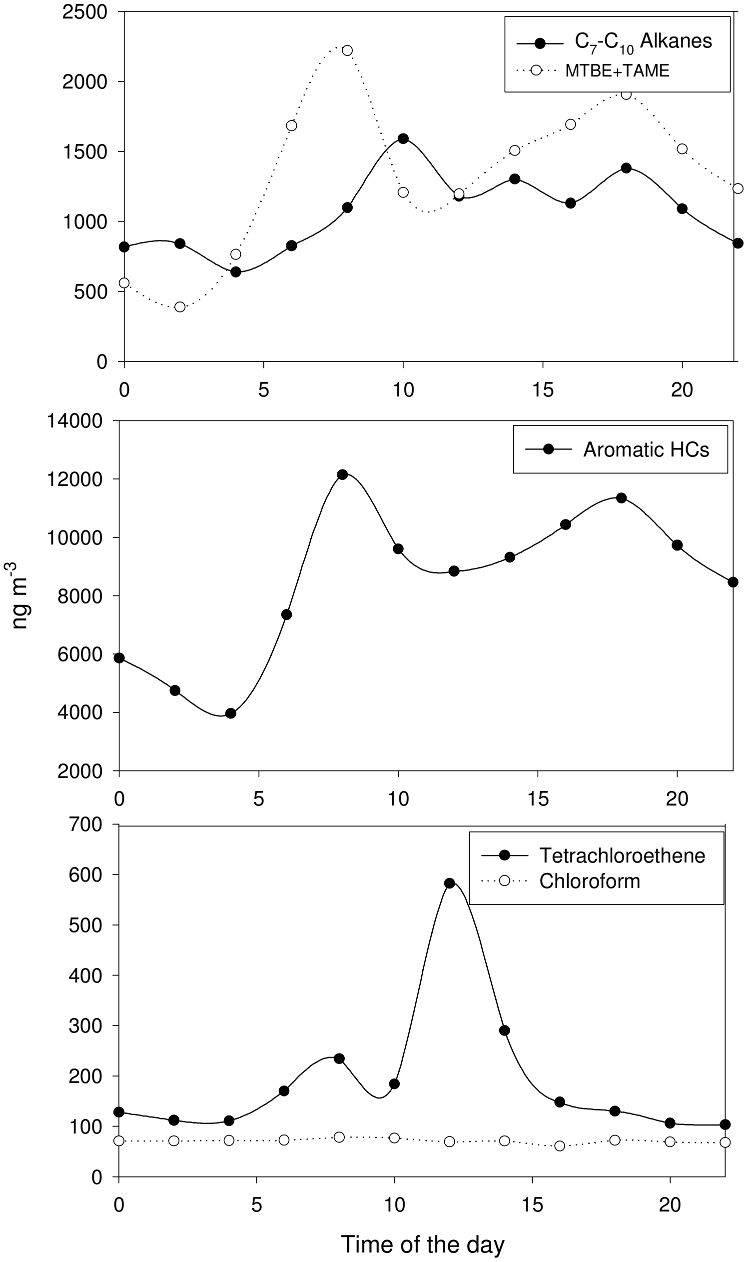

Figure 7. Diurnal variation of some VOCs at the urban background station of Kallio in Helsinki. Data is from the Tenax TA-carbopack B samples from the sampling campaign 4.2.-23.2.2004 described in paper IV.

4.2.3. Alkenes

Alkenes have been studied in papers III and IV. Of the alkenes, ethene has the highest concentrations, almost 2000 ng m^{-3} in Helsinki in the winter of 2004 (Figure 8). Average concentrations of the other measured alkenes varied between 50 and 600 ng m^{-3}. At the rural station of Utö, concentrations of alkenes were low and even below the detection limits. This is because the lifetimes of alkenes are short (Table 1) and they are not transported far from their sources.

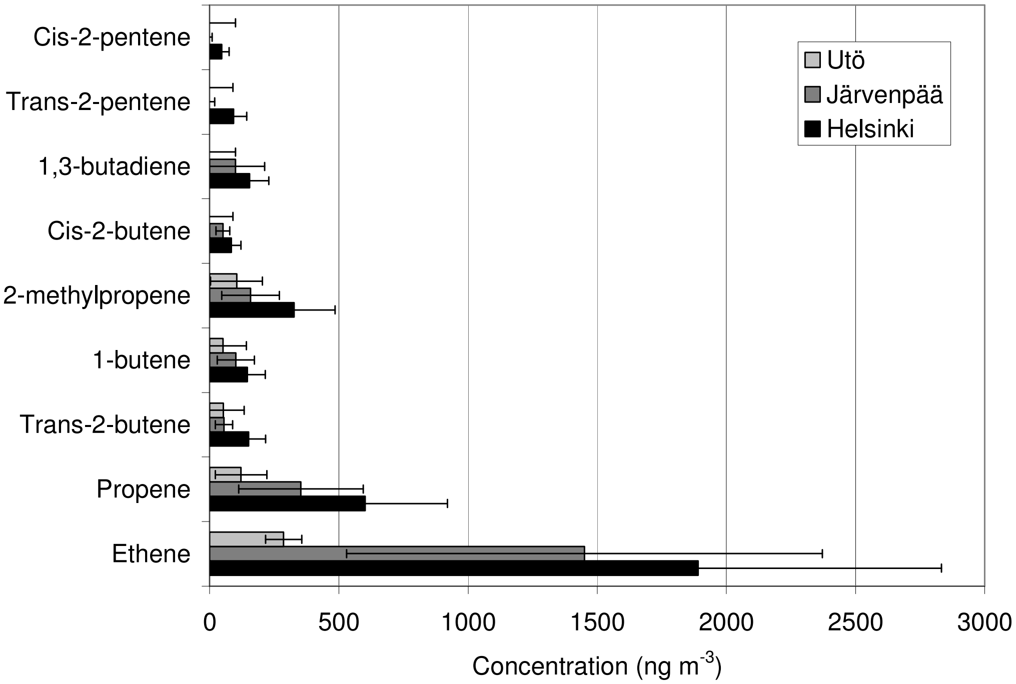

Figure 8. Concentrations of alkenes at the urban background station in Helsinki in February 2004, at the residential site in Järvenpää in December 2004 and January 2005 and at the background station of Utö at the beginning of March 2004. (Error bars for Helsinki and Järvenpää represent the standard deviation of daily averages. For Utö there were only two daily average values with a very low deviation, and therefore the uncertainty of the determination method was used as error bars for this station).

Although concentrations of alkenes are much lower than concentrations of halogenated hydrocarbons or alkanes, their contribution to the local chemistry is more important. This is shown in Figure 5 and Table 5, where concentrations and OH-reactivity-scaled concentrations (propylene-equivalents) are compared. In addition to the hydroxyl radicals they also react with ozone.

The chemical mass balance study in paper IV showed that local sources are much more important for the alkenes than for example for the alkanes. The main source of the alkenes in Helsinki was traffic, while at the residential site in Järvenpää it was wood combustion.

According to the *U.S. EPA* (2002 and 2005b), there is evidence that 1,3-butadiene is a human carcinogen. Average measured concentrations of 1,3-butadiene varied from 90 ng m^3 in June to 180 ng m^{-3} in March 2001 in Helsinki (paper III). In paper IV the chemical mass balance calculations showed that traffic was the main source of 1,3-butadiene in Helsinki, but at the residential site in Järvenpää wood combustion was the main contributor (91 %).

4.2.4. Alkynes

Of the alkynes, ethyne has the highest concentrations (Figure 9). Concentrations of propyne are much lower and often below the detection limits. For ethyne, the propylene-equivalent concentration is also low compared to many other VOCs, and therefore alkynes have little effect on the local chemistry of Helsinki (Table 5). Ethyne has sometimes been considered as a tracer for traffic (*Curren et al.*, 2006). However, as shown in paper IV wood combustion can also be a significant source of ethyne.

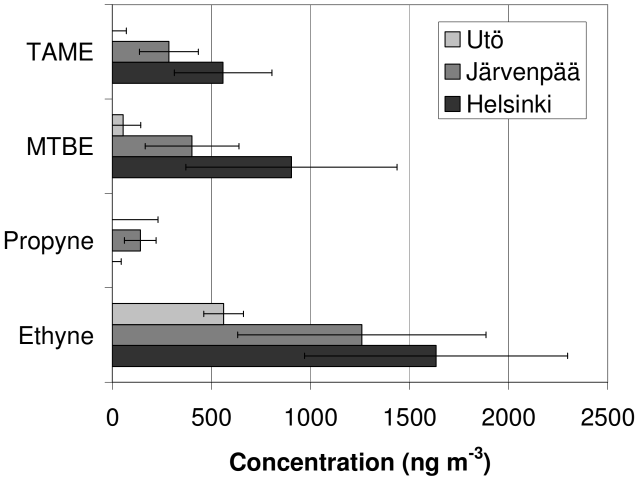

Figure 9. Concentrations of alkynes and gasoline additives at the urban background station in Helsinki in February 2004, at the residential site in Järvenpää in December 2004 and January 2005 and at the background station of Utö at the beginning of March 2004. (Error bars for Helsinki and Järvenpää represent the standard deviations of daily averages. For Utö there were only two daily average values with a very low deviation, and therefore the uncertainty of the determination method was used as error bars for this station).

4.2.5. Aromatic hydrocarbons

Aromatic hydrocarbons are of interest since some of them are toxic and carcinogenic. They have been studied in papers I-IV. Of the aromatics, toluene, benzene and the xylenes have the highest concentrations at urban, residential and background sites in Finland (Figure 10).

In paper I, sampling methods for aromatic hydrocarbons were tested; it was shown that diffusive sampling with Carbopack B adsorbent is a suitable method for following their concentration levels in urban air. Using this sampling method, concentrations of aromatic hydrocarbons have been measured in several locations in Helsinki thereafter. In most cases, the highest two-weekly mean concentrations have occurred at the urban station of Töölö, but annual averages at the suburban station of Tikkurila have been equally high. As expected, the lowest concentrations have been observed at the regional background station of Luukki. The diurnal variation of aromatic hydrocarbon concentrations can be found in Figure 7. It shows that concentrations follow the intensity of the traffic; the highest concentrations are measured during the rush hours and the lowest in the early hours of the morning.

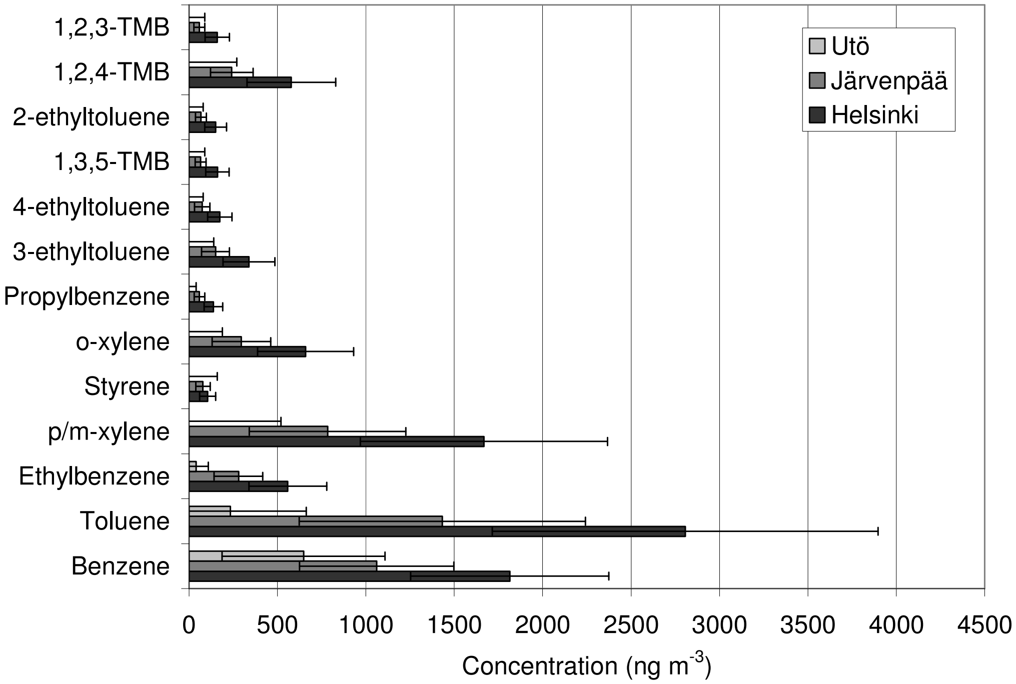

Figure 10. Concentrations of aromatic hydrocarbons at the urban background station in Helsinki in February 2004, at the residential site in Järvenpää in December 2004 and January 2005 and at the background station of Utö at the beginning of March 2004. (Error bars for Helsinki and Järvenpää represent the standard deviations of daily averages. For Utö there were only two daily average values with a very low deviation, and therefore the uncertainty of the determination method was used as error bars for this station).

A more detailed study was conducted for benzene, which is a carcinogenic compound and for which the European Union has set limit values: the annual average ambient air concentration may not exceed 5 μg m^{-3} (paper II). Annual average concentrations did not exceed the limit value during any of the measurement periods in Helsinki. However, there are also upper and lower assessment thresholds; the lower assessment threshold (2 μg m^{-3}) was exceeded in 2000 at the urban traffic station of Töölö in Helsinki. Dispersion modelling was used to get a wider picture of the benzene concentrations in Helsinki. The predicted concentrations were highest in the vicinity of major roads and streets, and at their junctions. The annual average concentrations from measurements and modelling agreed fairly well. A comparison of the benzene concentrations at the urban background station of Kallio and those in rural and remote areas showed that in winter the average concentrations at the rural station of Hyytiälä are close to those of Kallio. At the remote stations of Utö and Pallas, the concentrations in winter were approximately half of the urban background concentrations. In summer, concentrations in Kallio were substantially higher.

Both in the UNMIX and CMB studies, the main local source of aromatic hydrocarbons in Helsinki was found to be traffic (papers III and IV), but at the residential site in Järvenpää wood combustion played an important role, especially for benzene (Figure 11). At both sites, the benzene contribution from distant sources was high, but this was not so for the other more reactive aromatic hydrocarbons. Both receptor models were in quite good agreement, and this gave confirmation of the results.

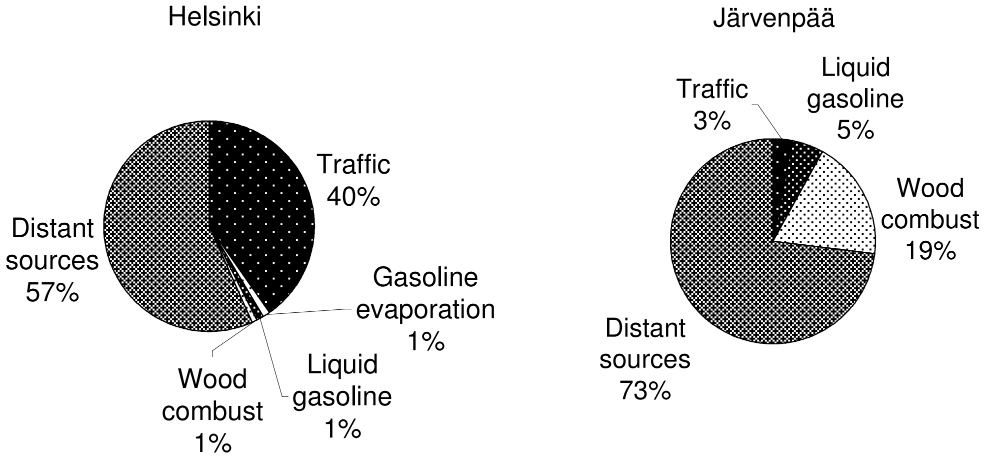

Figure 11. Source apportionment of benzene in Helsinki (urban) and Järvenpää (residential).

4.2.6. Gasoline additives

In the winter of 2004, the average concentration of MTBE in Helsinki was almost 1000 ng m^{-3} and that of TAME was over 500 ng m^{-3}, but at the rural location of Utö the MTBE concentration was only 50 ng m^{-3} and TAME was below the detection limit (Figure 9). MTBE has been studied in papers I, III and IV and TAME in papers III and IV. In paper I the diffusive sampling method developed for the aromatic hydrocarbons was also found to be suitable for MTBE.

The diurnal variation of MTBE and TAME in Helsinki follows the intensity of the traffic; highest concentrations are measured during the rush hours and lowest in the early hours of the morning (Figure 7). CMB studies also showed that the main source is local traffic, while the contribution of distant sources is low. The main source of TAME and MTBE in Järvenpää was found to be liquid gasoline.

MTBE has been used as a tracer for automobile exhausts (*Chang et al.*, 2003). In this study, traffic-related sources were able to explain the measured concentrations, and these results support the use of MTBE as a tracer. However, gasoline vehicle exhausts are not the only source of gasoline additives: gasoline vapour and liquid gasoline also contribute their share.

4.2.7. Biogenic hydrocarbons

Concentrations of biogenic hydrocarbons in Helsinki are lower than those at the forested site of Hyytiälä (*Hakola et al.*, 2003). However, even in winter time in Helsinki concentrations of isoprene and some monoterpenes are above detection limits (Table 5). In addition to vegetation, which is the main source of terpenes in the atmosphere, landfills, household products, processing of wood and biowastes, for example, can be sources of terpenes as well. Isoprene can also be found in traffic emissions. In the chemical mass balance study in Helsinki, the contribution of traffic or traffic-related sources to the measured isoprene concentration was 33 % (Figure 12).

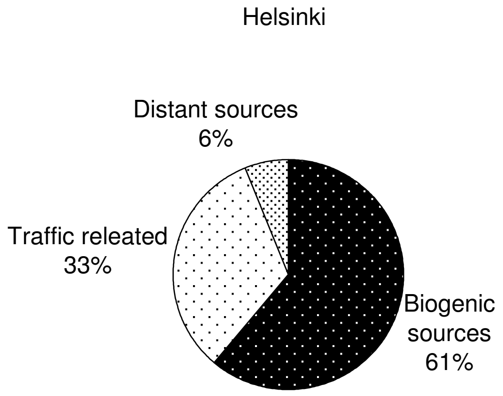

Figure 12. Source apportionment of isoprene in Helsinki.

4.2.8. Halogenated hydrocarbons

Halogenated hydrocarbons were studied in paper IV. Their concentrations in Helsinki were at the same level as in the background air of Utö (Figure 13). This indicated that there are no major sources of these compounds in Helsinki. Emission profile measurements and CMB calculations confirmed this. The only exception was tetrachloroethene, whose concentration was several times higher in Helsinki than in Järvenpää or on Utö. As can be seen from Figure 7, the concentration of chloroform is very stable over the whole day, as is the case for most of the measured halogenated HCs, but the tetrachloroethene concentration has a very pronounced diurnal variation. The chemical mass balance study showed that background air explains only 20 % of the measured tetrachloroethene concentrations. Dry cleaners were found to be a source of this compound in Helsinki. Halogenated hydrocarbons are not expected to have any significant effect on local chemistry since their propylene-equivalent concentrations are very low (Table 5 and Figure 5).

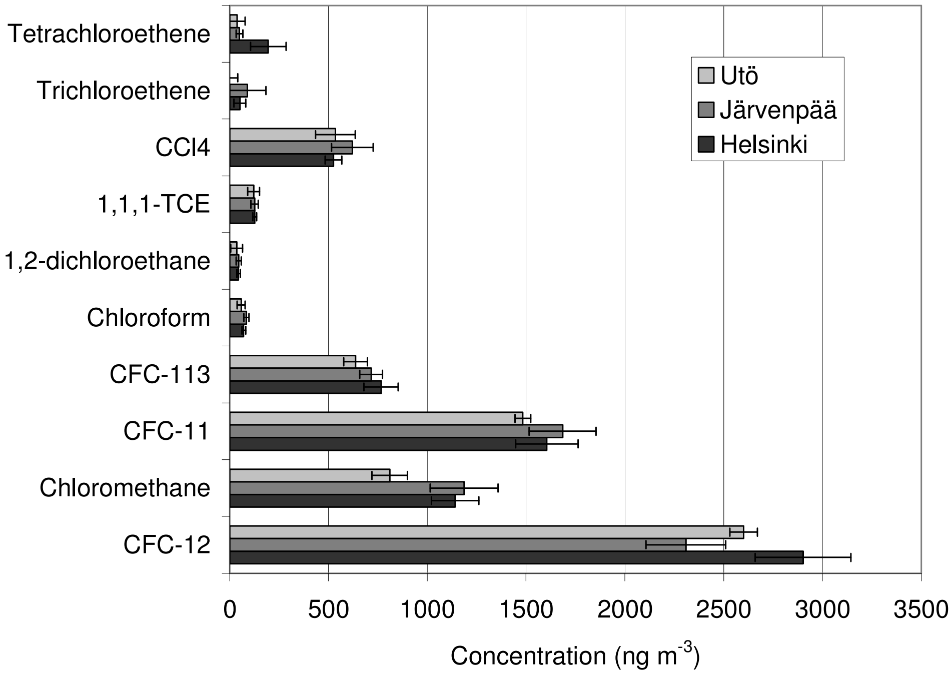

Figure 13. Concentrations of halogenated hydrocarbons at the urban background station in Helsinki in February 2004, at the residential site in Järvenpää in December 2004 and January 2005 and at the background station of Utö at the beginning of March 2004. (Error bars for Helsinki and Järvenpää represent the standard deviations of daily averages. For Utö there were only two daily average values with a very low deviation, and therefore the uncertainty of the determination method was used as error bars for this station).

4.2.9. Carbonyls

Carbonyls have been studied in papers IV and V. Winter concentrations of carbonyls at the urban site in Helsinki and the residential site in Järvenpää were found to be at the same level, but at the rural site of Utö concentrations were much lower (Figure 14). Carbonyl concentrations were also measured in Spring 2003 at the rural forested site at Hyytiälä and were close to the levels found in Helsinki. The most abundant carbonyls in Helsinki, Järvenpää and Hyytiälä were acetone (820 ng m^{-3} in Helsinki), formaldehyde (750 ng m^{-3} in Helsinki) and acetaldehyde (540 ng m^{-3} in Helsinki), but also concentrations of large alkanes, decanal and nonanal were over 100 ng m^{-3}.

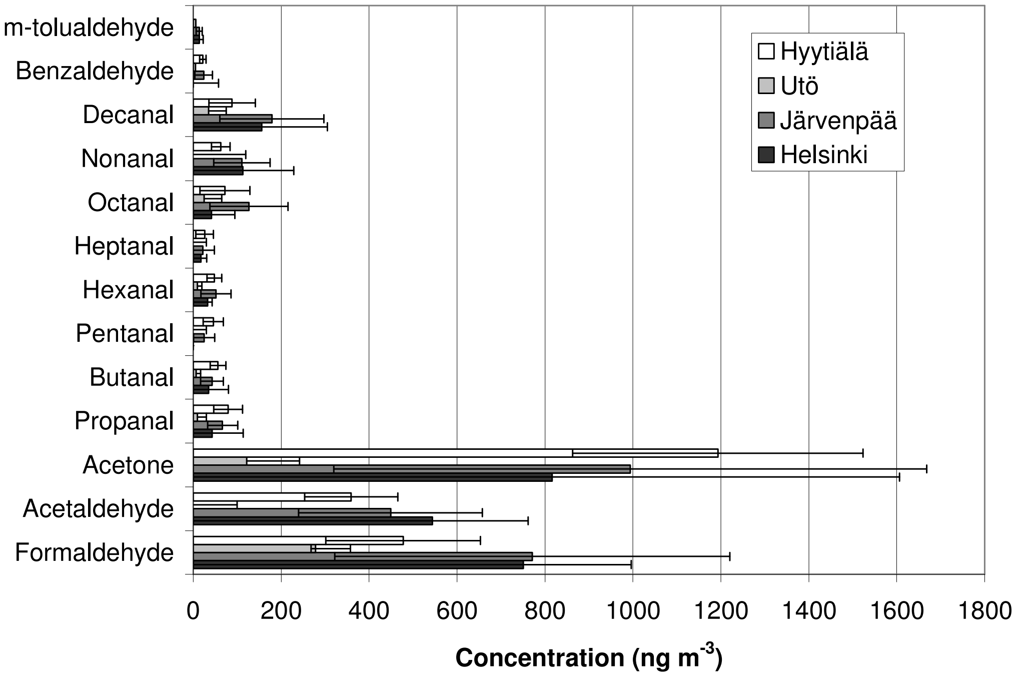

Figure 14. Ambient air concentrations of carbonyls at the urban background station in Helsinki in February 2004, at the residential site in Järvenpää in December 2004 and January 2005, at the background station of Utö at the beginning of March 2004 and at the forest research station of Hyytiälä in March/April 2003. (Error bars for Helsinki, Hyytiälä and Järvenpää represent the standard deviations of daily averages. For Utö there were only two daily average values with a very low deviation, and therefore the uncertainty of the determination method was used as error bars for this station).

The sources of carbonyls are highly uncertain. These compounds have direct primary sources and they are produced in the air in the reactions of other VOCs. In paper V the concentrations of carbonyls were compared between the urban area of Helsinki and the rural area of Hyytiälä. This showed that concentrations are at the same level indicating that secondary production or biogenic sources are significant sources for the carbonyls in the air of Hyytiälä, since for the other VOCs (e.g. trimethylbenzenes) with direct anthropogenic sources, the concentrations in Hyytiälä are much lower or below detection limits.

CMB source estimates of the carbonyls in Helsinki and Järvenpää (paper IV) gave acceptable results only for formaldehyde and for acetaldehyde in Helsinki. This indicates that the contribution of secondary production or unknown sources is significant. For formaldehyde, the main source was traffic in Helsinki and wood combustion in Järvenpää.

The impact of carbonyls on OH-radical chemistry can be important. In spring in the rural area of Hyytiälä, carbonyls were found in paper V to be higher OH sink than aromatic hydrocarbons and monoterpenes. As the hydroxyl-radical-scaled concentrations in Table 5 show, carbonyls also have quite an important role to play in Helsinki.

5. CONCLUSIONS

The measurement and receptor modelling methods used were found to be suitable for the VOCs studied. Different sampling and analysis methods were needed for the various different compounds or compound groups. The performance of the receptor models was found to vary significantly for different compounds. However, for most of the compounds studied the results were acceptable. The results from both receptor models used were in quite good agreement.

Alkanes had the highest concentrations in the urban air of Helsinki, but when the concentrations were scaled against the reactivity with hydroxyl radicals, aromatic hydrocarbons and alkenes were found to have the highest effect on local chemistry. Comparisons with the rural sites showed that concentrations at Utö and Hyytiälä were generally lower than in Helsinki, especially for the alkenes and aromatic hydrocarbons, but concentrations of halogenated hydrocarbons at Utö and carbonyls at Hyytiälä were at the same level as in Helsinki. At Hyytiälä, carbonyls had an important effect on the local hydroxyl radical chemistry in spring. The contribution of carbonyls as an OH sink was higher than the contribution of monoterpenes and aromatic hydrocarbons.

Different compounds were found to have totally different sources, but for most VOCs the main sources at the urban site in Helsinki were distant sources and traffic. At the residential site in Järvenpää, the contribution due to traffic was minor while distant sources, liquid gasoline and wood combustion made higher contributions. In the Nordic countries, wood is a domestic and renewable energy source, and the use of wood as a fuel source has increased lately (*Hedberg et el.*, 2002; *Haaparanta et al.*, 2003). Many of the VOCs emitted during wood combustion are very harmful or toxic; this study showed that wood combustion can be an important source of some VOCs usually considered to be traffic-related compounds (e.g., benzene). However, by using the right burning techniques and proper fireplaces emissions can be minimized. More research on this subject is needed.

Recently, fine particles have been of particular interest due to their health and climatic implications. Information on the VOCs presented here may be useful for secondary organic aerosol studies; some results have already been used in particle formation studies by *Boy et al.* (2005).

Even though emissions of ozone precursors have decreased in Europe (*Jonson et al.*, 2006), ozone concentrations have increased in Finland (*Laurila et al.,* 2004; *Aarnio et al.*, 2005). More research on this topic is therefore needed, and the data presented in this study will be used in the future in ozone modelling studies.

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