Interim Report IR-00-066

Secondary Organic Aerosol – Formation Mechanisms and Source Contributions in Europe

Ulrike Dusek

Approved by

Markus Amann (amann@iiasa.ac.at)
Project Leader
Transboundary Air Pollution

November 2000

Contents

Abstract

Fine particulate matter (PM2.5) as an atmospheric pollutant is strongly related to increased mortality and morbidity. The empirically established link between aerosol concentration and human health compels increased efforts to reduce the atmospheric concentrations of fine particles. Organic material accounts for about 20-60% of the total PM2.5 and contains substances of known toxicity. It has been shown that in some areas secondary organic aerosol (SOA) accounts for 20% of the total organic aerosol throughout the year but can contribute up to 70% in smog episodes. The estimation of the sources and concentrations of organic aerosol is therefore crucial to the proper assessment of related health effects.

Part of this work attempts a critical review of the literature on SOA. The goal is to describe formation mechanisms, to identify likely precursor gases, and to estimate the SOA contribution to PM2.5. SOA forms by oxidation of volatile organic compounds (VOC). The aerosol yield varies significantly among different VOC species as well as source sectors and the contribution of SOA to the total particulate organic material is dependent on the time of the day and the season. The consequences of these findings for reduction strategies are discussed.

The knowledge gained in the literature review is further used to exemplify a possible procedure to assess and compare the aerosol formation potential of some source sectors used in the RAINS model. It is found that traffic and solvent use in the printing industry and paint are important sectors for SOA production.

Acknowledgments

About the Author

Ulrike Dusek earned her master's degree in physics from the University of Vienna. She is now working on her PhD in atmospheric sciences at the University of Washington in Seattle, WA, USA. At IIASA, Dusek is working with the TAP project, where the goal of her work is to assess the importance of secondary organic aerosol and, specifically, its contribution to PM2.5 (particulate matter with particle diameters less than 2.5 μm).

Secondary Organic Aerosol – Formation Mechanisms and Source Contributions in Europe

Ulrike Dusek

1   Introduction

1.1   Secondary Organic Aerosol as an Atmospheric Pollutant

Atmospheric aerosols are suspended liquid or solid particles in the ambient air. Airborne particles have natural and anthropogenic sources and span a large range of sizes from a few nanometers to several micrometers in diameter. They are composed of many different chemical compounds, of which sulfate, ammonium, nitrate and organic species are the largest fraction (e.g. Heintzenberg *et al*. 1989). Ambient aerosol particles can be primary or secondary in origin. Primary particles are emitted directly from their respective sources, whereas secondary particles are formed in the atmosphere from gaseous precursors.

Particulate matter is recognized as a serious pollution problem, because of the adverse health effects of respirable particles. The exact mechanisms by which aerosol particles damage human health are not well understood but epidemiological evidence shows a clear link between ambient particle concentration and increased morbidity (i. e. the number of sick persons or cases of disease in relationship to a specific population) and mortality (Panyacosit, 2000). This fact leads to an increased awareness that the reduction of particulate pollution is a matter of importance.

A considerable fraction of the atmospheric aerosol (10-60%, e.g. Seinfeld *et al*. 1998) consists of organic compounds. While the inorganic aerosol chemistry is relatively well investigated, the composition and formation processes of the organic fraction are not as well known. One reason for this is that the organic fraction is composed of hundreds of individual species that are difficult to characterize with current analytical methods. Especially the secondary organic aerosol (SOA), formed through oxidation of volatile organic carbon (VOC) in the atmosphere is not very well understood. However, as up to 70% of the organic material can be secondary in origin under smog conditions, SOA should not be neglected as a contributor to anthropogenic pollution. The effective control and reduction of SOA requires knowledge of the precursor gases, formation and properties of the secondary organic species. This knowledge can be used to incorporate SOA in air quality models and integrated assessment models to find cost-effective reduction strategies.

Although many details in the formation process of SOA are still unknown, a basic overview of SOA formation can be given as shown in Figure 1.1. VOC precursor gases are oxidized in the atmosphere mainly by O_3, NO_3 and OH. The oxidation process adds functional groups to the organic gas molecules and thus lowers their vapor pressure. This process partly results in gases that are again volatile and do not contribute to the aerosol formation. Another part of the reaction products however might be semi-volatile and condense to form aerosol particles, if ambient conditions are favorable.

PRECURSOR

REACTION PRODUCTS

VOC

VOC 1+
VOC2+
...

Volatile organic carbon

O_3, OH, NO_3

SVOC1+
SVOC2+
...

Semivolatile organic carbon

AEROSOL
PARTICLES
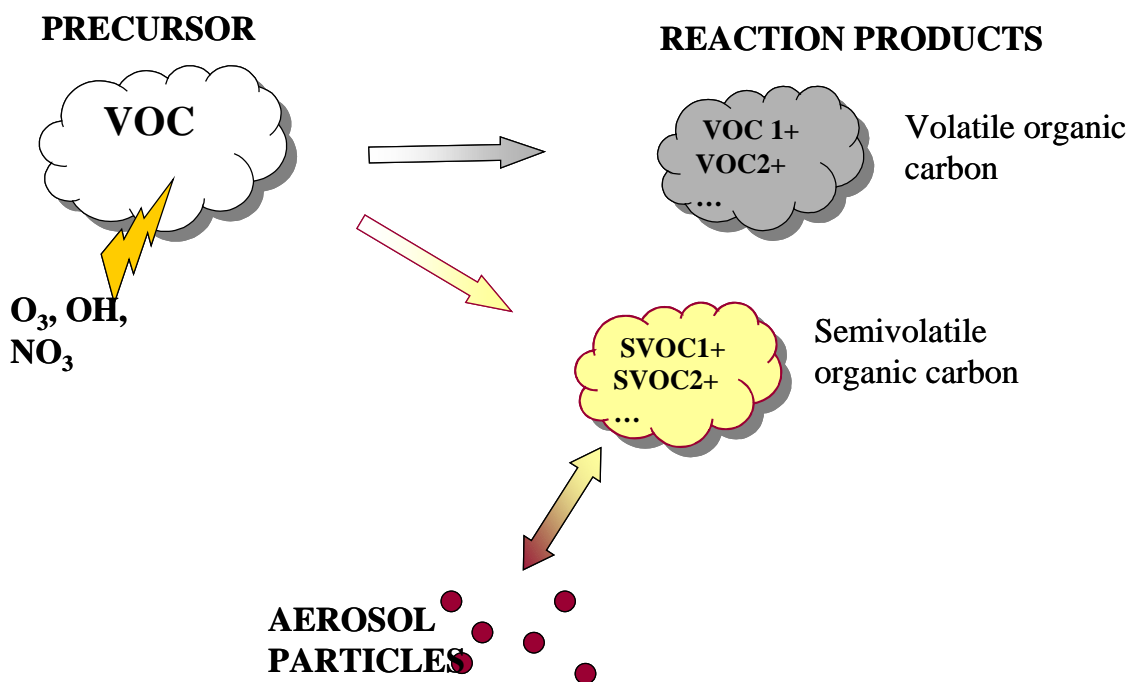
Figure 1.1: Schematic overview of SOA formation

Due to the complexity of the formation mechanism of SOA and the great number of individual chemical species involved, it is especially challenging to incorporate secondary organic particles into air quality models. The increasing evidence of the health effects of particulate pollution, however, compels increased efforts to reduce the ambient concentration of fine particles. To find cost-effective reduction strategies aerosol particles will have to be incorporated into integrated assessment models like the Regional Air Pollution Information and Simulation (RAINS) model (Amann *et al*. 1998, Alcamo *et al*. 1990). This will require the modeling of aerosol formation, transport, and deposition and it might be important to consider secondary organic aerosols into those models. Because of the complexity of the organic chemistry involved in SOA formation, it seems worthwhile to provide a preliminary assessment of the importance of SOA as an atmospheric pollutant and to identify the most important precursor gases and sources.

1.2 Aim of this Paper

The aim of this work is to summarize the current state of knowledge on the formation processes of the secondary organic aerosol and to apply this knowledge to evaluate the aerosol formation potential of source sectors in Europe. There is considerable evidence for the occurrence of SOA in the atmosphere and estimates of the contribution of SOA to the total organic aerosol are available, at least for selected locations. In the United States a considerable fraction of the organic aerosol is secondary in origin (Seinfeld and Pandis, 1998). This makes it necessary to shed some light on the complicated formation processes. The gas phase oxidation pathways are still speculative at present and there is also some debate about the nature of the gas/particle conversion processes. However, some empirical data on the aerosol formation potential of many natural and anthropogenic precursor gases are available in the literature. For example, fractional aerosol coefficients (FAC) (i.e., the fraction of the precursor gas that will end up as aerosol after oxidation) are derived by Grosjean and Seinfeld (1989). Although these FAC values are only rough estimates and can vary considerably in different atmospheric conditions, they can be used to make relative comparisons of the SOA formation potential of different source sectors in Europe. This provides a practical application for the knowledge gained in the literature review about importance and formation mechanisms of the secondary organic aerosol.

2 SOA in the Ambient Atmosphere - Conclusions from Measurements

Measurements of ambient organic aerosols can provide information about SOA formation and its contribution to the total aerosol mass. This section provides an overview of the results of some field studies that give evidence for the contribution of SOA to the ambient aerosol. Most of this evidence is indirect, because there is no a priori way of separating secondary from primary species in the ambient aerosol. By combining measurements with theoretical considerations, some conclusions about the importance of SOA as an atmospheric pollutant can be drawn.

2.1 Measurement Methods

The sampling and analysis of the organic aerosol component has some inherent difficulties that should be discussed before presenting measurement results. A thorough and comprehensive review of sampling and analytical methods has been given by Turpin *et al*. (2000). This section summarizes their main conclusions.

2.1.1 Sampling

The most common sampling method for the analysis of organic aerosol components is by means of filter measurements. Sampling errors mostly arise because of the semi-volatile nature of the particulate organic species. If there is a large pressure drop across the filter, particulate phase organics can volatilize causing negative artifacts of up to – 80%. On the other hand organic gas phase species can adsorb to the filter. If these adsorbed gases are erroneously interpreted as particulate matter, they can cause positive artifacts of up to 50%. (Turpin *et al.*, 2000 and references therein).

A common correction for positive artifacts caused by the adsorbed gases is to install a backup filter behind the first filter that is used for particle sampling. The first filter collects all particulate material and some gaseous species, whereas the organic mass collected at the second filter arises from adsorption of gaseous compounds only. The particulate carbon mass can thus be calculated by subtracting the mass found on the backup filter from the mass found on the first filter.

There is no such simple way to correct for negative artifacts, because the species that evaporate - due to the low pressures - from the particles on the first filter are not likely to adsorb to the second filter, where the pressure is just as low. A relatively safe technique for avoiding both positive and negative sampling artifacts is the use of a denuder system, followed by a filter and an adsorbent bed. The denuder first removes all gas phase organics so that only particles are collected on the filter downstream. This removal of the gaseous species however disturbs the gas/particle equilibrium and causes increased volatilization of particulate organics from the filter. These volatilized particulate compounds are then collected on the adsorbent bed downstream of the filter. The sum of the organic mass on the filter and on the adsorbent bed gives the total particulate organic mass.

2.1.2 Analysis

A variety of methods are used to characterize the organic particulate material. Analytical methods can either target the total organic carbon content, attempt speciation of individual compounds, or determine functional groups of the organic molecules. In the following an example of each of those approaches is briefly discussed.

- **Thermal analysis** can be used to quantify the total carbon content of particulate samples. The basic principle of this method is to volatilize organic carbon from the sample by heating it in the absence of oxygen. The evaporated compounds are then oxidized to CO_2, reduced to methane and quantified in a flame ionization detector. Afterwards the remaining elemental carbon is combusted by addition of oxygen at a temperature of about 750-800°C and quantified like the organic carbon. An intercomparison of different thermal analysis systems showed considerable interlaboratory variation in the split between elemental and organic carbon, e.g. 34% for elemental carbon (Turpin *et al.* 2000). Thermal analysis only measures the total amount of carbon molecules contained in the organic fraction of the aerosol sample. To obtain the total organic material, the organic carbon concentration has to be multiplied by the average ratio of carbon mass to the total organic mass in the sample. The magnitude of this conversion factor is still debated. Estimates range from 1.2 for primary organic carbon to 3.2 for the water-soluble fraction of the organic aerosol.

- Extraction followed by **gas chromatography and mass spectroscopy (GC/MS)** can be used to identify single organic species in a sample. Currently it is only possible to resolve a small fraction (10-20%, e.g., Forstner *et al.* 1997, Rogge *et al.* 1993) of the ambient organic mass concentration by this technique. There are several reasons for this difficulty in analyzing particulate organic species: First it is most often impossible to extract all the organic compounds from the filter. Then the signatures of many hydrocarbons cannot be resolved in the GC/MS system and form a continuum in the mass spectra. In addition, high molecular weight (>C40) and highly polar organic compounds do not elute through the GC column and thus cannot be analyzed. As most of the secondary organic carbon consists predominantly of polar molecules, it is especially difficult to speciate the secondary organic aerosol.

- **Fourier transformed infrared spectroscopy (FTIR)** provides information about functional groups and molecular bonds in the aerosol sample. The advantage of this method is that no prior extraction or sample preparation is necessary for analysis. The results of FTIR are thus representative of the whole organic aerosol component and not just of the extractable, elutable and resolvable part as in GC/MS. However at present this method has very high uncertainties in quantification and is mostly used for qualitative information. It can provide information on the functional loading of an 'average molecule' (e.g., Palen *et al.* 1992, Holes *et al.* 1997, Blando *et al.* 1998) but gives no information on individual species.

2.2 Evidence for SOA in the Atmosphere

No analytical method by itself is able to distinguish between primary and secondary organic material. Additional information or assumptions have to be used to make an estimate of the relative contributions of primary and secondary organic compounds to the ambient aerosol. The following section summarizes some efforts to identify and quantify SOA in the ambient atmosphere.

2.2.1 Estimate of SOA using Source OC/EC Ratios

Secondary organic carbon can be estimated by a relatively simple empirical method, if the ratio of organic carbon (OC) to elemental carbon (EC) of the major primary emissions is known (see Turpin and Huntzicker, 1990, 1991a,b, 1995). EC is often used as a tracer of primary anthropogenic emissions, and is inert in the atmosphere. The secondary organic carbon in the ambient aerosol can then be estimated as the excessive organic carbon, which cannot be explained by common origin with the elemental carbon according to primary OC/EC ratios. This secondary organic carbon is given as:

$$OC_{sec} = OC_{tot} - OC_{pri} \,,$$

$$OC_{pri} = EC * (OC/EC)_{pri}$$

where OC_{sec} is the secondary organic carbon, OC_{pri} the primary organic carbon, OC_{tot} the total measured organic carbon, and $(OC/EC)_{pri}$ the estimate of the primary OC/EC ratio.

One of the major uncertainties of this method is the estimate of the (OC/EC) ratio for primary emissions. The OC/EC ratios are strongly source dependent and therefore quite variable. In practice $(OC/EC)_{pri}$ is defined as the ambient OC/EC ratio at times when the formation of SOA is supposed to be negligible. This is the case on days that are characterized by lack of direct sunlight, low ozone concentrations and an unstable air mass. The estimates for $(OC/EC)_{pri}$ lie between 1.7 and 2.9 (Turpin *et al*. 1995).

An example of the relative contributions of primary and secondary organic carbon during a smog episode in the LA basin is shown in Figure 2.1, adapted from Turpin *et al*. 1995. It can be seen that the contribution of secondary OC is highest in the early afternoon, when the photochemical activity and the production of OH radicals are at their peak. In those time periods the correlation between EC (a marker for primary carbon emissions) and OC completely vanishes (Turpin *et al*. 1995), excluding additional primary sources that might be responsible for the sudden increase in secondary OC. In these early afternoon smog episodes secondary OC can contribute up to 70% to the total particulate organic carbon. The contribution to the total organic mass will likely be even higher, because a higher mass of organic material is associated with each secondary carbon atom than with each primary carbon atom. Secondary organic carbon is generally more oxidized and thus contains more functional groups than primary organic carbon.
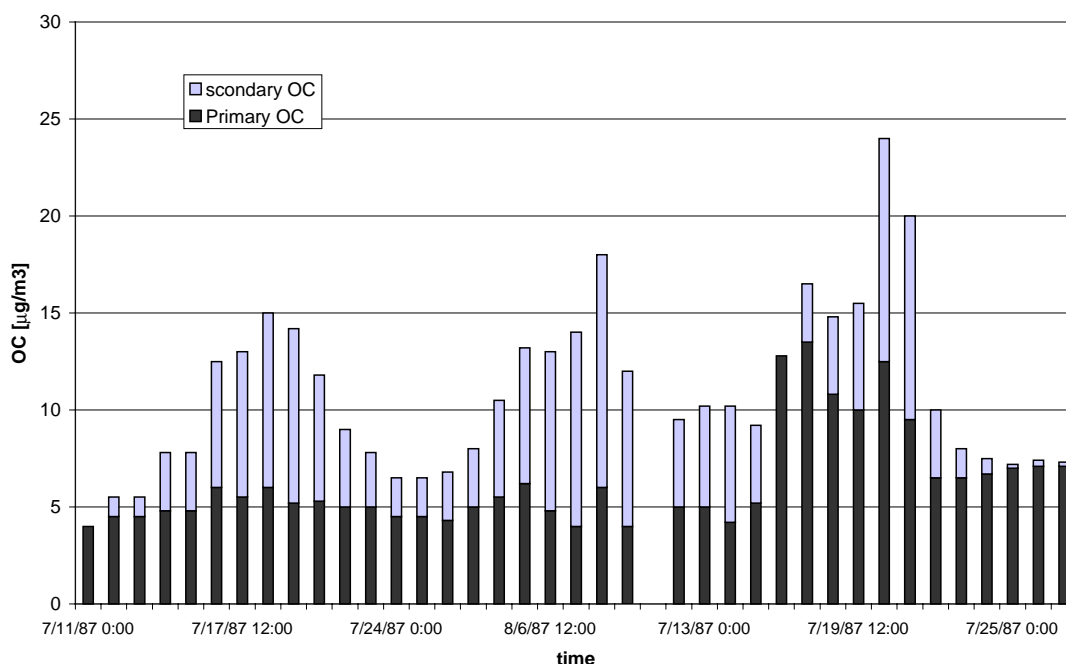
Figure 2.1: Contributions of secondary organic carbon to Los Angeles smog aerosol

In addition to the daily variation with the midday peak, SOA concentration is likely to have a seasonal variation as well, with low amounts in the winter, due to the reduced photochemical activity. Strader *et al.* (1999) showed that the SOA formation in the LA basin during winter time is reduced compared to the summertime estimates by Turpin *et al.* (1995), but by no means negligible. The daily average contributions of SOA to the observed OC concentrations is on average 20% and can be significantly higher during afternoon periods.

According to the estimates described above the secondary organic aerosol seems to contribute significantly to the total organic aerosol at least in the LA basin. Summertime smog episodes in Los Angeles might not be easily comparable to European conditions, but the wintertime study with its lower temperatures might be more representative for European cities.

2.2.2 Estimates of SOA using Models

The contribution of SOA to the ambient aerosol can also be estimated by measuring the total organic aerosol and by modeling the organic aerosol contributed by primary emissions. Source-receptor modeling is an example of this approach and can be summarized as follows. Measurements of the organic aerosol composition at a receptor site *k* are made. If detailed species profiles for the most important primary OC sources are known, the concentration of chemical constituent *i* at receptor site *k*, c_{ik} can be expressed as:

$$c_{ik} = \sum_{j=1}^{m} f_{ijk} a_{ij} s_{jk} \qquad (2.1)$$

7

where s_{jk} is the contribution to total particle mass at receptor site k arising from source j, a_{ij} is the fraction of constituent i in the emissions from source j and f_{ijk} accounts for selective loss of constituent i between source and receptor (Schauer *et al.*, 1996). Equation 2.1 can be solved for the unknown source contributions s_{jk} to the ambient aerosol mass. The organic mass that remains unaccounted for by this approach can originate from unknown sources as well as secondary production and provides thus an upper estimate for SOA. Schauer *et al.* (1996) estimate that as an upper limit SOA contributes 30% to the total organic aerosol in Roubidoux (CA) averaged over the year. This site is located downwind of LA and has traditionally high SOA formation (e.g. Turpin and Huntzicker 1991). For other sites in the LA basin the maximum SOA contribution was lower, ranging from 15-18% on a yearly average.

Another possibility of estimating SOA is to model its formation directly. Using a refined gas phase reaction model and empirical aerosol yields Pandis *et al.* (1992) estimated the SOA contribution to the organic aerosol to be 18% on August 28, 1987 at Claremont in the LA basin.

2.2.3 Other Evidence for SOA in the Ambient Atmosphere

There is also more direct evidence that indicates the presence of SOA in the atmosphere without providing quantification. Rogge *et al.* (1992) measured the seasonal variation of selected organic aerosol species. They concluded that most primary organic species are enriched in the wintertime, whereas lower weight n-Alkanoic acids, dicarboxylic acids and aromatic carboxylic acids have their maximal concentration during spring and early summer. This early summer maximum is consistent with secondary production in the atmosphere that is highest when the O_3 and OH radical concentrations are high. Since both oxidizing agents are produced photochemically, they are abundant in summertime.

Schauer *et al.* (1996) compared ambient concentrations of many organic aerosol species to their primary emissions from sources. The ratio of atmospheric concentration to emission rate (in µg/m3 per kg/day) for inert aerosol species generally lies around 0.1. Some species (n-Alkandioic acids and aromatic dicarboxylic acids) showed a ratio that was orders of magnitude higher. These species are most likely formed in the atmosphere. A similar conclusion is drawn for alkanoic acid found in the alpine environment in Austria, (Limbeck and Puxbaum, 1999). Although the evidence summarized here allows no quantitative estimate of SOA formation, it identifies certain organic species that are likely to be secondary in origin.

2.3 Natural and Anthropogenic Sources of SOA

For air pollution modeling and reduction policies it is important to distinguish between natural and anthropogenic emissions of a pollutant. In the case of SOA this is not trivial. Even if the precursor VOCs are classified as either natural or anthropogenic, the formation of SOA however requires also the presence of oxidizing agents like OH and ozone, which in polluted regions are often anthropogenic. The formation of SOA from natural VOCs can thus be enhanced by anthropogenic production of ozone. Kanakidou *et al.* (2000) estimate an increase in the SOA production from 17-28 Tg/yr in pre-industrial times to 61-79 Tg/yr at present due to increase in ozone from anthropogenic sources. This is probably a conservative estimate, because they only consider oxidation of the natural VOCs by ozone and not by OH and NO_3, which take part in the gas phase

chemistry as well. This indicates not only that the contribution of natural precursors to SOA formation is by no means negligible (see also Griffin *et al.* 1999), but also that not all SOA derived from natural precursor gases can be classified as 'natural'. This has important implications for the interpretation of modeling results.

3 Formation of Secondary Organic Aerosol in the Atmosphere

Secondary organic aerosol (SOA) is a product of the atmospheric oxidation of reactive organic gases (ROG). ROGs are emitted by many anthropogenic and natural sources such as burning of fossil fuels and wood, biomass burning, solvent use, emission by vegetation and the oceans (e.g. Seinfeld and Pandis 1998, Duce *et al*. 1983, Jacobson *et al*. 2000). Common atmospheric ROGs include alkanes, alkenes, aromatics and phenols.

The formation of secondary organic aerosol involves two crucial steps: First volatile organic precursor ROGs have to be oxidized to form semi-volatile organic carbon (SVOC). The distinction between volatile and semi-volatile gases is somewhat arbitrary, usually species with saturation vapor pressures below a certain threshold pressure (e.g. 10^{-1} or 30 mm Hg) are called semi-volatile (see Turpin *et al*., 2000). Subsequently those semi-volatile organic compounds partition to the aerosol phase. Because of this two step process there are two criteria for substantial aerosol formation: (i) The oxidization of the ROG precursors has to be fast and (ii) sufficient SVOC with low saturation vapor pressure has to be produced. If either the precursor gases are oxidized too slowly or the reaction products have high vapor pressures no aerosol will be produced. Aerosol formation can thus be 'reactivity limited' or 'volatility limited' (Grosjean and Seinfeld, 1989).

3.1 Oxidation of ROGs

3.1.1 *Gas phase Oxidation*

As a first condition for substantial aerosol production the precursor ROGs have to have high reactivity towards the major oxidizing species present in the atmosphere. These are ozone, the hydroxyl radical (OH) that is produced by the photolysis of ozone during daytime and the nitrate radical (NO_3), that is active during the night. Most of the saturated aliphatics (alkanes and cycloalkanes), the oxygenated aliphatics (e.g., alcohols and esters) and aromatics are not very reactive and only vulnerable to the attack of the OH radical, the most aggressive oxidizing species. Only ROGs that have a double bond are reactive enough to be oxidized by O_3 and NO_3. Alkenes, cycloalkenes, dienes, and natural ROGs like terpenes and styrene can thus react with all three oxidizing species. The reactivity of the major ROG classes toward oxidizing species is summarized in Table 3.1.

Table 3.1: Reactivity of ROGs towards oxidizing species in urban air (units: cm^3 $molecule^{-1}s^{-1}$ at 289K) originally compiled by Grosjean and Seinfeld, 1989.

	Ozone	OH radical	NO$_3$ radical	Important removal process with
Alkanes, Cycloalkanes	$\leq 10^{-23}$	$0.3\text{-}8\bullet 10^{-11}$	$\leq 10^{-17}$	OH
Oxygenated aliphatics	$\leq 2.2\bullet 10^{-21}$	$0.2\text{-}6\bullet 10^{-11}$	$\leq 1.4\bullet 10^{-16}$	OH
Aromatics	$\leq 6\bullet 10^{-21}$	$0.1\text{-}6\bullet 10^{-11}$	$\leq 10^{-17}$	OH
Alkenes, cycloalkenes, other olefins	$2\bullet 10^{-18}\text{-}1.5\bullet 10^{-15}$	$0.8\text{-}12\bullet 10^{-11}$	$6\bullet 10^{-17}\text{-}3\bullet 10^{-11}$	O$_3$, OH, NO$_3$

Generally the oxidation of ROGs produces single and multifunctional oxygenated compounds such as carboxylic acids, dicarboxylic acids, alcohols, carbonyls. The addition of functional groups makes the molecules more heavy and polar and thus lowers the vapor pressure of the organic gas. Most of the aldehydes, alcohols ethers and monocarboxylic acids however are still too volatile to form particles. They are mostly intermediate reaction products, which are further oxidized to semi-volatile species (Pun *et al*. 2000). Some of those final oxidation products have sufficiently low vapor pressure to be found in the particulate phase. These end products are usually highly oxidized (Holes *et al*. 1997) and are proposed to include dicarboxylic acids, polyols, amino acids and other multifunctional compounds (Saxena and Hildemann 1996). Some of those proposed compounds have been identified in the aerosol formed in smog chamber studies (e.g. Forstner *et al*. 1997 a, b, Holes *et al*. 1997) as well as in the ambient atmosphere (e.g. Limbeck and Puxbaum, 1999, Blando *et al*. 1998, Rogge *et al*. 1993). The reaction products of atmospheric precursors with low carbon numbers (alkanes C2-C7, alkenes C2-C6, isoprene and benzene) are generally too light to have sufficiently low vapor pressure for condensation. These precursor gases are not expected to contribute to the atmospheric aerosol formation.

The oxidization pathways of individual ROG that lead to reaction products in the particle phase are very speculative at present. The main reason for this lack of understanding is that only a fraction of the reaction products resulting from the oxidization of each individual precursor ROG can be identified with current analytical methods. GC/MS methods only identify a fraction of the organic species in the aerosol and the pathways derived from this method do not account for the total SOA mass. Other methods like Fourier Transform Infrared (FTIR) microscopy provide information about the average molar loadings of functional groups in the organic aerosol. This method is thus more representative of the entire organic aerosol, but can not give

conclusive evidence about individual species (e.g. Holes *et al.* 1997, Blando *et al.* 1998). Thus the information on oxidization pathways of VOCs and the composition of the resulting aerosol remains fragmental.

An example of those difficulties in determining oxidation pathways is given for the oxidization of trimethylbenzene. The first step in the oxidization of higher aromatics like toluene, xylene, or trimethylbenzene by the OH radical can be either the abstraction of a hydrogen atom or the addition of the radical to the aromatic ring as shown in Figure 3.1 for the example of tri-methylbenzene. The hydrogen abstraction pathway is of minor importance (approximately 10%) compared to the OH addition pathway (Seinfeld and Pandis, 1998).
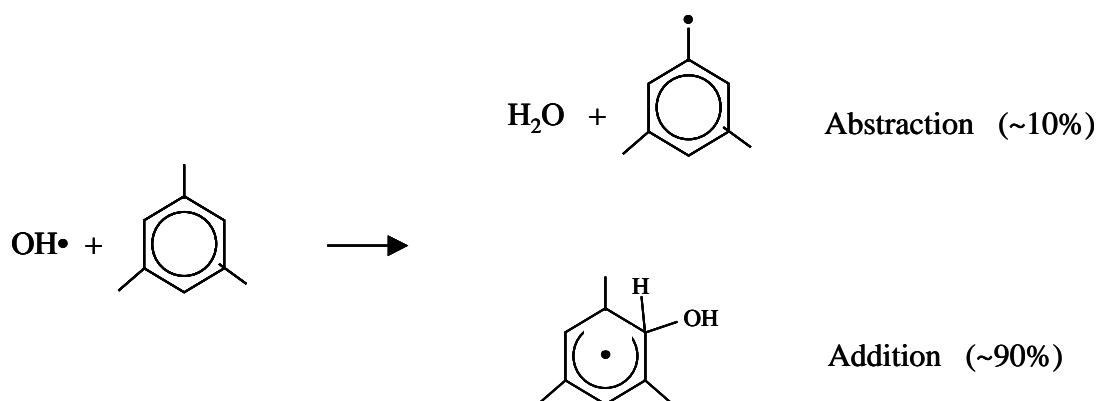
Figure 3.1: Schematic drawing of the addition and abstraction pathways, from: Holes *et al.* 1997.

The hydrogen abstraction pathway leads to end products like aromatic aldehydes and aromatic nitrates. The addition of the OH radical to the aromatic ring can either yield polyfunctional aromatics with nitrate and hydroxyl groups or it can split the ring to form unsaturated dicarbonyls. Those can be further oxidized to polycarbonyls with or without hydroxy groups. FTIR analysis of the oxidization products of 1,3,5 Trimethylbenzene shows that the aerosol is formed mostly by ring opening reactions, because the fraction of aromatic species in the particles is only 5-10% (Blando *et al.*, 1998). The organic species in the aerosol phase are highly oxidized and contain about three carbonyl groups and one hydroxy group per average molecule. The main reaction pathway leading to this 'average molecule' is shown in Figure 3.2.
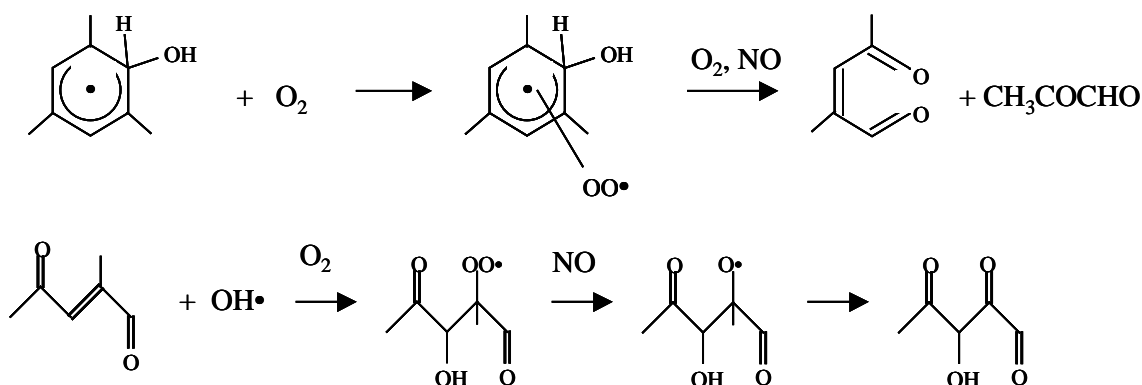
Figure 3.2: Pathway leading to the 'average molecule' in the aerosol phase after oxidation of 1,3,5 Trimethylbenzene

Using gas chromatography those more highly oxidized species are not identified. The analyzable fraction of the particulate oxidization products of 1,2,4 Trimethylbenzene shows an equal split between ring-retaining and ring-fragmentation products (Forstner *et al.*, 1997). Thus this analyzable fraction does not seem to be representative of the total organic aerosol formed by the oxidation of Trimethylbenzene. On the other hand a large part of the identified fraction consists of furandiones, which can not be specified using FTIR spectroscopy. Furandione is formed by a different pathway than the 'average molecule' constructed from FTIR analysis. This shows that the pathways leading to the average molecule are not necessarily representative of the actual atmospheric oxidation pathways. There is some chance however that some differences in SOA composition might be caused by a different chemistry of 1,3,5 and 1,2,4 trimethylbenzene.

3.1.2 Liquid phase Oxidation

It is possible that at least some of the VOC oxidation steps involved in SOA formation take place in cloud or fog droplets. Liquid phase production of secondary organic aerosol (SOA) would require the following combination of processes: The dissolution of volatile soluble precursor gases in water droplets and the subsequent oxidation in the liquid phase to form semi-volatile organics. Upon evaporation of the droplets a part of the semi-volatile material can remain in the particle phase. This alternate way of SOA production has only recently gotten some attention in the literature.

Although many of the anthropogenic precursor gases are water insoluble immediately after emission, they get more water-soluble as they are oxidized in the gas phase. Those intermediate, water-soluble VOC oxidation products could dissolve in cloud or fog droplets and take part in the liquid-phase chemistry. Those are mostly monocarboxylic acids, aldehydes, alcohols, acetone and organic peroxides. This production of water-soluble VOCs is probably enhanced in the interstitial spaces of clouds and fogs, because these spaces are enriched in oxidizing agents. The particle phase products formed from cloud and fog processing that are hypothesized by Blando *et al.* (2000) are carboxylic acids (e.g. dicarboxylic acids, oxo-acids), glyoxal, esters, and organosulfur compounds.

Blando *et al.*, (2000) summarize evidence that liquid-phase oxidation might be a possible pathway in the production of SOA: First organic compounds like monocarboxylic acids, aldehydes, alcohols are found frequently in cloud and fog water

(e.g. Facchini *et al.*, 1999, Blando *et al.*, 2000 and references therein, Saxena *et al.*, 1996 and references therein). Many of these compounds are found in the gas phase as well as in the liquid phase, which supports the hypothesis that soluble VOCs can partition to cloud and fog droplets. Moreover, there is also a considerable overlap between some species found in the liquid and in the aerosol phase (e.g. aldehydes, carboxylic acids, esters). It has also been shown that organic species can participate in liquid phase reactions. For example, in the ambient atmosphere formaldehyde is scavenged efficiently into fog droplets and reacts there with sulfate (Facchini *et al.*, 1992). An additional piece of evidence for the aqueous phase production of at least some water soluble secondary organic carbon species is provided by Aumont *et al.*, 2000. The authors claim that the high carboxylic acid concentration in cloud water samples cannot be explained by a gas-phase source. This suggests that carboxylic acid formation is probably dominated by VOC oxidation in cloud and fog water.

The importance of liquid phase oxidation for the atmospheric production of SOA is not yet clear and its relative contribution to VOC oxidation cannot yet be assessed. The evidence for this process is mostly speculative at present, but indicates the need for further research.

3.2 Gas/Particle Partitioning of SVOCs

Once semi-volatile organic species (SVOCs) are produced by oxidation of VOCs, they form secondary organic aerosol particles. There are several possible mechanisms by which semi volatile organic gases are distributed between the gas and the particle phase. The following is a brief review of the processes considered in the literature and a discussion about which of them are the most important in the atmosphere.

3.2.1 Condensation

3.2.1.1 Description:

Condensation is the simplest gas to particle conversion mechanism, because it does not involve interaction of the condensing gas with the already existing aerosol phase. The amount of SVOC partitioning to the aerosol phase depends only on the properties of the condensing gases.

A SVOC species that does not interact with already either existing aerosol or other gaseous components condenses by **homomolecular nucleation**. An organic compound *i* produced by the oxidation of the mother ROG accumulates in the gas phase till its vapor pressure p exceeds its saturation vapor pressure p_0. The amount of *i* necessary to sustain the saturation vapor pressure (c_i^0) remains in the gas phase, the rest partitions to the particle phase either by condensing homogeneously or on existing particles. The concentration of i in the aerosol phase ($c_{ae,i}$) is either:

$$c_{ae,i} = 0 \qquad \text{if} \qquad c_i < c_i^0$$

$$c_{ae,i} = c_{i,t} - c_i^0 \qquad \text{if} \qquad c_i > c_i^0$$

where c_i and $c_{i,t}$ are the gas phase and the total concentration of species i respectively.

Two or more organic compounds can also condense by **heteromolecular nucleation** to form a multi component solution. The saturation vapor pressure of a component over an ideal solution ($p_{i0}*$) is lower than the saturation vapor pressure over the pure substance i p_{i0}. Thus in heteromolecular condensation each of the species i can condense at a vapor pressure $p_{i0}*$ which is lower than the vapor pressure p_{i0} required for homomolecular condensation. Heteromolecular condensation facilitates thus the formation of secondary organic aerosol. Since many of the secondary organic compounds are water-soluble (Saxena *et al.* 1996) binary nucleation of organic compounds with water vapor could be possible, but not much is known about this process.

3.2.1.2 Importance as an atmospheric process:

The early literature on secondary organic aerosol formation (e.g. Grosjean, 1977) suggests that homomolecular nucleation is the governing process for condensation of semi volatile compounds. However, later studies (e.g. Pankov *et al.*, 1994, Odum *et al.* 1996) indicate that ad- or absorption mechanisms seem to be of greater importance. These mechanisms facilitate gas to particle conversion, so condensation gives a lower limit of the amount of material in the particle phase. The concept of homomolecular nucleation is still sometimes used as a simplified gas – particle partitioning mechanism in modeling studies (e.g. Pandis 1992).

Heteromolecular nucleation has mostly been studied for inorganic compounds like sulfuric acid. Not very much information is currently available on the binary nucleation properties of organic compounds.

3.2.2 Absorption and Adsorption

3.2.2.1 Description:

Gas to particle conversion by absorption and adsorption involves interaction of the SVOC with the preexisting aerosol particles. These gas/particle partitioning mechanisms are more complicated than condensation, since they depend not only on the properties of the condensing SVOC, but also on the properties of the particles that act as sorption sites. The effectiveness of the partitioning of a semi-volatile species i to the particle phase can be expressed by the so-called partitioning coefficient K_i. It is defined as the ratio of the concentration of i in the aerosol phase ($c_{ae,i}$) to the concentration of i in the gas phase ($c_{g,i}$):

$$K_i = \frac{c_{ae,i}}{c_{g,i}} \tag{3.1}$$

Adsorption is the partitioning of a gas to a particle surface. If inorganic particles are present in the atmosphere gas molecules can attach themselves to the particle surfaces and pores. This happens at gas phase concentrations much lower than required for homomolecular condensation. Adsorption transfers a fraction of the organic vapor to the particle phase when the gas phase is still undersaturated. The adsorption equilibrium is determined by the Van der Waals (or in some case acid-base) interactions of the adsorbed molecules with the particle surface. The adsorption partitioning coefficient for van der Waals interactions at 20 °C can be written as (Goss and Schwarzenbach, 1998):

$$\ln\left(K_i^{ad}\right) = -0.133\sqrt{\gamma^{vdw}}\ln\left(p_{i0}\right) + 2.09\sqrt{\gamma^{vdw}} \tag{3.2}$$

where γ^{vdw} is the Van der Waals parameter of the surface and p_{i0} is the saturation vapor pressure of compound i.

Absorption is the partitioning of a gas into the particle bulk phase. If organic particles are already present in the atmosphere (for example primary organic material) organic vapors can dissolve into the preexisting organic aerosol (e.g. Pankow, 1994 a, b). No threshold vapor pressure p_0 is necessary for this process. The partitioning coefficient for absorption can be expressed as

$$K_i^{abs} = \frac{RT \cdot m_{ae}}{\gamma_i \, p_{i,0} M_{ae}}, \tag{3.3}$$

where R is the universal gas constant, T the temperature, m_{ae} the mass concentration of the absorbing aerosol, γ_i the activity coefficient of species i in the solution, and M_{ae} the molecular weight of the absorbing aerosol.

It can be seen from Equation 3.3 that the partitioning coefficient is proportional to the preexisting aerosol mass and indirectly proportional to the vapor pressure of the dissolved gas. The activity coefficient γ describes the non-ideal interaction between the SVOC and the absorbing aerosol. An increase of γ above 1 means that the SVOC is not easily miscible with the absorbing aerosol and that it partitions more readily to the gas phase. γ is characteristic for each absorber/absorbent pair and can vary strongly for one SVOC in different absorbers. For example γ for alkylbenzenes in octanol is close to 1 whereas for alkylbenzenes in water it is higher than 1000 indicating good miscibility with octanol and poor miscibility with water (Goss and Schwarzenbach, 1998).

3.2.2.2 Importance as an atmospheric process:

There is strong evidence that gas to particle conversion in the ambient atmosphere is dominated by sorption processes rather than by condensation. For example Odum *et al*., (1996), Odum *et al*. (1997 a, b) have shown that aerosol yields in smog chamber experiments depend on the mass concentration of organic aerosol produced. If condensation was the main gas to particle conversion process in those experiments, the aerosol yield would be independent of the aerosol mass in the chamber. The authors state that this dependence of aerosol yield on organic aerosol mass concentration is likely to be the main reason for the discrepancies between previously measured aerosol yields (e.g. Grosjean and Seinfeld, 1989).

It is more difficult to determine whether absorption or adsorption is the prevalent gas to particle conversion mechanism in the ambient atmosphere. Several results suggest however that, at least in urban aerosol, absorption is more important than adsorption. Odum *et al*. (1996) propose that adsorption will only play a role till a monolayer of organic material forms on the adsorbing inorganic aerosol. Then organic vapors can start to dissolve into the newly formed organic layer and the sorption process is further dominated by absorption. Liang *et al*. (1997), find that the aerosol production is reduced if SVOCs partition to ammonium sulfate particles rather than to organic aerosol. The reason for this reduced aerosol production might be that the partitioning to ammonium sulfate is caused by adsorption whereas the partitioning to organic aerosol is caused by absorption. The same authors find that the gas/particle conversion of SVOCs in the

presence of ambient urban aerosol is similar to absorption in certain model organic compounds. Goss and Schwarzenbach (1998) state that measured ambient values of the partitioning constant are orders of magnitude higher than values that could be explained by adsorption theory. This also corroborates the domination of the absorption over the adsorption mechanism in urban areas.

3.3   Effects of Relative Humidity and Temperature on SOA Formation

3.3.1   Temperature

The oxidation of the ROGs becomes more efficient with increasing temperature. But the partitioning coefficient (i.e., the fraction of reaction products in the aerosol phase) decreases with increasing temperature. This is because all gas to particle conversion processes depend inversely on the saturation vapor pressure p_0 of the SVOC in question. p_0 increases exponentially with temperature, which means that low temperatures facilitate the gas to particle conversion. This decrease of the partitioning coefficient with temperature has been verified in gas chamber experiments (Leach *et al.* 1999). Consequently there exists an ideal temperature for SOA formation, when the temperature is already high enough for fast oxidation but still low enough for effective condensation. A model study (Strader *et al.* 1999) suggests that this temperature lies between 15 and 20°C. This result is exemplified in Figure 3.3. The dashed line shows the increase in oxidized reaction products with temperature. The dotted line shows the decrease of the fraction of those reaction products that are found in the particulate phase. The resulting total concentration of SOA (shown in the solid line) has a maximum around 17°C.
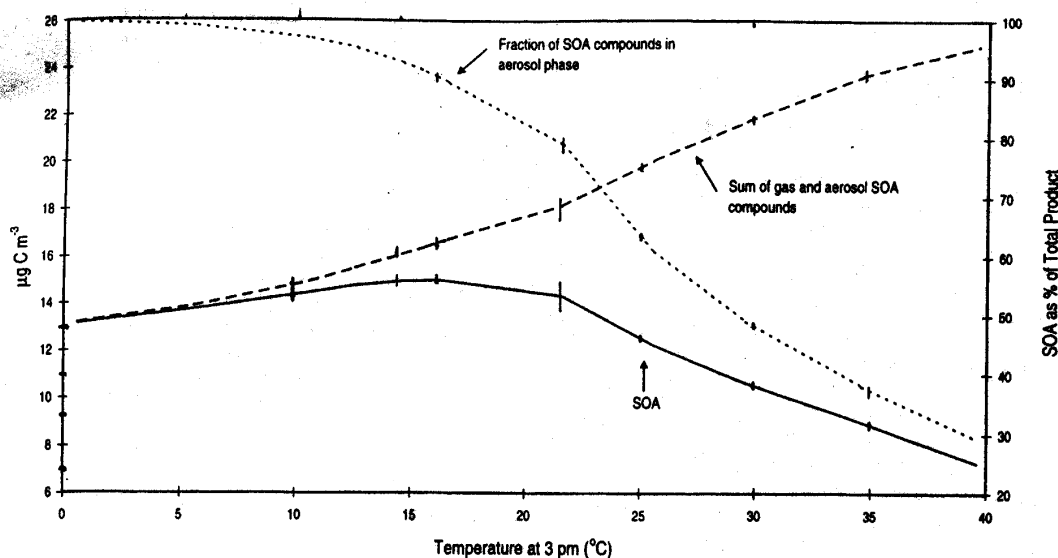
Figure 3.3: Variation of SOA formation with temperature from Strader *et al.* 1999

17

3.3.2 Relative Humidity

There is some evidence that changes in the relative humidity (r.h.) can alter gas phase oxidation pathways of ROGs. For example different reaction products were found on the aerosol formed by the ozonolysis of 1-tetradecene at low and at high relative humidity (Tobias *et al.* 2000). Not very much is known about these effects of relative humidity on gas phase chemistry.

Relative humidity has a different effect on condensation, ad- and absorption. Soluble SVOC could nucleate binarily with water vapor. This has been observed for inorganic compounds but presently not much is known about a possible binary nucleation of SVOC and water vapor (Seinfeld and Pandis, 1998). **Adsorption** of SVOCs to solid particle surfaces decreases with relative humidity (e.g. Storey *et al.* 1995), because the organic gas molecules have to compete for the same sorption sites with an increasing number of water molecules (e.g., Storey *et al.* 1995). Only at very high relative humidity, when a complete water film covers the particle surface adsorption of SVOCs starts to increase again. Changes in relative humidity can have a drastic effect on the **absorption** of SVOCs into the ambient aerosol. Much of the ambient aerosol contains hygroscopic substances and forms solution droplets at elevated relative humidity The activity coefficient for the dissolution of SVOC in dry organic aerosol can differ strongly from the activity coefficient of the same SVOC in water (Goss and Schwarzenbach, 1998). Changes in relative humidity can favor or hinder the partitioning of a certain species to the particle phase. If at high relative humidity the absorbing aerosol is liquid, the non-polar and insoluble species are more likely to be found in the gas phase whereas the polar and acidic species will dissolve more easily. This effect has not yet been experimentally investigated, because most of the smog chamber studies are conducted at low relative humidity.

3.4 Parameterization of Aerosol Formation Potential

Both the actual gas-phase reaction pathways and the condensation mechanisms in secondary aerosol formation are still speculative at present. However, the aerosol formation potential of important precursor gases can be characterized by establishing empirical expressions for the total amount of aerosol formed by the oxidation of a precursor gas. Two examples of such simplified treatments of aerosol formation potential are the fractional aerosol coefficient and the aerosol yield.

3.4.1 Fractional Aerosol Coefficient

The fractional aerosol coefficient (FAC) is defined as the percentage of an emitted precursor VOC that eventually ends up in the aerosol phase.

$$FAC = \frac{aerosol\ formed\ (kg/day)}{VOC\ emitted\ (kg/day)} \qquad (3.4)$$

This coefficient is a very crude first order approximation to SOA formation, which is not very accurate. It summarizes the complicated oxidation-condensation processes that govern the SOA formation in only one constant for each precursor ROG. With its help the secondary organic aerosol can be treated to a first approximation like primary emissions: The emissions of each precursor VOC can be multiplied with the FAC to get 'emissions' of secondary organic particles. It is only a crude approximation, however, to

regard the fractional aerosol coefficient for each VOC species as a constant, because it is likely to change with the oxidant concentration, temperature, relative humidity, and preexisting aerosol concentration in the ambient air. The quantitative results from this parameterization should therefore be regarded with care.

3.4.2 Aerosol Yields

Another possible way to parameterize aerosol formation potential is to define and measure aerosol yields, which relate the total amount of aerosol produced by the oxidation of a ROG to the amount of precursor gas that has reacted. This aerosol yield Y is defined as

$$Y = \frac{c_a}{\Delta ROG},$$

(3.5)

where c_a is the mass concentration of the newly formed aerosol (in μg/m^3) and ΔROG is the reacted precursor concentration (usually in μg/m^3 or in ppm).

3.4.2.1 An expression for the aerosol yield considering absorption into the preexisting organic aerosol

If absorption is the dominant gas to particle conversion mechanism, the aerosol yield of a certain precursor gas will depend on the available absorbing organic aerosol concentration M_o. The total aerosol yield thus has to be parameterized as a function of M_o. If a reactive organic gas undergoes oxidation to produce products P_1, P_2, …

ROG $\longmapsto$ $\alpha_1 P_1 + \alpha_2 P_2 + …$
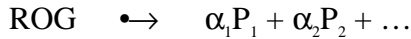
and the reaction products are absorbed into the preexisting aerosol phase the aerosol yield can be written as (e.g. Odum *et al.* 1996):

$$Y = M_o \sum_i \left(\frac{\alpha_i K_{om,i}}{1 + K_{om,i} M_o} \right),$$

(3.6)

where α_i is the mass-based stoichiometric coefficient for the reaction product i and $K_{om,i}$ is the partitioning coefficient K of product i normalized by the mass concentration of the absorbing organic aerosol:

$$K_{om,i} = \frac{c_{om,i}}{c_{g,i} M_o},$$

(3.7)

where $c_{om,i}$ is the concentration of i in the aerosol phase and $c_{g,i}$ is the concentration of i in the gas phase. For ideal solutions the non-normalized partitioning coefficient is the inverse of the saturation concentration of the pure substance i:

$$K_i = \frac{1}{c_i^0},$$

(3.8)

which makes it possible to use saturation vapor pressure data from the literature in Equation 3.7.

Due to the insufficient knowledge of oxidation pathways not all coefficients α_i and not all partitioning coefficients $K_{om,i}$ are known for all reaction products. But for each ROG the total aerosol yield Y and M_o can be determined experimentally (see e.g. Odum *et al.* 1996) and the unknown parameters α_i and $K_{om,i}$ are obtained by fitting Equation (3.6) to the Y-M_o data pairs. The hundreds of different reaction products can usually be represented by two hypothetical compounds with different α_1, α_2, $K_{om,1}$, and $K_{om,2}$. An example of the dependence of Y on M_o is shown in Figure 3.4.
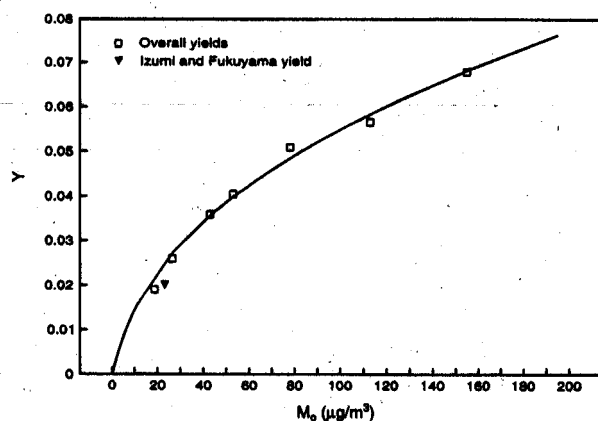
Figure 3.4: SOA yield of α-pinene as a function of M_o from Odum *et al.* 1996.

3.4.2.2 Applicability to the atmosphere

Experimentally determined parameterizations of aerosol yields of single ROGs are only useful if they are applicable to the ambient atmosphere. Whereas in experimental settings only one ROG is oxidized, the ambient atmosphere contains a complex mixture of many different precursor ROGs. Also the preexisting absorbing aerosol might differ between the experiment and the real atmosphere.

The first problem in characterizing a ROG by its aerosol yield is that a ROG could have different reaction pathways and products in a mixture of different precursor gases than if it is present alone. In a mixture it has to compete with the other ROGs for the same oxidants. The aerosol yield of a mixture of ROGs does therefore not necessarily equal the sum of the yields of each ROG alone. The smog chamber experiments of Odum *et al.* (1997 a, b) show however that, e.g., for whole gasoline vapor, the aerosol yield can be represented very well by the sum of the yields of its aromatic components. This result does not necessarily apply to all other sources and VOC mixtures, but gives some confidence in the smog chamber data.

The second problem is that when the aerosol yield of a single precursor is measured the absorbing aerosol is only formed by the reaction products of the precursor gas itself. The absorbing fraction in the ambient aerosol however is a more complex mixture of secondary and primary aerosol of different origins. It might have different absorption characteristics than the aerosol formed by one single precursor. Liang *et al.* (1997) compared the sorption of semi-volatile organic compounds to model organic aerosols with the sorption to ambient aerosol. They found that the sorption properties of ambient

smog aerosol were similar to the sorption properties of chamber generated aerosol from the oxidation of gasoline vapor and to tobacco smoke aerosol. This finding is consistent with the relatively high fraction of secondary organic aerosol in the Los Angeles area (e.g. Turpin *et al*. 1991 a, b, Turpin *et al*., 1995). Direct measurements of gas-particle partitioning coefficients (Falconer and Bidleman, 1994) suggest that the partitioning coefficients K_{om} for a single SVOC are quite similar even in different cities. However a more thorough analysis by Goss and Schwarzenbach (1998) casts doubt on this conclusion and shows that the absorption characteristics of the urban aerosol can vary even at the same location. They conclude that there exists no typical urban aerosol in regard to its absorption properties. Despite those uncertainties the parameterization of aerosol yields as a function of absorbing organic aerosol concentration is a considerable improvement over the simple FAC values.

4 Quantitative Determination of the Aerosol Formation Potential

The aerosol formation potential of different precursors can be determined experimentally by measuring either the fractional aerosol coefficients (FAC) or the aerosol yields defined in the previous chapter. This is usually done in smog chamber experiments that simulate the atmospheric oxidation of precursor VOCs in a controlled environment. The measured FAC or yield data can then be used to parameterize the SOA formation in air quality models.

If FAC values are used, the formation of secondary organic aerosol can be treated like primary emissions (Grosjean *et al.*, 1989, Barthelmie and Pryor, 1997). The emissions of each VOC species are multiplied by the corresponding FAC to obtain an emission rate of secondary organic aerosol, which can be further incorporated in a simple dispersion model. This method is comparatively simple but not very accurate, because the FAC can change with the concentration of oxidizing species, ambient temperature, relative humidity, and the amount and nature of the ambient absorbing aerosol, as discussed in Section 3.4.

If yield data are used, it is necessary to determine the amount of reacted precursor species (ΔROG) by a detailed gas phase chemical model (e.g. Pandis *et al.*, 1992, Strader *et al.*, 1999). ΔROG can then be multiplied by the corresponding aerosol yield to get the SOA production at each model time step or location. This approach is expected to give better results, because the gas phase oxidation and its dependence on temperature and oxidant concentration are treated explicitly. Both approaches allow the speciated VOC emissions to be linked to SOA concentrations and can thus provide information about the importance of different VOC sources for SOA formation.

4.1 Smog Chamber Experiments

Smog chamber experiments have been conducted since the 1960s to study the formation of secondary organic aerosols (e.g. Grosjean and Seinfeld, 1989 and references therein, Pandis *et al.* 1990, Odum *et al.*, 1996). SOA formation experiments are usually conducted in an enclosed chamber, that consists most often of Teflon, but also glass, aluminum and stainless steel are sometimes used as chamber materials (Grosjean and Seinfeld, 1989). The chamber size can vary considerably from 3.5 m^3 (Grosjean *et al.* 1992) to 60 m^3 (Pandis *et al.*, 1990). Both indoor (e.g. Kleindienst *et al.*, 1999) and outdoor chambers (e.g. Pandis *et al.*, 1990) are used. The latter can take advantage of the natural sunlight whereas indoor chambers have to be irradiated using UV lamps. However the temperature in outdoor chambers often gets unrealistically high, which can lead to aerosol yields that differ from ambient conditions.

The two major types of experiments conducted in smog chambers are photochemistry experiments that are conducted in sunlight and ozonolysis experiments that take place in the dark. For photochemistry experiments the chamber is filled with purified air, NO_x, and the organic precursor gas. In many cases propene or propylene are added as a photochemical initiator and to facilitate the production of OH radicals. Propene and propylene have the advantage that their main oxidation products (formaldehyde and acetaldehyde) do not participate in the aerosol formation (Kleindienst *et al.* 1999). The photochemical reactions produce O_3, OH and the NO_3 radical, all of which are potential

oxidizing agents towards the precursor VOC. The ozonolysis experiments are conducted to study the reactivity and aerosol yields of alkenes and biogenic hydrocarbons towards ozone. In these experiments ozone is mixed with purified air and seed aerosol in a dark chamber. Subsequently the precursor gas is injected into the chamber and oxidized by ozone alone.

Most experiments also use an inert tracer gas for calibration purposes and a seed aerosol to facilitate initial condensation. The concentration of precursor gases and oxidizing species are sometimes much higher than ambient, especially in the early experiments (Grosjean and Seinfeld, 1989). It is still debated if this can considerably change the aerosol yields. Forstner et al. (1997) claim that even when initial aromatic hydrocarbon concentration in the chamber are an order of magnitude higher than in the ambient atmosphere, the hydroxyl radical chemistry stays the same. However, subsequent OH – aromatic adduct reactions could be more significant than in the ambient atmosphere due to the higher NO_x concentrations. Kleindienst et al. (1999) used realistic ambient gas phase concentrations in their flow-trough chamber and found lower aerosol yield for toluene compared to Odum et al. (1997a). They speculate that the NO_x levels, which were more than a factor of two higher in the experiments of Odum et al. (1997a) could be responsible for this difference.

Once the precursor gas has reacted and the particle concentration reaches a maximum the aerosol yields can be calculated as the quotient of newly formed particle mass and reacted precursor gas (ΔROG). If the yields are calculated long after the beginning of the experiment particle losses to the wall and by gravitational settling can be substantial, especially for small chambers. These particle losses should be corrected for and yields should be calculated right when the particle concentration reaches a maximum.

Figure 4.1 shows an example of a typical dark smog chamber experiment in which α-pinene is oxidized by O_3 (from Leach et al. 1999). O_3 (triangles) is injected into the chamber two hours (hr) before the injection of α-pinene. Once the ozone concentration reaches 0.65 ppm α-pinene (circles) is injected and the experiment starts at t = 0 hr. The concentration of both gases starts to decrease rapidly as α-pinene reacts with O_3 and with some delay particulate matter (squares) is formed. The particle concentration reaches a peak and starts to decrease indicating particle loss to the walls, by deposition and leaks.
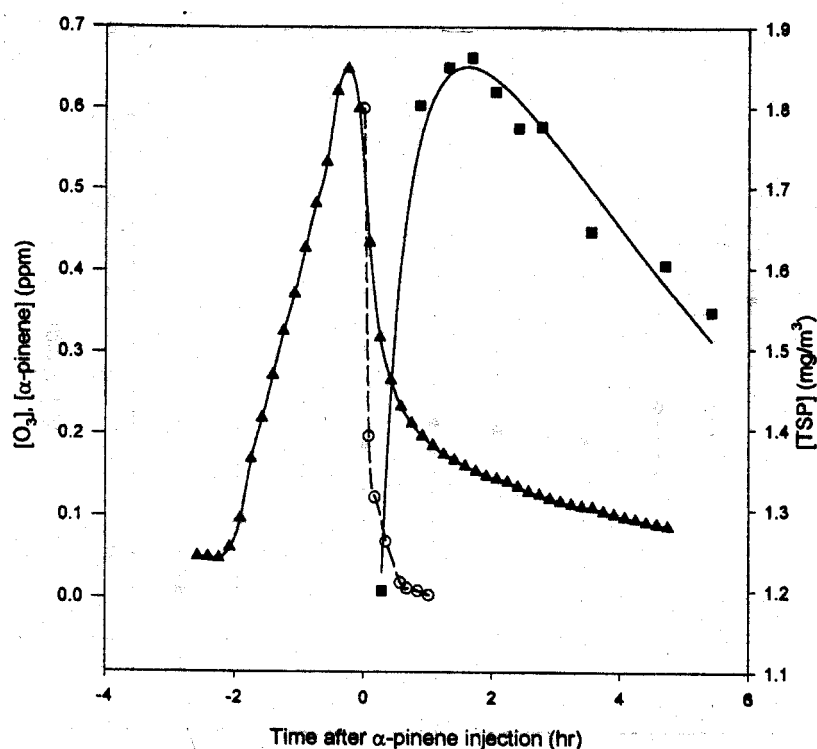
Figure 4.1: Concentration profiles of O_3 (triangles), α - pinene (circles), and secondary organic aerosol mass concentration (TSP, shown in squares) for a typical a-pinene/O3 experiment (from Leach *et al.*,1999)

There are some problems comparing smog chamber aerosol yields to ambient values. The temperatures in the chambers are usually higher than ambient changing gas phase reaction speed and the gas/particle partitioning coefficient of the reaction products. The concentration of precursor VOC and oxidant gases are often orders of magnitude higher than in the ambient atmosphere. This can change reaction pathways and possibly aerosol yields especially if the proportions in oxidant, NO_x and VOC concentrations differ from typical ambient values. Wall losses can lead to an underestimate of the aerosol yields if they are not corrected for. The gas/particle partitioning of the reaction products in smog chamber experiments can deviate from ambient values due to differences in the absorbing aerosol phase. In chamber experiments the absorbing aerosol phase consists mostly of the chamber-generated aerosol itself, while in the atmosphere it is usually a more complex mixture of compounds. In particular, smog chamber experiments are usually conducted at low relative humidity, where the absorbing aerosol phase contains no water, whereas water usually is a major constituent of the aerosol particles at ambient relative humidity. All these factors could be responsible for biased aerosol yields in smog chambers. However, the current state of knowledge about oxidation pathways and reaction products of VOCs requires that those empirical aerosol yields have to be used in air quality models. This empiricism will remain necessary until substantial advances in the knowledge of reaction kinetics and thermodynamics of SOA formation have been made.

24

4.2 Yield Data

Various authors have started to parameterize aerosol yields as a function of absorbing aerosol mass, as in Equation 3.5, first suggested by Odum *et al.* (1996). In all cases one or two hypothetical reaction products are sufficient to fit the experimentally determined SOA yields. Equation 3.5 can thus be written as:

$$Y = M_o \left(\frac{\alpha_1 K_{om,1}}{1 + K_{om,1} M_o} + \frac{\alpha_2 K_{om,2}}{1 + K_{om,2} M_o} \right), \qquad (4.1)$$

where α_1, $K_{om,1}$ and α_2 and $K_{om,2}$ refer to the stoichiometric coefficient and the partitioning coefficient of the first and second reaction product respectively.

Table 4.1 shows the SOA yield data for selected anthropogenic aromatic VOCs as determined by Odum *et al.* (1996, 1997a,b). Some aromatic species of similar structure seem to have similar aerosol yields and can be lumped into "high yield" aromatic precursors and "low yield" aromatic precursors. A common α and K_{om} for all "high yield" precursor gases is determined by making one fit of Equation 4.1 to the yield data of all included species. The same is done for the "low yield" species. For comparison α and K_{om} that were determined separately for two of the low yield aromatics by Odum *et al.* (1996) are also shown. This gives an estimate of the uncertainty associated with the use of the high and low yield categories. It also should be mentioned that the grouping into low and high yield species classes is somewhat doubtful considering the experimental uncertainties and the possible differences between chamber and ambient conditions mentioned above. The results of Kleindienst *et al.* (1999) show that in a slightly different experimental setup with gas-phase concentrations and absorbing aerosol composition more representative of the urban ambient atmosphere, toluene yields seem to be more indicative of a low yield than a high yield species.

The anthropogenic species listed in Table 4.1 are the only ones for which empirical parameters α and K are available so far. Studies of Odum *et al.* (1997a,b) indicate that the aromatic species might be the most important anthropogenic source of SOA. They show that the SOA yield from the oxidation of whole gasoline vapor can be approximated by the aerosol formation of its aromatic components, and that the contribution of aliphatic hydrocarbons can be neglected in their experiments.

Table 4.1: Aerosol yield parameters for aromatic compounds

Yield Class	Species	α_1	$K_{om,1}$	α_2	$K_{om,2}$
High Yield Aromatics	Toluene Ethylbenzene m,o,p-Ethyltoluene n-Propylbenzene	0.071	0.053	0.138	0.0019
Low Yield Aromatics	m,o,p-Xylene 1,3,5 and 1,2,4-Trimethylbenzene 1,2-Dimethyl-4-ethylbenzene 1,4-Dimethyl-2-ethylbenzene 1,2,4,5 and 1,2,3,5 Tetramethylbenzene	0.038	0.042	0.167	0.0014
	m-Xylene [a]	0.03	0.032	0.167	0.0019
	1,2,4-Trimethylbenzene [a]	0.0324	0.053	0.166	0.002
	1-Methyl-3-n-propylbenzene	0.05	0.054	0.136	0.0023
	p-Diethylbenzene	0.0083	0.093	0.22	0.001

(a) Odum *et al.* 1996

Table 4.2 shows a comprehensive summary of yield parameters for biogenic VOC compounds. Biogenic VOC compounds contain unsaturated carbon-carbon bonds, which make them very reactive and vulnerable to attack by of all three major oxidizing species, O_3, OH, NO_3. This makes their gas-phase chemistry more complex than that of most anthropogenic species that are only oxidized by the OH radical. Table 4.2 thus summarizes yields for different conditions, for full photochemistry (O_3, OH, and NO_3) and for oxidation by O_3, and by NO_3 separately. The data are compiled by Griffin *et al.* (1999).

Table 4.2: Aerosol yield parameters for biogenic alkenes

Species	α_1	$K_{om,1}$ [m^{3}µg^{-1}]	α_2	$K_{om,2}$ [m^{3}µg^{-1}]
Full photochemistry				
Δ^3-Carene	0.054	0.043	0.517	0.0042
β-Caryophyllene	1	0.0416	-	-
α-Humulene	1	0.0501	-	-
Limonene	0.239	0.055	0.363	0.0053
Linalool	0.073	0.049	0.053	0.0210
Ocimene	0.045	0.174	0.149	0.0041
α-Pinene	0.038	0.171	0.326	0.0040
β-Pinene	0.130	0.044	0.406	0.0049
Sabinene	0.067	0.258	0.399	0.0038
α&γ-Terpinene	0.091	0.081	0.367	0.0046
Terpinene-4-ol	0.049	0.159	0.063	0.0045
Terpinolene	0.046	0.185	0.034	0.0024
Ozone				
Δ^3-Carene	0.128	0.337	0.068	0.0036
α-Pinene	0.125	0.088	0.102	0.0788
β-Pinene	0.026	0.195	0.485	0.0030
Sabinene	0.037	0.819	0.239	0.0001
Nitrate Radical				
Δ^3-Carene	0.743	0.0088	0.257	0.0091
β-Pinene	1	0.0163		
Sabinene	1	0.0115		

The aerosol yields of biogenic precursor VOCs are generally higher than the yield of anthropogenic VOCs, which makes them effective sources of aerosols. Different biogenic hydrocarbons have a wide range of yields, as can be seen in Figure 4.2, which compares the aerosol yields of different biogenic precursors at a preexisting absorbing aerosol concentration of 20µg/m^3. Sesquiterpenes have the highest SOA yields of the organic compounds tested, a behavior that reflects the high carbon number of those molecules. Among the other species, b-pinene, limonene and sabinene have high aerosol yields.
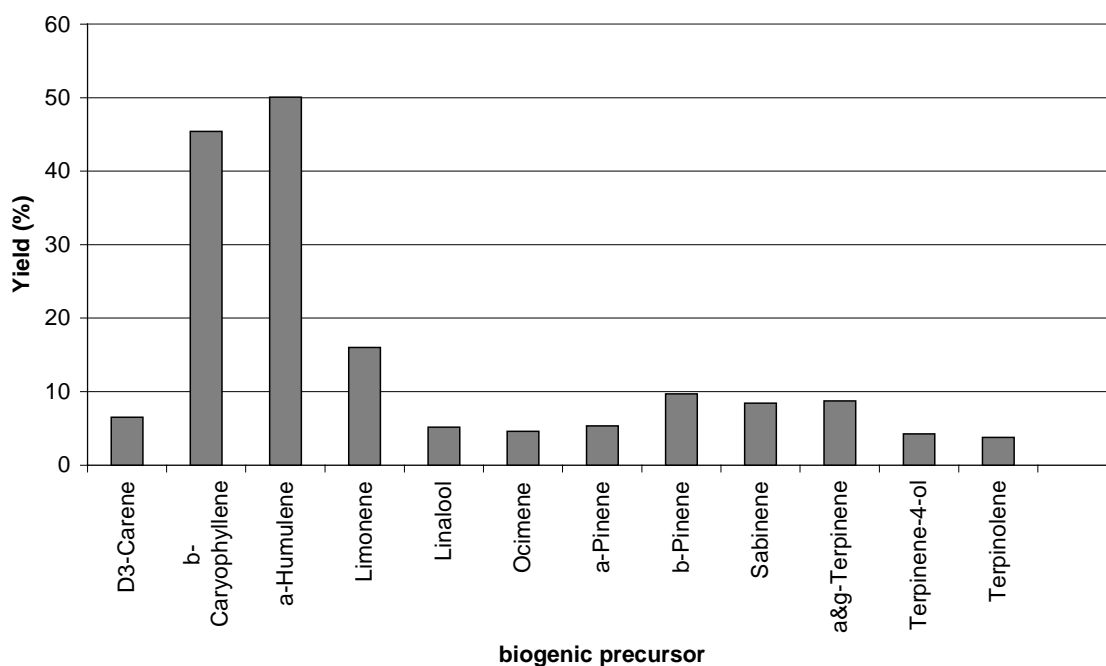
Figure 4.2: Comparison of the aerosol yields of different organic precursors, $M_o = 20\mu g/m^3$

The overall high aerosol yields of biogenic precursor VOCs can make them important for organic aerosol formation even in urban areas. Pandis *et al*. (1992) estimated, for example, that up to 16% of the SOA during a high-smog episode in the Los Angeles basin could be attributed to biogenic precursors. This shows that the contribution of biogenic precursors to anthropogenic pollution cannot be neglected in this area. Compared to North America, biogenic non-methane VOCs in Europe are relatively less important. However, according to a recent estimate (Simpson *et al.,* 1999) natural sources in Europe still emit about half as much non-methane VOC compounds as anthropogenic sources. Taking into account the much higher SOA formation potential of biogenic VOCs, the overall contribution of natural sources to the SOA concentrations could still be significant. This has been confirmed by a recent modeling study (Andersson-Sköld and Simpson, 2000). This study shows that, at least in the Scandinavian boreal region, where natural VOC emissions exceed anthropogenic emissions, biogenic emissions are much more important for SOA formation than anthropogenic emissions. Kavouras *et al*. (1999) also provide some in-situ evidence for particle production through oxidation of monoterpenes in Portuguese forests

4.3   Fractional Aerosol Coefficient Data

The fractional aerosol coefficient (FAC) is a coarser approach to parameterize the aerosol formation potential. It summarizes both gas-phase chemistry and gas/particle conversion in one constant and provides a rough estimate of what percentage of a VOC precursor will end up as aerosol. As ambient conditions (like oxidant concentration, temperatures, preexisting aerosol, …) vary strongly from one location to another and between different times, these coefficients should not be used to predict SOA

concentrations quantitatively. They can, however, provide a basis for a comparison of the aerosol formation potential of different precursor gases and VOC sources. That means they could provide rough estimates of whether, under identical ambient conditions, one emission source would produce more SOA per VOC emitted than another. In this section FAC values derived by Grosjean and Seinfeld (1989) will be used to compare the aerosol formation potential of different source sectors used in the Regional Air Pollution Information and Simulation (RAINS) model. Those FAC values have been used previously to predict SOA formation either from emissions (Grosjean and Seinfeld, 1989) or from gas-phase measurements (Barthelmie and Pyor, 1997).

4.3.1 FAC Values for Different VOC Precursor Gases

The fractional aerosol coefficients used in the following calculations were taken from Grosjean and Seinfeld (1989), Table 9. They include FAC values for 17 alkenes, over 40 alkanes and cycloalkanes, 20 aromatics and various miscellaneous anthropogenic and natural VOC precursors. The authors derived FAC values partly from a review of experimental data and partly from theoretical considerations.

In order to arrive at a consistent data set of experimental values, wall loss corrected data were used whenever possible. Some of the data sets were reevaluated to use maximal values of aerosol concentration for the calculation of FAC values instead of final values at the end of the experiment, when particle losses can be considerable. Yields were converted to fractional aerosol coefficients using either the fraction of reacted ROG reported by the authors or that estimated from concentration – time profiles shown in the original reference.

The fractional aerosol coefficients for VOC species, for which experimental data are not available were estimated from theoretical considerations. Several low weight precursor gases (e.g. C1-C6 alkanes and alkenes, benzene, C2-C4 aldehydes) have only volatile reaction products, that do not partition to the particle phase. A FAC of 0 is recommended for these and similarly low-weight VOC species. The FAC of higher weight species can be estimated from structure-reactivity relationships and the gas phase vapor pressures of the low volatile reaction products. If necessary, vapor pressures of reaction products can be derived from existing relationships between vapor pressure and compound size within each structural family of VOC.

Figure 4.3 shows selected FAC values for different VOC species. The aromatic compounds have relatively high aerosol formation potential compared to the aliphatic compounds. It can be noted that according to Grosjean and Seinfeld (1989) o-xylene has a higher aerosol formation potential than p- or m- xylene, although the experimentally determined aerosol yields of all three species are similar (compare Table 4.1). It is not possible to tell if this results from higher gas phase reactivities of o-xylene or from erroneous assumptions of the authors.

The FAC values presented in this section will in general tend to underestimate the aerosol formation for several reasons (Grosjean and Seinfeld, 1989). Not all of the experimentally derived FAC values could be corrected for wall losses and some of the smog chamber studies were conducted without seed aerosol, thereby retarding aerosol formation and growth. The theoretical analysis uses the assumption that semi-volatile species only condense when they exceed their saturation vapor pressure and neglects possible ad- and absorption effects. This gives a lower limit of aerosol formation.
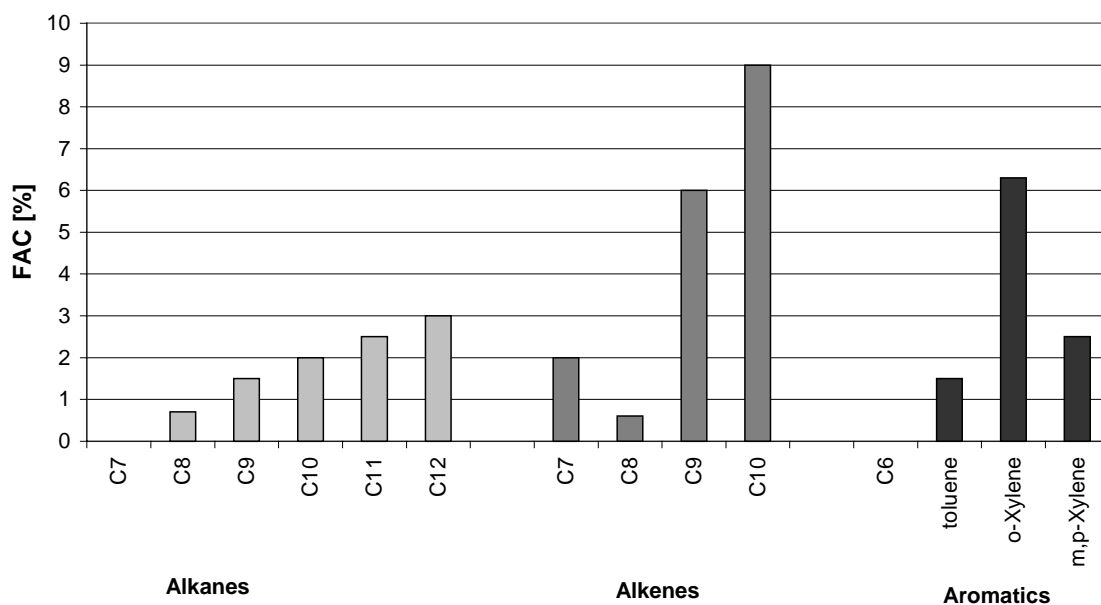
Figure 4.3: FAC of selected VOCs. Data from Grosjean and Seinfeld (1989)

4.3.2 Aerosol Formation Potential of Different VOC Sources Relevant to the RAINS Model

The FAC values for single VOC species compiled by Grosjean and Seinfeld (1989) can be used to characterize and compare the SOA formation potential of different VOC sources. If a detailed profile of the non methane VOCs emitted by one source is known, the aerosol formation potential of the respective source can be calculated as the weighted average of the FACs of the single components i:

$$FAC = \sum_i f_i \cdot FAC_i \qquad (4.2)$$

where f_i is the fractional contribution of species i to the emitted non-methane VOC.

These weighted averages can be applied to evaluate the relative aerosol formation potential of the source sectors in the RAINS model. These source sectors are closely related to the EMEP/CORINAIR SNAP categories, for some of which the speciated profiles can be found in the EMEP/CORINAIR guidebook (EEA, 1996). These species profiles often have low data quality according to the EMEP/CORINAIR internal ranking system, but they provide a first guideline for a rough estimation of the fractional composition for each source sector. If possible, more than one estimate of the species profiles was used to get a range of possible FAC values for each source. Table 4.3 shows the FAC values for different RAINS source sectors. The individual species profiles used for each source sector and the discussion of some necessary assumptions made in the calculations of the FAC values can be found in the Appendix A1-A19.

30

Table 4.3: FAC values for different source sectors used in the RAINS model

Sector	RAINS code	FAC	Detailed Source profile in
Solvent use			
Architectural use of paint	ARCH_P	0.2	A1
Manufacture of automobiles	AUTO_P	1.5-2.0	A2
- " - new installations	AUTO_P_NEW	1.5-2.0	A2
Domestic use of solvents	DOM_OS	0.1-0.3	A5
Domestic use of paint	DOM_P	1.5-2.0	A2
Other industrial use of solvents	IND_OS	-	n.a.
Other industrial use of paints	IND_P	1.5-2	A2
Products incorporating solvents	PIS	-	n.a.
Printing, offset	PRT_OFFS	1.5	A9
Printing offset, new installations	PRT_OFFS_NEW	1.5	A9
Flexography and rotogravure in packing	PRT_PACK	1.5	A9
-"- , new installations.	PRT_PACK_NEW	1.5	A9
Rotogravure in publication	PRT_PUB	1.5	A9
Rotogravure in publication, new installations	PRT_PUB_NEW	1.5	A9
Screen printing	PRT_SCR	1.5	A9
Screen printing, new installations	PRT_SCR_NEW	1.5	A9
Vehicle refinishing	VEHR_P	1.5-2.0	A2
Vehicle refinishing, new installations	VEHR_P_NEW	1.5-2.0	A2
Treatment of vehicles	VEHTR	-	n.a.
Preservation of wood	WOOD	2.1	A13
Preservation of wood – new installations	WOOD_NEW	2.1	A13
Treatment and distribution of oil products			
Conversion	CON_COMB	-	n.a.
Gasoline distribution – service stations	D_GASST	0.07-1.8	A4
Gasoline distribution – transport, depots	D_REFDEP	-	n.a.
Degreasing	DEGR	-	n.a.
Degreasing – new installations	DEGR_NEW	-	n.a.
Extraction, proc., distribution of gaseous fuels	EXD_GAS	-	n.a.
Distribution of gaseous fuels – new mains	EXD_GAS_NEW	-	n.a.
Extraction, proc., distribution of liquid fuels	EXD_LQ	-	n.a.
- " - including new (un)loading procedures	EXD_LQ_NEW	-	n.a.
Refineries, process	REF_PROC	0.1-0.2	A10
Transport			
Evaporative emissions from cars	CAR_EVAP	0.03-0.4	A3
Air transport (LTO)	TRA_AIR	0.2	A11
Transport other –2-stroke engines	TRA_OT_LF2	1.0-2.1	A12
Transport other – large size ships	TRA_OTS_L	1.5-2.7	A14
Transport other – medium size ships	TRA_OTS_M	1.5-2.7	A14
Transport road – 2-stroke engines	TRA_RD_LF2	1.0-2.1	A12
Diesel engines	TR_RD_LD4 (MD)	1.5-2.7	A14
Gasoline engines, 4-stroke, no catalyst	TR_RD_LD4	1.2-1.3	A15
Gasoline engines, 4-stroke, catalyst	TR_RD_LD4	1.2-1.3	A16

Sector	RAINS code	FAC	Detailed Source profile in
Combustion			
Industrial boilers	IN_BO	*	A17-A19
Other industrial combustion	IN_OC	*	A17-A19
Power plants, existing other	PP_EX_OTH	*	A17-A19
Power plants, existing wet bottom	PP_EX_WB	0.05-0.3	A19
New power plants	PP_NEW	-	n.a.
Combustion in residential and commercial sector	RESID	*	A17-A19
Wood combustion		0.15-0.2	A17
Coal combustion		0.05-0.3	A18
Gas combustion		0	A19
Fuel oil combustion		-	n.a.
Other sectors			
Agricultural waste burning	AGR_BURN	-	n.a.
Dry cleaning	DRY	0	A6
Dry cleaning (new installations)	DRY_NEW	-	n.a.
Food and drink industry	FOOD	>0.3	A7
Application of glues and adhesives in industry	GLUE	-	n.a.
Other industrial sources	IND_OTH	-	n.a.
Inorganic chemical industry	INORG	-	n.a.
Organic chemical industry, production	ORG_PROC	0.01	A8
Organic chemical industry, storage	ORG_STORE	-	n.a.
Pharmaceutical industry	PHARMA	-	n.a.
Products not incorporating solvents	PNIS	-	n.a.
Waste treatment and disposal	WASTE	-	n.a.

* FAC values for these sectors have to be calculated using the relative contribution of wood, oil, coal and gas combustion for each country and year

Selected FAC values from Table 4.3 are presented graphically in Figure 4.4.
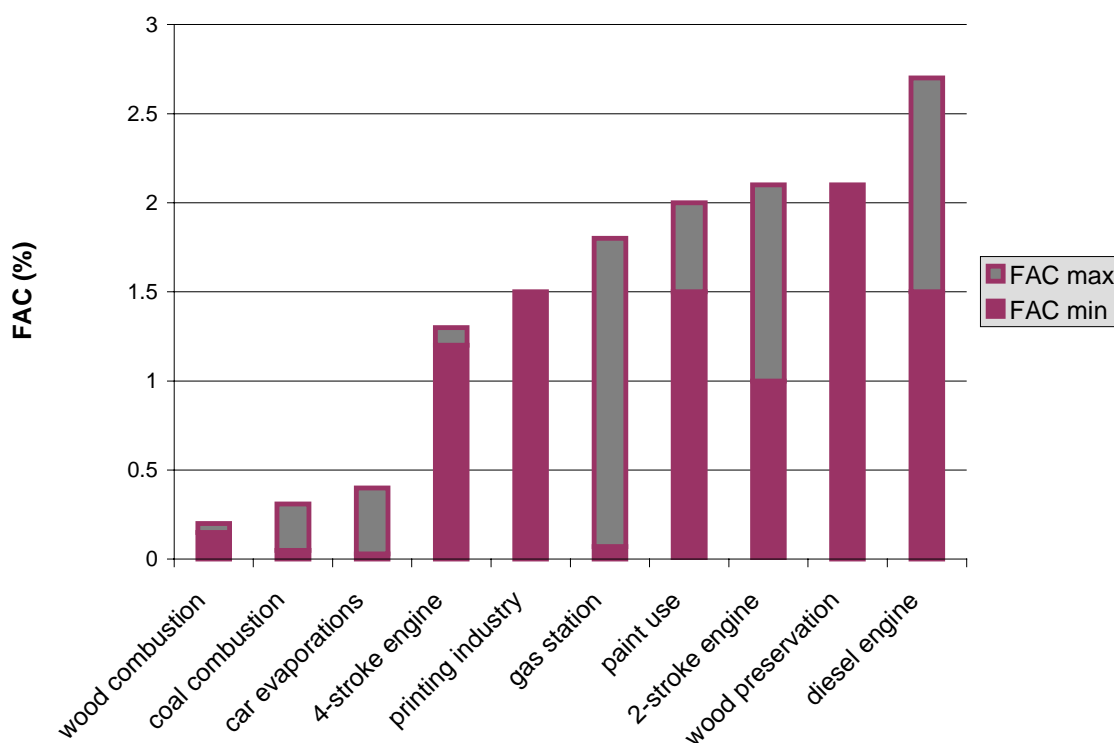
Figure 4.4: FAC values of selected VOC sources

The FAC values presented in Table 4.3 should not be regarded as more than a rough estimate of the relative aerosol formation potential of the different source sectors. This is partly due to uncertainties in the FAC values of individual species and partly due to the poor data quality in the VOC profiles of different source sectors. In some cases not a single, but a range of FAC values is assigned to a source sector. There are two possible reasons for assigning a range of values. Sometimes more than one estimate of species profiles is available and the different estimates result in different FAC values. In other cases, one species profile is available but is ambiguous (for example, it contains the category alkanes >C7) and a range of FAC values has to be assigned to a species class. The Appendix should be consulted for details of the calculation of the FAC values for each source sector. Different species profiles for old and new installations of various activities were not available. Thus it has to be assumed that the species profile remains unaltered by implementing new technologies, even though this might not be valid.

Some of the source sectors deserve special comment:

- For most of the different types of **paint use** (except for architectural paint) only one species profile of solvent use in paint is available (see Appendix A2). Although it is not very realistic to assume that activities like domestic paint use and car painting have the same species profile, the species profile shown in A2 is the only information that is available at this point. The paint considered in this one available species profile consists to a large part of white spirit, which is a mixture of high molecular weight alkanes. This explains the relatively high FAC value assigned to paint use. For other paint types not based on white spirit the FAC could be considerably lower, as is the case for the solvent-based architectural paint.

- The use of just one overall VOC species profile for the very different activities involved in **printing** is not realistic. Moreover the species profile is very crude and the error in the FAC for printing activities might therefore be very large.

- **Diesel** emissions are supposed to contain a high fraction of high molecular weight alkanes, which lead to high FAC values. However, some recent experiments with gasoline vapor (Odum *et al*. 1997 a, b) suggest that the aerosol yield of this complex gaseous mixture can be explained by the aerosol formation of the aromatic components alone. If this result is transferable to diesel emissions the FAC value assigned to diesel emissions might be an overestimate. It is, however, not possible to verify this speculation at present. The same considerations apply to exhaust and evaporative emissions from gasoline cars. The overestimation of the FAC in these latter cases would be smaller however, because the higher alkanes are a less important constituent of gasoline vapor than of diesel.

- An upper limit to the FAC of **food production** could not be given, because carboxylic acids are supposedly a large part of the VOCs emitted (the species profile is very uncertain for this sector). The FAC or aerosol yield of carboxylic acids has not been measured. There is evidence, however, that carboxylic acids are an important intermediate product in SOA formation, that although itself volatile, is effectively further oxidized to semi-volatile species (e.g. Pun *et al*., 2000). The aerosol yield from the oxidation of carboxylic acids might be substantial but is presently unknown.

- The aerosol formation potential of **gasoline cars** with and without catalyst is almost identical, which might lead to the conclusion that the installation of a catalyst has no influence on SOA production of gasoline cars. This is somewhat misleading, because the FAC values presented in Table 4.3 represent the percentage of non-methane VOCs that form secondary aerosol. The installation of a catalyst, however, considerably reduces the emissions of non-methane VOC in favor of methane (Hewitt, 1999), which does not form aerosol. The aerosol formation potential with respect to all VOC emissions (including methane) is thus considerably reduced by a catalyst.

4.4 Relative Importance of Selected RAINS Sectors for SOA Formation in Europe

The relative importance of each sector for SOA formation in Europe can be estimated by multiplying its yearly emissions with the corresponding FAC values. The results are 'emission rates' for SOA. For the following comparison of the SOA formation of different source sectors, the VOC emissions from the year 1990 for the 15 EU states are used, as previously published by Amann *et al.* (2000). This year was chosen because the new technologies implemented in certain sectors - like 'Manufacture of automobiles, new installations' (AUTO_P_NEW) or 'Vehicle refinishing, new installations' (VEHR_P_NEW) - contribute only negligible amounts to total emissions. As it is still unclear how most of those new installations change the species profile of the emissions, we refrain from evaluation of more recent years or future scenarios, where the share of new installations in total emission is larger.

SOA emissions have been calculated for all sectors for which FAC values were available. Table 4.4 shows SOA emission rates for the selected source sectors.

Table 4.4 shows that the highest contribution to the SOA formation comes from mobile sources (cars, ships, and also two-stroke vehicles) due to their overall high emissions combined with a high aerosol formation potential. For example, the non-road traffic using two-stroke engines (TRA_OT_LF2) has lower VOC emissions than residential combustion, but contributes more strongly to the formation of SOA. Car evaporations (CAR_EVAP), emissions from gas stations (D_GASST) and domestic paint use (DOM_P) also have potentially high contributions to the SOA formation. Their SOA 'emissions' are comparable, although their VOC emission rates range from 224 to 1414.

Table 4.4: Importance of selected RAINS sectors for SOA formation

Sector	RAINS code	FAC [%]	VOC Emissions [kT/year]	SOA Emissions [kT/year]	Share [%]
Architectural use of paint	ARCH_P	0.2	359	0.7	1
Manufacture of automobiles	AUTO_P	1.5-2.0	144	2-3	2
Evaporative emissions from cars	CAR_EVAP	0.03-0.4	1414	0.5-6	<1-4
Gasoline distribution – service stations	D_GASST	0.07-1.8	328	0.2-6	<1-4
Domestic use of solvents	DOM_OS	0.1-0.3	679	0.6-2	1
Domestic use of paint	DOM_P	1.5-2.0	224	3-4	3-4
Dry cleaning	DRY	0	104	0	0
Industrial boilers	IN_BO*	0.16-0.3	9	0.01-0.03	<1
Other industrial combustion	IN_OC**	0.3-0.56	42	0.1-0.2	<1
Other industrial use of paints	IND_P	1.5-2	770	11-15	11-12
Organic chemical industry, production	ORG_PROC	0.01	332	0.03	<1
Power plants, existing other	PP_EX_OTH+	0.07-0.27	36	0.02-0.1	<1
Power plants, existing wet bottom	PP_EX_WB	0.05-0.3	1	0	0
Printing	PRT_^^	1.5	314	5	3-5
Refineries, process	REF_PROC	0.1-0.2	208	0.2-0.4	<1
Combustion in residential and commercial sector	RESID++	0.15-0.27	682	1-2	1
Air transport (LTO)	TRA_AIR	0.2	60	0.1	<1
Transport other –2 stroke engines	TRA_OT_LF2	1.0-2.1	427	4-9	5-6
Transport other – medium size ships	TRA_OTS_M	1.5-2.7	12	0.2-0.3	<1
Transport other – large size ships	TRA_OTS_L	1.5-2.7	14	0.2-0.4	<1
Transport road – 2 stroke engines	TRA_RD_LF2	1.0-2.1	943	9-20	10-14
Vehicle refinishing	VEHR_P	1.5-2.0	117	2	2
Preservation of wood	WOOD	2.1	111	2	2
Preservation of wood – new installations	WOOD_NEW	2.1	1	0.01	0
Diesel engines	TR_RD_LD4 (MD)	1.5-2.7	631	10-17	10-12
Gasoline engines, 4-stroke	TR_RD_LD4 ^	1.2-1.3	3449	41-44	32-44
Other sectors		-	2699	n.a.	

^ catalyst and no catalyst vehicles are combined because of their similar FAC; ^^eight printing sectors are combined because of their similar FAC

* calculated as: 17% coal, 29% gas, 6% diesel, 48% wood, contribution of fuel oil ignored

** calculated as: 17% coal, 34% gas, 17% diesel, 32% wood, contribution of fuel oil ignored

\+ calculated as: 69% coal, 9% gas, 1%diesel, 21% wood, contribution of fuel oil ignored

\++ calculated as: 24% coal, 3% gas, 2% diesel, 71% wood, contribution of fuel oil is negligible

Figure 4.5 shows the contributions of the most important sectors to the total SOA emissions. Since most of the FACs have a range of values, the shares are calculated for the case in which each source is assigned the estimated minimum FAC (a) and also for the case in which each source is assigned the estimated maximum FAC (b).

Contribution of most important source sectors to total emissions
(a)   FAC = min
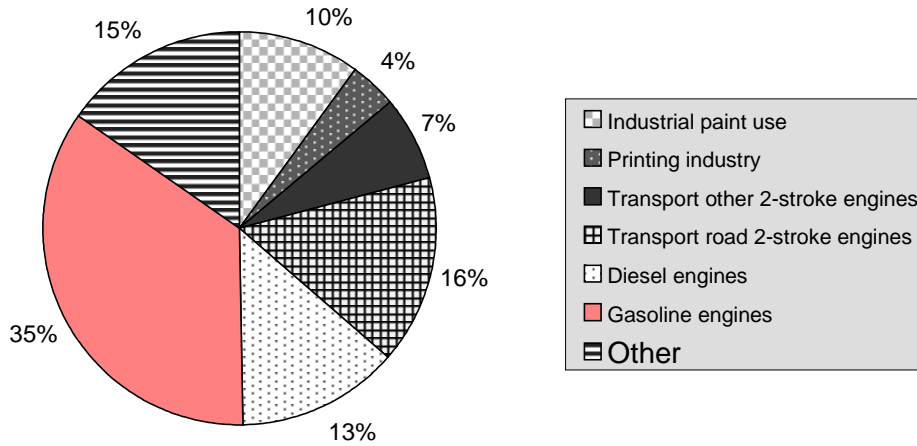
(b)   FAC = max
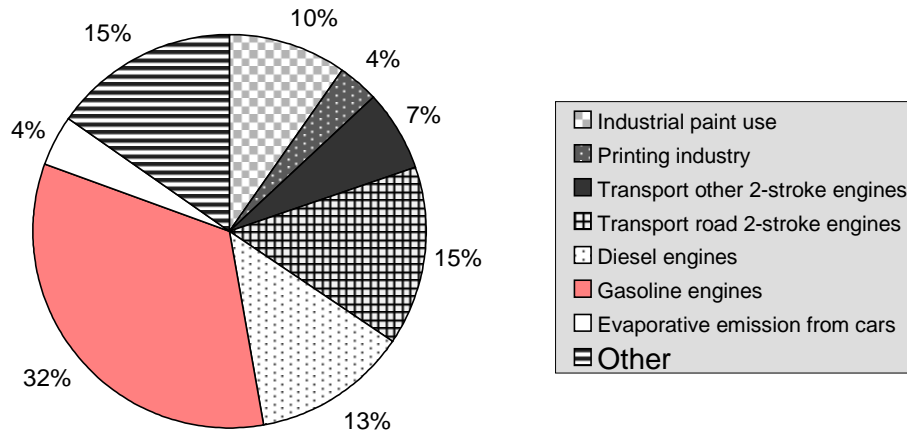
Figure 4.5: Contribution of individual source sectors to total SOA emissions

5 Conclusions

Importance of secondary organic aerosol

It is shown that secondary organic aerosol (SOA) contributes significantly to the aerosol mass concentration. It has been estimated that in smog episodes in Los Angeles up to 70% of the organic aerosol mass is of secondary origin, which reflects peak SOA concentrations. The long-term contribution of secondary material to the total organic aerosol mass lies around 20% according to various estimates. The high SOA concentration in urban smog situations suggests that SOA should not be neglected as an atmospheric pollutant.

Formation mechanisms

The formation of SOA involves two steps: The production of semi-volatile organic compounds by oxidation of VOC precursor gases and the subsequent gas-to-particle conversion of those semi-volatile compounds. SOA formation is, therefore, strongly coupled to photochemical activity and the availability of oxidizing agents (O_3, NO_3 and OH) in the atmosphere. The hydroxyl radical OH is the most important of those oxidizing species. Since OH is produced by the photolysis of ozone, maximum SOA formation can be expected when the ozone concentrations are high (e.g. smog episodes) and enough sunlight is available. Thus, the SOA production is strongest around noon and in early summer. This has been confirmed through observations (e.g. Turpin and Huntzicker 1990, 1991 a,b, 1995). However, even wintertime formation of SOA in the Los Angeles Basin cannot be neglected because the efficiency of gas – particle conversion processes is greater at lower temperatures.

In general, the aerosol formation potential of VOC species within a compound class increases with the molecular weight. The most important anthropogenic precursor gases are the long-chain alkanes and alkenes (greater than 6 carbon atoms) and aromatics other than benzene (e.g. toluene, trimethylbenzene). These precursor gases for SOA have both natural and anthropogenic sources.

Fractional aerosol coefficients as indicators of formation potential

Although the details of SOA formation and its chemical composition are only partially known, empirical data can be used to estimate the SOA formation potential of certain precursor gases and, if their species profile is available, of VOC sources. For example, fractional aerosol coefficients (FAC), defined as the percentage of a precursor gas that will end up as organic aerosol, have been compiled by Grosjean and Seinfeld (1989). The VOC emission rates from a certain source can multiplied by their respective FAC to obtain 'emission rates' of SOA. To a first approximation, this allows secondary particles to be treated as if they were primary emissions.

This approach, however, is not suited for quantitative estimates of ambient SOA concentration due to several conceptual difficulties. It neglects the dependence of SOA formation on all environmental variables like oxidant concentration, temperature and preexisting aerosol concentration. It does not consider any timescales involved in the SOA formation, nor the fact that secondary particles are often formed far from their sources. Moreover, it neglects possible interactions of VOC species, like the

competition for the same oxidants. A more detailed modeling approach is needed to predict ambient SOA concentrations accurately.

Despite these problems, FACs can be used to compare the relative importance of VOC sources for SOA formation. At present this approach is rather limited, because good estimates of species profiles are only available for a few sources and source sectors. A first estimate of the SOA formation potential for RAINS source sectors is presented in this paper, using primarily the species profiles published in the EMEP/CORINAIR emission inventory guidebook (EEA, 1996). According to those estimates, road traffic is the most important source for SOA in the EU in 1990 because of its high VOC emission rates and the high FAC of gasoline and diesel exhaust. It should be mentioned that the estimates of the FAC values could substantially change when more accurate species profiles become available. Because of the low data quality of some of the source profiles, the accomplishment of Sections 4.3.2 and 4.4 is more to exemplify a possible procedure to assess the formation potential of VOC sources rather than providing accurate numbers. The details on the calculations of the FAC values given in the Appendix can be used to judge the quality of the source profiles available for each sector.

Options for reducing secondary organic aerosol

Despite these difficulties in quantification, some qualitative conclusions can be drawn from the literature about SOA formation reviewed in this paper. There are two general alternatives for reducing SOA:

- The reduction of the precursor gases, which are VOCs with high carbon numbers. The most important sectors emitting SOA precursor gases are traffic and solvent use in print and paint. These VOCs have generally a low potential for producing ozone as estimated by the photochemical ozone creation potentials (POCP) published by Derwent and Jenkin, 1991.

- The reduction of ozone, because ozone and its photolysis product, the OH radical, are the necessary oxidants for the production of SOA. All measures that reduce ozone are thus likely to also reduce SOA. This hypothesis is supported by some modeling studies (Kanakidou et al., 2000) and the fact that peak SOA concentrations coincide with smog episodes (Turpin et al. 1995). Consequently, the reduction of short-chain VOCs, that have low FAC but high POCP, or even the reduction of NOx, could reduce SOA.

Because the reduction of VOCs with both high and low carbon numbers is likely to eventually reduce SOA concentration, targeting selected VOC species might not be as important as it seems at first sight. It is at the present time not yet possible to decide which of the two options given above (reducing long-chain precursor gases or reducing ozone) is more cost-effective. More analysis and more detailed modeling efforts are needed to draw further conclusions.

SOA is also formed from natural sources (e.g. Griffin et al., 1999), and natural precursors have been found to contribute significantly to the SOA production in smog episodes (Pandis et al., 1992). To reduce SOA via the reduction of ozone would be effective in controlling even the SOA formed from natural precursors.

6 References

Alcamo, J., Shaw, R. and Hordijk, L*., The RAINS Model of Acidification: Science and Strategies in Europe*. Kluwer Academic Publishers, Dordrecht, Netherlands, 1990.

Amann M., Bertok I., Cofala J., Gyarfas F., Heyes C., Klimont Z., Makowski M., Schöpp W., Shibayev S., Cost-effective Control of Acidification and Ground-level Ozone. ISBN 92-828-4346-7, European Communities, Brussels, Belgium, 1998.

Amann, M., Bertok, I., Cofala, J., Gyarfas, F., Heyes, C., Klimont, Z., and Schöpp, W., Cost-effective Control of Acidification and Ground-Level Ozone - Eighth Interim Report, IIASA, Laxenburg, Austria, 2000.

Andersson-Sköld, Y. and Simpson, D., Secondary organic aerosol formation in Northern Europe: a model study, submitted to J. Geophys. Res., 2000.

Aumont, B., Madronich, S., Bey, I., Tyndall, G. S., Contribution of secondary VOC to the composition of aqueous atmospheric particles: A modeling approach, J. Atmos. Chem. 35, 59-75, 2000.

Blando, J. D., Turpin, B. J., Secondary organic aerosol formation in cloud and fog droplets: a literature evaluation of plausibility, Atmos. Environ. 34, 2000.

Blando, J. D., Porcia, R. J., Li, T.-H., Bowman, D., Lioy, P. J., Turpin, B. J., Secondary formation and the Smoky Mountain aerosol: An examination of aerosol polarity and functional group composition during SEAVS, Environ. Sci. Technol. 32, 604-613, 1998.

Barthelmie, R. J. Pryor, S. C. Secondary organic aerosols: Formation potential and ambient data, Sci. Total Environ. 205, 167-178, 1997.

Derwent, R. G. and Jenkin, M.E., Hydrocarbons and the long-range transport of ozone and PAN across Europe, Atmos. Environ., 25A, 1661-1678, 1991.

Desecari, S., Faccini, M. C. and Fuzzi, S., Characterization of water-soluble organic compounds in atmospheric aerosol: A new approach, J. Geophys. Res., 105, 1481-1489, 2000.

EEA (European Environmental Agency) *Joint EMEP/CORINAIR Atmospheric Emission Inventory Guidebook, First Edition.* Copenhagen, 1996.

Faccini, M. C., Fuzzi, S., Lind, J. A., Fierlinger-Oberlinninger, H., Kalina, M., Puxbaum, H., Winiwarter, W., Arends, B. G., Wobrock, W., Jaeschke, W., Berner, A. and Kruisz, C., Phase partitioning and chemical reactions of low molecular weight organic compounds in fog, Tellus 44B, 1992.

Faccini, M. C., Fuzzi, S., Zappoli, S., Andrachio, A., Gelencser, A., Kiss, G., Krivacsy, Z., Meszaros, E., Hannson, H.-C., Alsberg, T., and Zebuehr, Y., Partitioning of the organic aerosol component between for droplets and interstitial air, J. Geophys. Res. 104, 26,821-26832, 1999.

Forstner, H. J. L., Flagan, R. C., and Seinfeld, J. H,. Secondary organic aerosol formation from the photo-oxidation of aromatic hydrocarbons: Molecular composition, Environ. Sci. and Technol. 31, 1345-1358, 1997.

Forstner, H. J. L., Flagan, R. C., and Seinfeld, J. H., Molecular speciation of secondary organic aerosol from the photo-oxidation of the higher alkenes: 1-octene and 1-decene, Atmos. Environ. 31, 1953-1964, 1997.

Goss, K.-U., Schwarzenbach, R. P. Gas/Solid and Gas/Liquid partitioning of organic compounds: Critical evaluation of equilibrium constants, Environ. Sci. Technol., 32, 2025-2032, 1998.

Griffin, R. J., Cocker, D. R. III, Flagan, R. C., and Seinfeld, J. H., Organic aerosol formation from the oxidation of biogenic hydrocarbons, J. Geophys. Res. 104, 3555-3567, 1999.

Griffin, R. J., Cocker, D. R. III, Seinfeld, J. H., and Dabdub, D., Estimate of global atmospheric organic aerosol from oxidation of biogenic hydrocarbons, Geophys. Res. Lett. 2721-2724, 1999.

Grosjean, D. and Seinfeld, J. H., Parameterization of the formation potential of secondary organic aerosols, Atmos. Environ., 23, 1733-1747, 1989.

Heintzenberg, J., Fine particles in the global troposphere: A review, Tellus 41B, 149-160, 1989.

Hewitt, C.N.(ed.), *Reactive Hydrocarbons in the Atmosphere*, Academic Press, San Diego, USA, 1999.

Hildemann, L. M., Cass, R.G., Mazurek, M. A., Mathematical modelling of urban organic aerosol: Properties measured by high-resolution gas chromatography, Environ. Sci. Technol. 27, 2045-2055, 1993.

Hildemann, L. M., Mazurek, M. A., Cass, C. R., Quantitative characterisation of urban sources of organic aerosol by high-resolution gas chromatography, Environ. Sci. Technol. 25, 1311-1325, 1991.

Hildemann, L. M., Mazurek, M. A., Cass, G. R., Simeoneit, B. R. T., Seasonal trends in Los Angeles ambient organic aerosol observed by high-resolution gas chromatography, Aerosol Sci. Technol. 20, 303-317, 1994.

Hoffmann, T., Odum, J. R. Bowman, F., Collins, D., Klockow, D., Flagan, R. C., and Seinfeld, J. H., Formation of organic aerosols from the oxidation of biogenic hydrocarbons, J. Atmos. Chem. 26, 189-222, 1997.

Holes, A., Eusebi, A., Grosjean, D., and Allen, D. T., FTIR analysis of aerosol formed in the photooxidation of 1,3,5 Trimethyl benzene, Aerosol Sci. Technol. 26, 517-526, 1997.

Jacobson, M. C., Hannson H.-C., Noone K. J., and R. J. Charlson, Organic atmospheric aerosols: Review and state of the science, Reviews of Geophysics, 38, 267-294, 2000.

Kanakidou, M., Tsigaridis K., Denetener, F. J., Crutzen, P. J., Human-activity-enhanced formation of organic aerosols by biogenic hydrocarbon oxidation, J. Geophys. Res. 105, 9243-9254, 2000.

Kavouras, I. G., Mihalopoulos, N., Stephanou, E. G., Secondary organic aerosol formation vs primary organic aerosol emission: In situ evidence for the chemical coupling between monoterpene acidic photooxidation products and new particle formation over forests, Environ. Sci. Technol. 33, 1028-1037, 1999.

Kleeman, M. J. Cass, G. R., Effects of emissions control strategies on the size and composition distribution of urban particulate air pollution, Environ. Sci. Technol. 1999, 33, 177-189.

Kleindienst, T. E., Smith, D. F., Li, W., Edney, E. O., Driscoll, D. J., Speer, R. E., and Weathers, W. S., Secondary organic aerosol formation from the oxidation of aromatic hydrocarbons in the presence of dry sub-micron ammonium sulfate aerosol, Atmos. Environ. 33, 3669-3681, 1999.

Limbeck, A., Puxbaum, H. Organic acids in continental background aerosols, Atmos. Environ. 33, 1847-1853, 1999.

Liang, C., Pankow, J. F., Odum, J. R., Seinfeld J. H., Gas/particle partitioning of semivolatile compounds to model inorganic, organic and ambient smog aerosols, Environ. Sci. Technol. 31, 3086-3092, 1997.

Leach, K. B., Kamens, R. M., Strommen, M. R., and Jang, M., Partitioning of semivolatile organic compounds in the presence of a secondary organic aerosol in a controlled atmosphere, J. Atmos. Chem. 33, 241-264, 1999.

Odum, J. R., Hoffmann, T., Bowman, F., Collins D., Flagan, R. C., Seinfeld J. H., Gas/Particle partitioning and secondary organic aerosol yields, Environ. Sci. Technol. 30, 2580-2585, 1996.

Odum J. R., Jungkamp T. W. P., Griffin, R. J., Flagan, R. C., Seinfeld J. H., The atmospheric aerosol formation potential of whole gasoline vapor, Science 274, 96-99, 1997a.

Odum J. R., Jungkamp T. W. P., Griffin, R. J., Forstner, J. H. L. Forstner, Flagan, R. C., Seinfeld J. H., Aromatics, reformulated gasoline and atmospheric organic aerosol formation, Environ. Sci. Technol. 31, 1890-1897, 1997b

Palen, E. J., Allen, D. T., Pandis, S. N., Paulson, S. E., Seinfeld, J. H., Flagan, R. C., Fourier transform infrared analysis of aerosol formed in the photooxidation of isoprene and β-pinene, Atmos. Environ. 26A, 1239-1251, 1992.

Pandis, S. N., Paulson, S. E., Seinfeld, J. H., and Flagan, R. C., Aerosol formation in the photooxidation of isoprene and β-pinene, Atmos. Environ. 25A, 997-1008, 1991.

Pandis, S. N., Harley, R. A., Cass, G. R., and Seinfeld, J. H., Secondary organic aerosol formation and transport, Atmos. Environ. 26A, 2269-2282, 1992.

Panyacosit, L., A review of particulate matter and health: Focus on developing countries, IIASA Interim Report, IR-00-005, IIASA, Laxenburg, Austria, 2000.

Paulson, S. E., Pandis, S. N., Baltensberger, U., Seinfeld J. H., Flagan, R. C., Palen, E. J., Allen, D. T., Schaffner, C., Giger, W., Portmann, A., Characterisation of photochemical aerosols from biogenic hydrocarbons, J. Aerosol Sci., 21, 245-248, 1990.

Pio, C. A., Castro, L. M., Cerqueira, M. A., Santos, I. M., Belchior, F., Salgueiro, M. L., Source assessment of particulate pollutants measured at the Southwest European Coast, Atmos. Environ., Vol. 30, No. 19, 3309-3320, 1996.

Pun, K. B., Seigneur, C., Grosjean, D., Saxena, P., Gas-phase formation of water-soluble organic compounds in the atmosphere: a retrosynthetic analysis, J. Atmos. Chem. 35, 199-223, 2000.

Pratsinis, S., Novakov, T., E. C. Ellis, Friedlander, S. K., The carbon containing component of the Los Angeles aerosol, J. Air Poll. Control Assoc., 34, 643-650, 1984.

Rogge, W. F., Mazurek, M. A., Hildemann, L. M., Cast, G. R., Simoneit, B. R. T., Quantification of urban organic aerosol at a molecular level: Identification, abundance, and seasonal variation, Atmos. Environ., 27A, 1309-1330, 1993.

Saxena, P, and Hildemann L. M., Water-soluble organics in atmospheric particles: A critical review of the literature and application of thermodynamics to identify candidate compounds, Journal of atmospheric chemistry, 24, 57-109, 1996.

Schauer J. J., Rogge W. F., Hildemann L. M., Mazurek, M. A., Cass, G. R. Source apportionment of airborne particulate matter using organic compounds as tracers, Atmos. Environ., Vol. 30, No. 22, 3837-3855, 1996.

Seinfeld, J. H. and Pandis, S. N*., Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, John Wiley & Sons, New York, 1998.

Simoneit, B. R. T, Characterization of organic constituents in aerosols in relation to their origin and transport: A Review, Intern. J. Environ. Anal. Chem., 23, 207-237, 1986.

Simpson, D. *et al.*, Inventorying emissions from Nature in Europe, J. Geophys. Res., 104, 8113-8152, 1999.

Strader, R., Lurmann, F., Pandis, S. N., Evaluation of secondary organic aerosol formation in winter, Atmos. Environ. 33, 4849-4863, 1999.

Tobias, H. J., Docherty, K. S., Beving, D. E., and Ziemann, P. J. Effect of relative humidity on the chemical composition of secondary organic aerosol formed from reactions of 1-tetradecene and O_3, Environ. Sci. Technol. 34, 2116-2125, 2000.

Turpin, B. J., Huntzicker, J. J., Larson S. M., Cass G. R., Los Angeles summer midday particulate carbon: Primary and Secondary Aerosol, Environ. Sci. Technol. 25, 1788-1793, 1991.

Turpin, B. J. Huntzicker, J. J., Secondary formation of organic aerosol in the Los Angeles Basin: A descriptive analysis of organic and elemental carbon concentrations, Atmos. Environ. 25A, 207-215, 1991.

Turpin, B. J., Huntzicker, J. J., Identification of secondary organic aerosol episodes and quantification of primary and secondary organic aerosol concentrations during SCAQS, Atmos. Environ. 29, 3527-3544, 1995.

Turpin, B. J., Saxena, P., Andrews, E., Measuring and simulating particulate organics in the atmosphere: problems and prospects, Atmos. Environ. 34, 2983-3013, 2000.

Zappoli, S., Andracchio, A., Fuzzi, S., Facchini M. C. Gelencser, A., Kiss, G., Krivacsy, Z., Molnar, A., Meszaros, E., Hansson, H.-C., Rosman, K., Zebuehr, Y, Inorganic, organic and macromolecular components of fine aerosol in different areas of Europe in relation to their water solubility, Atmos. Environ. 33, 2733-2743, 1999.

Appendix

This appendix contains the details of the FAC estimation of the different source sectors. Unless otherwise indicated the species profiles are taken from the EMEP/CORINAIR emission inventory guidebook (EEA, 1996). The FAC of each source sector is calculated as the average of the FAC values of the single compounds weighted by their fractional contribution f to the emitted non-methane VOC.

A1 Source profile of water-based architectural surface coating

VOC compound	% of emissions (f*100)	FAC (%)	f*FAC
Acetone	3.2	0.00	0.00
n-Butyl acetate	2.5	0.00	0.00
n-Butyl alcohol	1.6	0.00	0.00
Cyclohexane	20.7	0.00	0.00
Dimethyl formamide	0.5	0.00	0.00
2-Ethoxyethyl acetate	1.3	0.00	0.00
Ethyl alcohol	0.6	0.00	0.00
Ethylbenzene	4.3	0.60	0.03
Ethylene glycol	0.6	0.00	0.00
n-Hexane	20.7	0.00	0.00
Isobutyl acetate	1.5	0.00	0.00
Isobutyl alcohol	0.6	0.00	0.00
Isobutyl isobutyrate	6.1	0.00	0.00
Isomers of xylene	2.6	3.77	0.10
Isopropyl alcohol	16.4	0.00	0.00
Methyl alcohol	3.9	0.00	0.00
Methyl ethyl ketone	5.6	0.00	0.00
Methyl isobutyl ketone	0.6	0.00	0.00
Methyl n-butyl ketone	0.7	0.00	0.00
Propylene glycol	0.8	0.00	0.00
Toluene	5.2	1.50	0.08
		FAC	**0.20**

A2 Source profile of solvent use in paint

Compound class ^	Specific compound ^^	% of emissions (f*100)	FAC (%)	f*FAC min	f*FAC max
Alkanes + Alkenes:		**29.70**			
	white spirit *	27.76	2.90	0.80	
	SBP solvents	1.94	0.05	0.00	
Aromatics:		**24.10**			
	toluene	6.38	1.50	0.10	
	xylenes	7.91	3.77	0.30	
	styrene	1.28	0.00	0.00	
	160-180 boiling fraction **	5.87	2.60	0.15	
	180-220 boiling fraction ***	2.68	6.30	0.17	
Alcohols:		**11.50**			
	ethanol	0.76	0.00	0.00	
	2-propanol	1.01	0.00	0.00	
	2methyl-1-propanol	2.27	0.00	0.00	
	1-butanol	4.55	0.00	0.00	
	2-butanol	1.90	0.00	0.00	
	4-methyl-4hydroxy-2pentanone	1.01	0.00	0.00	
Ketones:		**9.90**			
	propanone	1.92	0.00	0.00	
	2-butanone	2.34	0.00	0.00	
	4-methyl-pentanone	4.36	0.00	0.00	
	cyclohexanone	0.64	0.00	0.00	
	other	0.64	0.00	0.00	
Esters		**17.70**			
	n-butyl acetate	9.37	0.00	0.00	
	ethyl acetate	5.90	0.00	0.00	
	other	2.43	?	0.00	0.07
Cellosolves		**6.90**			
	2-butoxyethanol	2.61	0	0.00	
	1-methoxy-2-propanol	1.49	0	0.00	
	others	2.80	?	0.00	0.08
				min	max
			FAC	**1.52**	**1.68**

^ general composition: Western Europe 1990
^^ specific components of main classes: UK 1995

* for composition of white spirit see wood preservation
** e.g. trimethylbenzene, ethyltoluene (boiling temperature=161)
***e.g diethylbenzene (boiling temperature=184) , tetramethylbenzene(boiling temperature=198)

A3 Source profile of evaporative emission of cars

1) Estimate by Veldt

Compound class	Specific compound ^^	% of emissions (f*100)	FAC (%)	f*FAC
Alkanes				
	propane	1	0	0.000
	n-butane	20	0	0.000
	i-butane	10	0	0.000
	n-pentane	15	0	0.000
	i-pentane	25	0	0.000
	hexane	15	0	0.000
	heptane	2	0	0.000
Alkenes				0.000
	1-butene	1	0	0.000
	2-butene	2	0	0.000
	1-pentene	2	0	0.000
	2-pentene	3	0	0.000
	1,3 hexene	1.5	0	0.000
Aromatics				0.000
	benzene	1	0	0.000
	toluene	1	1.5	0.015
	m,p xylene	0.5	2.5	0.013
			FAC	**0.028**

2) Estimate by Derwent

Compound class	Specific compound	% of emissions (f*100)	FAC (%)	f*FAC
Alkanes				
	n-butane	19.99	0	0.000
	i-butane	10.48	0	0.000
	n-pentane	7.22	0	0.000
	i-pentane	10.15	0	0.000
	n-hexane	2.02	0	0.000
	2-methylpentane	3.02	0	0.000
	3-methylpentane	2.01	0	0.000
	2,2 dimethylpentane	0.6	0	0.000
	2,3 dimethylpentane	0.74	0	0.000
	n-heptane	0.7	0	0.000
	2-methylhexane	0.92	0	0.000
	3-methylhexane	0.93	0	0.000
	n-octane	0.27	0.7	0.002
	methylheptanes	0.67	0.5	0.003
Alkenes				
	1-butene	1.49	0	0.000
	2-butene	2.55	0	0.000
	2-pentene	2.35	0	0.000
	1-pentene	0.49	0	0.000

Compound class	Specific compound	% of emissions (f*100)	FAC (%)	f*FAC
	2-methyl-1-butene	0.67	0	0.000
	3-methyl-1-butene	0.67	0	0.000
	2-methyl-2-butene	1.31	0	0.000
Aromatics				
	benzene	2.34	0	0.000
	toluene	5.66	1.5	0.085
	o-xylene	1.59	6.3	0.100
	m-xylene	1.88	2.5	0.047
	p-xylene	1.88	2.5	0.047
	ethylbenzene	1.32	0.6	0.008
	n-propylbenzene	0.41	0.7	0.003
	i-propylbenzene	0.12	0.7	0.001
	1,2,3-trimethylbenzene	0.31	1.4	0.004
	1,2,4-trimethylbenzene	1.6	1.7	0.027
	1,3,5-trimethylbenzene	0.39	2.6	0.010
	o-ethyltoluene	0.37	2.6	0.010
	m-ethyltoluene	0.64	2.6	0.017
	p-ethyltoluene	0.64	2.6	0.017
			FAC	**0.381**

A4 Source profile of emissions from gas stations

Compound class	Individual compound	% of emissions (f*100)	FAC [%]	f*FAC min	f*FAC max
Alkanes					
	C4+	89	0-1	0	0.98
Alkenes					
	C3+	7	0-2	0	0.14
Aromatics					
	Benzene	1.1	0	0	0
	Toluene	2	1.5	0.03	0.03
	Xylene	0.8	4.4	0.04	0.04
				min	max
			FAC	**0.07**	**1.1**

A5 Species profile for all consumer products

species	% of emissions (f*100)	FAC [%]	f*FAC
aliphatic hydrocarbons	22	0-1*	0-0.22
alcohols	50	0	
amines	1	0	
ketones	1	0	
esters	1	0	
ethers	19	0	
aromatic hydrocarbons	3	3.1**	0.093
chlorinated hydrocarbons	1	0	
organic acids	1	0	
		FAC	**0.1-0.3**

* FAC=0 if predominantly butane or propane, FAC=1 if predominantly C9-C10
** calculated as average over major aromatic hydrocarbons

A6 Species profile of dry cleaning emissions

PER, CFC FAC = 0

A7 Species profile of emissions of food production

species	% of emissions (f*100)	FAC [%]	f*FAC
ethanol	20	0	0
other alcohols	10	0	0
aldehydes	20	0	0
sulfur compounds*	10	0	0
carboxylic acids	10	?	?
alkanes	10	0-2	0-0.2
aromatics**	10	3.1	0.3
ethers	10	0-0.65	0-0.065
		FAC	**0.3-?**

* known to produce sulfates, but not to produce SOC
** average over major aromatic species

A8 Species profiles from the production of organic chemicals

chemical produced	species	% of emissions	FAC [%]	% aerosol
Ethylene 0.3	methane	12.5	0	0
FAC=0.01	ethane	37.8	0	0
	propane	23.9	0	0
	n-butane	15	0	0
	n-pentane	8.1	0	0
	benzene	2.1	0	0
	toluene	0.5	1.5	0.0075
	methanol	0.3	0	0
Propylene 0.2	methane	58	0	0
FAC=0-?	ethylene	11.5	0	0
	propylene	6.8	0	0
	benzene	1	0	0
	other HC	22	?	?
1,2 Dichloret+Vinylchloride 0.01	methane	1.2	0.0	0.00
FAC=0.003	ethylene	10.9	0	0
	1,2 dichloroethane	42.3	0.0	0.00
	toluene	0.2	1.5	0.003
	ClHcs	43.8	0	0.00
	other HCs	1.6	0	0.00
Polyvinylchloride 0.1	vinylchloride	100	0	0
FAC=0				
Polypropylene 0.1	isobutanol	3.8	0	0
FAC=0	propylene	96.2	0	0
Styrene 0.01	methane	10.8	0	0
FAC=0.4-?	ethylene	1.6	0	0
	styrene	18.5	0	0
	benzene	2.8	0	0
	toluene	25.8	1.5	0.387
	other HC	40.5	?	?
Polystyrene 0.01	ethylbenzene	10.0	0.6	0.06
FAC=0.06	styrene	90.0	0	0
Styrene-Butadiene 0.02	styrene	95	0	0
FAC=0	butadiene	5	0	0
SB 0.02				
FAC=0				
Ethylbenzene 0.01	methane	2.6	0	0
FAC=0.36	ethylene	8.1	0	0
	benzene	44.2	0	0
	toluene	10.2	1.5	0.15
	ethylbenzene	35.1	0.6	0.21
Phthalic Anhydride 0.1	FAC=?			
Acrylonitrile 0.01	FAC=?			
			FAC	**0.01**

A9 Species profile for solvent use in printing industry

compound class	speciation	% of emissions (f*100)	FAC%	f*FAC
Alkanes	e.g. decane	50.00	2.00	1.00
Alcohols	e.g. isopropanol	35.00	0.00	0.00
Aromatics	e.g. toluene	15.00	3.28	0.49
Ketones	e.g. methyl ethyl ketone	10.00	0.00	0.00
			FAC	**1.49**

A10 Species profile for emissions from petroleum products processing

Estimate 1				Estimate 2			
species	% of emissions (f*100)	FAC [%]	f*FAC	species	% of emissions (f*100)	FAC [%]	f*FAC
Methane	0	0	0	Methane	13	0	0
Ethane	5	0	0	Ethane	6.5	0	0
Propane	20	0	0	Propane	19.7	0	0
Butane	20	0	0	Butane	11	0	0
Pentanes	20	0	0	Pentanes	21	0	0
hexanes	10	0	0	hexanes	8	0	0
heptanes	5	0	0	heptanes	1.87	0	0
> heptanes	5	1.5	0.075	octanes	2.13	0.7	0.01491
Ethene	1	0	0	nonanes	1.01	1.5	0.01515
Propene	1	0	0	decanes	1.01	2	0.0202
Butene	0.5	0	0	cyclohexane	0.08	0	0
Benzene	2	0	0	cycloheptane	2.27	1	0.0227
Toluene	3	1.5	0.045	cyclooctane	0.66	2	0.0132
o-Xylene	0.7	6.3	0.0441	cyclononane	0.11	3	0.0033
m,p-Xylene	1.3	2.5	0.0325	propene	1.75	0	0
Ethylbenzene	0.5	0.6	0.003	butene	0.15	0	0
		FAC	**0.1996**	toluene	0.44	1.5	0.0066
				xylenes	0.19	4.4	0.00836
				formaldehyde	8.88	0	0
						FAC	**0.10442**

A11 Species profile for air traffic

based on an average LTO cycle for commercial aircraft and general aviation

1)Commercial aircraft

Specific compound	% of emissions (f*100)	FAC (%)	f*FAC
ethylene	17.4	0	0
formaldehyde	15	0	0
C6H18O3Si	9.1	0	0
Methane	9.6	0	0
Propane	5.2	0	0
Acetaldehyde	4.6	0	0
C8H24O4Si4	2.9	0.7	0.0203
Ethyne	4.2	0	0
Acetone	2.4	0	0
Glyoxal	2.5	0	0
Acrolein	2.3	?	?
Butene	2	0	0
Benzene	1.9	0	0
1,3 butadiene	1.8	0	0
Methylglyoxal	2	0	0
n-dodecene	1.1	15	0.165
Butyraldehyde	1.2	0	0
		FAC	**0.19**

2) General aviation

Specific compound	% of emissions (f*100)	FAC (%)	f*FAC
ethylene	15.5	0	0
formaldehyde	14.1	0	0
C6H18O3Si	11.8	0	0
Methane	11	0	0
Propane	4.6	0	0
Acetaldehyde	4.3	0	0
C8H24O4Si4	4.2	0.7	0.0294
Ethyne	3.7	0	0
Acetone	2.9	0	0
Glyoxal	2.5	0	0
Acrolein	2.1	?	
Butene	1.8	0	0
Benzene	1.8	0	0
1,3 butadiene	1.6	0	0
Methylglyoxal	1.8	0	0
n-dodecene	1.2	15	0.18
Butyraldehyde	1.2	0	0
		FAC	**0.21**

A12 Species profile for emissions from a 2-stroke Otto engine

Source: Hewitt, 1999

Compound class	Specific compound	% of emissions (f*100)	FAC (%)	f*FAC min	F*FAC max
Alkanes					
	Methane	7	0.00	0.00	
	Ethane	1	0.00	0.00	
	Butane	2	0.00	0.00	
	Isobutane	0.3	0.00	0.00	
	Pentane	3	0.00	0.00	
	Isopentane	4	0.00	0.00	
Alkenes					
	Ethene	5	0.00	0.00	
	Propene	2	0.00	0.00	
	cis-2-Butene	0.4	0.00	0.00	
	trans-2-Butene	0.2	0.00	0.00	
Alkynes					
	Ethyne	4	0.00	0.00	
Aromatics					
	Benzene	5	0.00	0.00	
	Toluene	12	1.50	0.18	
	Xylene**	11	3.77	0.41	
	Ethylbenzene	2.8	0.60	0.02	
	C9 Aromatics	8.3	0.7-2.6	0.06	0.22
Aldehydes					
	Formaldehyde	0.6	0.00	0.00	
	Acetaldehyde	0.2	0.00	0.00	
	Acrolein	0	0.00	0.00	
	Benzaldehyde	0.2	0.00	0.00	
	Tolualdehyde	0.2	0.00	0.00	
Ketones					
	Acetone	0.1	0.00	0.00	
Other VOCs*		30.6	1-3	0.31	0.92
				min	max
			FAC	**0.98**	**2.11**

* Hewitt (1999) suggests higher alkanes

** assume equal mixture of o,m,p xylene

A13 Source profile of solvent use in wood preservation

mixture of white spirit other petroleum distillates and creosote in undefined ratios
Assumption: equal ratios of white spirit, creosote and other petroleum distillates

WHITE SPIRIT:

compound class	species	% of emissions (f*100)	FAC [%]	f*FAC
Paraffins:	C9	15.0	1.5	0.23
	C10	20.0	2.0	0.40
	C11	13.0	2.5	0.33
	C12	4.0	3.0	0.12
Cycloalkanes	C9	7.0	0.5	0.04
	C10	16.0	4.0	0.64
	C11	9.0	5.0	0.45
	C12	2.0	6.0	0.12
Aromatics	C8	2.0	3.0	0.06
	C9	9.0	1.9	0.17
	C10	8.0	4.5	0.36
			FAC	**2.90**

SBP SOLVENTS:*

compound class	species	% of emissions (f*100)	FAC [%]	% aerosol
paraffins	pentane	10.7	0.0	
	hexane	18.0	0.0	
	heptane	6.3	0.0	
	2-methyl-butane	0.3	0.0	
	2,2 dimethyl-butane	0.7	0.0	
	2,3 dimethyl-butane	3.0	0.0	
	2 methyl-pentane	19.3	0.0	
	3-methyl-pentane	9.7	0.0	
	dimethylpentanes	3.0	0.0	
	methylhexanes	10.7	0.0	
cycloparaffins	cyclopentane	2.3	0.0	
	methylcyclopentane	4.3	0.0	
	cyclohexane	6.3	0.0	
	dimethylcyclopentane	3.0	1.0	0.03
	methylcyclohexane	2.3	1.0	0.02
			FAC	**0.05**

CREOSOTE OIL

high fraction of aromatics and PAH(54-85%), assume 75% PAH (naphthalene)

species	% of emissions	FAC(%)	f*FAC
naphthalene	75.0	4.0	3.00
others	25.0	0-3	0-0.75
		FAC	**3-3.75**

FAC total = 2.1

A14 Source profile of diesel engine exhaust

Estimate by C. Veldt

Compound class	Specific compound	% of emissions (f*100)	FAC (%)	f*FAC
Alkanes				
	Ethane	1.00	0.00	0.00
	Propene	1.00	0.00	0.00
	n-Butane	2.00	0.00	0.00
	n-Pentane	2.00	0.00	0.00
	C13	30.00	3.50	1.05
Alkene				
	Ethene	12.00	0.00	0.00
	Propene	3.00	0.00	0.00
	1,3 Butadiene	2.00	0.00	0.00
	2-Pentene	1.00	0.00	0.00
	C13	2.00	15.00	0.30
Alkynes				
	Propylene	2.00	0.00	0.00
Aromatics				
	Benzene	2.00	0.00	0.00
	Toluene	1.50	1.50	0.02
	o-Xylene	0.50	6.30	0.03
	m,p Xylene	1.50	2.50	0.04
	Ethylbenzene	0.50	2.50	0.01
	C13*	20.00	6.30	1.26
Other				
	Formaldehyde	6.00	0.00	0.00
	Acetaldehyde	2.00	0.00	0.00
	Other aldehydes	1.50	0.00	0.00
	Acrolein	1.50	?	
	2-Butanal	1.00	0.00	0.00
	Benzaldehyde	0.50	0.00	0.00
	Acetone	1.50	0.00	0.00
			FAC	**2.71**

2) Estimate by Derwent

Compound class	Specific compound	% of emissions (f*100)	FAC (%)	f*FAC
Alkanes				
	methane	3.70	0.00	0.00
	ethane	0.50	0.00	0.00
	n-butane	2.50	0.00	0.00
	i-butane	2.50	0.00	0.00
	n-pentane	2.50	0.00	0.00
	i-pentane	2.50	0.00	0.00
	n-hexane	2.50	0.00	0.00
	2-methylpentane	2.50	0.00	0.00
	3-methylpentane	2.50	0.00	0.00
	2,2 dimethylbutane	2.50	0.00	0.00

Compound class	Specific compound	% of emissions (f*100)	FAC (%)	f*FAC
	2,3 dimethylbutane	2.50	0.00	0.00
	n-heptane	2.50	0.00	0.00
	2-methylhexane	2.50	0.00	0.00
	3-methylhexane	2.50	0.00	0.00
	n-octane	2.50	0.70	0.02
	methylheptanes	2.50	0.50	0.01
	n-nonane	2.50	1.50	0.04
	methyloctanes*	2.50	0.50	0.01
	n-decane	2.50	2.00	0.05
	methylnonanes	2.50	2.00	0.05
	n-undecane	2.50	2.50	0.06
	n-duodecane	2.50	3.00	0.08
Alkenes				
	ethene	11.00	0.00	0.00
	propene	3.40	0.00	0.00
	1-butene	0.50	0.00	0.00
	1-pentene	0.70	0.00	0.00
	3-methyl-1-butene	0.50	0.00	0.00
	2-methyl-2-butene	0.50	0.00	0.00
Alkynes				
	acetylene	3.20	0.00	0.00
Aromatics				
	benzene	2.60	0.00	0.00
	toluene	0.80	1.50	0.01
	o-xylene	0.80	6.30	0.05
	m-xylene	0.80	2.50	0.02
	p-xylene	0.80	2.50	0.02
	ethylbenzene	0.80	0.60	0.00
	n-propylbenzene	0.50	0.70	0.00
	i-propylbenzene	0.50	0.70	0.00
	1,2,3 trimethylbenzene	0.50	1.40	0.01
	1,2,4 trimethylbenzene	0.50	1.70	0.01
	1,3,5 trimethylbenzene	0.50	1.60	0.01
	o-ethyltoluene	0.50	2.60	0.01
	m-ethyltoluene	0.50	2.60	0.01
	p-ethyltoluene	0.50	2.60	0.01
others				
	formaldehyde	5.90	0.00	0.00
	acetaldehyde	1.00	0.00	0.00
	proprionaldehyde	1.00	0.00	0.00
	butyraldehyde	1.00	0.00	0.00
	i-butyraldehyde	1.00	0.00	0.00
	acetone	2.00	0.00	0.00
			FAC	**0.49**

Estimate by Hewitt (1999)

Compound class	Specific compound	% of emissions (f*100)	FAC (%)	f*FAC
Alkanes				
	>C10*	53.28	2.75	1.47
Alkenes				
	Ethene	12.30	0.00	0.00
	Propene	4.30	0.00	0.00
	i-Butene	0.82	0.00	0.00
	cis-2-Butene	0.82	0.00	0.00
	trans-2-Butene	0.72	0.00	0.00
	1,3 Butadiene	1.13	0.00	0.00
Alkynes				
	Ethyne	2.87	0.00	0.00
Aromatics				
	Benzene	1.95	0.00	0.00
	Toluene	0.82	1.50	0.01
	Xylene**	0.82	3.77	0.03
	Ethylbenzene	0.31	0.60	0.00
Others				
	Formaldehyde	8.30	0.00	0.00
	Acetaldehyde	4.30	0.00	0.00
	Acrolein	2.15	0.00	0.00
	Benzaldehyde	1.84	0.00	0.00
	Tolualdehyde***	1.02	1.50	0.02
	Acetone	1.54	0.00	0.00
			FAC	**1.53**

*assume equal mixture of C10,C11,C12, C13
** assume equal mixture of o,m,p-Xylene
*** assume: equals toluene

A15 Source profile of 4-stroke gasoline engine exhaust

Estimate by Veldt

Compound class	Specific compound	% of emissions (f*100)	FAC (%)	f*FAC
Alkanes	Ethane	1.40	0.00	0.00
	Propane	0.10	0.00	0.00
	n-Butane	3.10	0.00	0.00
	i-Butane	1.20	0.00	0.00
	n-Pentane	2.10	0.00	0.00
	i-Pentane	4.30	0.00	0.00
	Hexane	7.10	0.00	0.00
	Heptane	4.60	0.00	0.00
	Octane	7.90	0.70	0.06
	Nonane	2.30	1.50	0.03
	>C10	0.90	3.50	0.03
Alkene	Ethene	7.20	0.00	0.00
	Propene	3.80	0.00	0.00
	Propadiene	0.20	0.00	0.00
	1-Butene	1.70	0.00	0.00
	1,3 Butadiene	0.80	0.00	0.00
	2-Butene	0.60	0.00	0.00
	1-Pentene	0.70	0.00	0.00
	2-Pentene	1.10	0.00	0.00
	1-Hexene	0.60	0.00	0.00
	1,3 Hexene	0.60	0.00	0.00
	>C7	0.30	10.00	0.03
Alkynes	Acetylene	4.50	0.00	0.00
	Methylacetylene	0.30	0.00	0.00
Aromatics	Benzene	4.50	0.00	0.00
	Toluene	12.00	1.50	0.18
	o-Xylene	2.50	6.30	0.16
	m,p Xylene	5.60	2.50	0.14
	Ethylbenzene	2.10	2.50	0.05
	Styrene	0.70	0.00	0.00
	1,2,3 Trimethylbenzene	0.50	2.60	0.01
	1,2,4 Trimethylbenzene	2.60	1.70	0.04
	1,3,5 Trimethylbenzene	0.80	2.60	0.02
	C9	3.80	6.30	0.24
	>C10	4.50	6.30	0.28
Other	Formaldehyde	1.70	0.00	0.00
	Acetaldehyde	0.30	0.00	0.00
	Other aldehydes	0.30	0.00	0.00
	Acrolein	0.20	?	
	Benzaldehyde	0.40	0.00	0.00
	Acetone	0.10	0.00	0.00
			FAC	**1.28**

Estimate by Derwent

Compound class	Specific compound	% of emissions (f*100)	FAC (%)	f*FAC
Alkanes	methane	8.00	0.00	0.00
	ethane	1.30	0.00	0.00
	propane	1.20	0.00	0.00
	n-butane	1.95	0.00	0.00
	i-butane	0.93	0.00	0.00
	n-pentane	2.78	0.00	0.00
	i-pentane	4.45	0.00	0.00
	n-hexane	1.76	0.00	0.00
	2-methylpentane	2.14	0.00	0.00
	3-methylpentane	1.49	0.00	0.00
	2,2 dimethylbutane	0.28	0.00	0.00
	2,3 dimethylbutane	0.54	0.00	0.00
	n-heptane	0.74	0.00	0.00
	2-methylhexane	1.39	0.00	0.00
	3-methylhexane	1.11	0.00	0.00
	n-octane	0.37	0.70	0.00
	methylheptanes	0.84	0.50	0.00
	n-nonane	0.18	1.50	0.00
	methyloctanes*	1.58	0.50	0.01
	n-decane	0.37	2.00	0.01
	methylnonanes	0.84	2.00	0.02
	n-undecane	2.75	2.50	0.07
	n-duodecane	2.75	3.00	0.08
Alkenes	ethene	7.90	0.00	0.00
	propene	3.60	0.00	0.00
	1-butene	1.40	0.00	0.00
	2-butene	0.50	0.00	0.00
	2-pentene	0.90	0.00	0.00
	1-pentene	0.70	0.00	0.00
	2-methyl-1-butene	0.70	0.00	0.00
	3-methyl-1-butene	0.70	0.00	0.00
	2-methyl-2butene	1.40	0.00	0.00
Alkynes	butylene	0.50	0.00	0.00
	acetylene	6.30	0.00	0.00
Aromatics	benzene	3.20	0.00	0.00
	toluene	7.20	1.50	0.11
	o-xylene	1.58	6.30	0.10
	m-xylene	2.06	2.50	0.05
	p-xylene	2.06	2.50	0.05
	ethylbenzene	1.20	0.60	0.01
	n-propylbenzene	0.16	0.70	0.00
	i-propylbenzene	0.13	0.70	0.00
	1,2,3 trimethylbenzene	0.40	1.40	0.01
	1,2,4 trimethylbenzene	1.60	1.70	0.03
	1,3,5 trimethylbenzene	0.50	1.60	0.01
	o-ethyltoluene	0.38	2.60	0.01
	m-ethyltoluene	0.63	2.60	0.02
	p-ethyltoluene	0.63	2.60	0.02

others	formaldehyde	1.60	0.00	0.00
	acetaldehyde	0.35	0.00	0.00
	proprionaldehyde	0.57	0.00	0.00
	butyraldehyde	0.07	0.00	0.00
	valeraldehyde	0.03	0.00	0.00
	benzaldehyde	0.39	0.00	0.00
	acetone	0.14	0.00	0.00
			FAC	**0.60**

Estimate by Hewitt(1999)

Compound class	Specific compound	% of emissions (f*100)	FAC (%)	f*FAC
Alkanes	ethane	0.83	0.00	0.00
	propane	0.31	0.00	0.00
	butane	3.13	0.00	0.00
	isobutane	2.08	0.00	0.00
	pentane	2.08	0.00	0.00
	isopentane	5.21	0.00	0.00
	>C10*	21.15	2.75	0.58
Alkenes	Ethene	7.29	0.00	0.00
	Propene	4.17	0.00	0.00
	1-Butene	0.42	0.00	0.00
	i-Butene	2.60	0.00	0.00
	cis-2-Butene	0.21	0.00	0.00
	trans-2-Butene	0.83	0.00	0.00
	1,3 Butadiene	0.63	0.00	0.00
	Pentene	1.15	0.00	0.00
Alkynes	Ethyne	5.73	0.00	0.00
Aromatics	Benzene	5.21	0.00	0.00
	Toluene	11.98	1.50	0.18
	Xylene**	10.42	3.77	0.39
	Ethylbenzene	2.60	0.60	0.02
	C9 aromatics****	7.81	1.86	0.15
Others	Formaldehyde	1.56	0.00	0.00
	Acetaldehyde	0.73	0.00	0.00
	Acrolein	0.42	0.00	0.00
	Benzaldehyde	0.31	0.00	0.00
	Tolualdehyde***	0.52	1.50	0.01
	Acetone	0.63	0.00	0.00
			FAC	**1.32**

*assume equal mixture of C10,C11,C12, C13
** assume equal mixture of o,m,p-Xylene
*** equal toluene
****average over all C9 aromatics listed in Grosjean et al. 1989

A16 Source profile of 4-stroke gasoline engine exhaust (engine with catalyst)

Estimate by Veldt

Compound class	Specific compound	% of emissions (f*100)	FAC (%)	f*FAC
Alkanes	Ethane	1.8	0.00	0.00
	Propane	1	0.00	0.00
	n-Butane	5.5	0.00	0.00
	i-Butane	1.5	0.00	0.00
	n-Pentane	3.2	0.00	0.00
	i-Pentane	7	0.00	0.00
	Hexane	6	0.00	0.00
	Heptane	5	0.00	0.00
	Octane	7	0.70	0.05
	Nonane	2	1.50	0.03
	>C10	3	3.50	0.11
Alkenes	Ethene	7	0.00	0.00
	Propene	4.5	0.00	0.00
	Propadiene	0	0.00	0.00
	1-Butene	1.5	0.00	0.00
	1,3 Butadiene	0.5	0.00	0.00
	2-Butene	0.5	0.00	0.00
	1-Pentene	0.5	0.00	0.00
	2-Pentene	1	0.00	0.00
	1-Hexene	0.4	0.00	0.00
	1,3 Hexene	0.4	0.00	0.00
	>C7	0.2	10.00	0.02
Alkynes	Acetylene	4.5	0.00	0.00
	Methylacetylene	2.5	0.00	0.00
Aromatics	Benzene	3.5	0.00	0.00
	Toluene	7	1.50	0.11
	o-Xylene	2	6.30	0.13
	m,p Xylene	4	2.50	0.10
	Ethylbenzene	1.5	2.50	0.04
	Styrene	0.5	0.00	0.00
	1,2,3 Trimethylbenzene	1	2.60	0.03
	1,2,4 Trimethylbenzene	4	1.70	0.07
	1,3,5 Trimethylbenzene	2	2.60	0.05
	C9	3	6.30	0.19
	>C10	6	6.30	0.38
Other	Formaldehyde	1.1	0.00	0.00
	Acetaldehyde	0.5	0.00	0.00
	Other Aldehydes	0.2	0.00	0.00
	Acrolein	0.2	?	
	Benzaldehyde	0.3	0.00	0.00
	Acetone	1	0.00	0.00
			FAC	**1.29**

Estimate by Hewitt

Compound class	Specific compound	% of emissions (f*100)	FAC (%)	% of emissions as SOA
Alkanes				
	ethane	2.33	0.00	0.00
	propane	0.58	0.00	0.00
	butane	6.98	0.00	0.00
	isobutane	3.49	0.00	0.00
	pentane	2.91	0.00	0.00
	isopentane	8.72	0.00	0.00
	>C10*	17.56	2.75	0.48
Alkenes				
	Ethene	5.23	0.00	0.00
	Propene	2.91	0.00	0.00
	1-Butene	0.12	0.00	0.00
	i-Butene	1.74	0.00	0.00
	cis-2-Butene	0.23	0.00	0.00
	trans-2-Butene	0.70	0.00	0.00
	1,3 Butadiene	0.47	0.00	0.00
	Pentene	0.81	0.00	0.00
Alkynes				
	Ethyne	3.49	0.00	0.00
Aromatics				
	Benzene	6.98	0.00	0.00
	Toluene	11.63	1.50	0.17
	Xylene**	10.47	3.77	0.39
	Ethylbenzene	2.33	0.60	0.01
	C9 aromatics****	6.98	1.86	0.13
Others				
	Formaldehyde	1.16	0.00	0.00
	Acetaldehyde	0.70	0.00	0.00
	Acrolein	0.23	0.00	0.00
	Benzaldehyde	0.23	0.00	0.00
	Tolualdehyde***	0.47	1.50	0.01
	Acetone	0.58	0.00	0.00
			FAC	**1.20**

*assume equal mixture of C10, C11, C12, C13
** assume equal mixture of o,m,p-Xylene
*** equal toluene
****average over all C9 aromatics listed in Grosjean et al. 1989

A17 Source profile for emissions from wood combustion

Hewitt (1999)

Compound class	Specific compound	% of emissions (f*100)	FAC (%)	f*FAC min	f*FAC max
Alkanes	ethane	10.00	0.00	0.00	
	propane	1.51	0.00	0.00	
	butane	0.51	0.00	0.00	
	>C4	3.00	0-1	0.00	0.03
Alkenes	ethene	30.00	0.00	0.00	
	propene	6.00	0.00	0.00	
	butene	0.51	0.00	0.00	
	pentene	2.00	0.00	0.00	
Alkynes	ethyne	10.00	0.00	0.00	
	propyne	0.51	0.00	0.00	
Aromatics	Benzene	15.00	0.00	0.00	
	Toluene	5.00	1.50	0.08	
	o-Xylene	0.51	6.30	0.03	
	m-Xylene	0.72	2.50	0.02	
	p-Xylene	0.73	2.50	0.02	
	Ethylbenzene	0.51	0.60	0.00	
Aldehydes	Formaldehyde	2.00	0.00	0.00	
	Acetaldehyde	1.00	0.00	0.00	
	Acrolein	2.00	0.00	0.00	
	Aldehydes C4	3.00	0.00	0.00	
Other VOCs	ketones	1.51	0.00	0.00	
	other	4.00	0-1	0.00	0.03
			FAC	**0.15**	**0.20**

A18 Source profile of emissions from coal combustion

Hewitt (1999)

Compound class	Specific compound	% of emissions (f*100)	FAC (%)	f*FAC (min)	f*FAC (max)
Alkanes	ethane	15.00	0.00	0.00	
	propane	10.00	0.00	0.00	
	>C4	5.00	0-1	0.00	0.05
Alkenes	ethene	30.00	0.00	0.00	
	propene	5.00	0.00	0.00	
	>C3	5.00	0-1	0.00	0.05
Alkynes	ethyne	5.00	0.00	0.00	
Aromatics	Benzene	5.00	0.00	0.00	
	Toluene	1.00	1.50	0.02	
	o-Xylene	0.36	6.30	0.02	
	m-Xylene	0.32	2.50	0.01	
	p-Xylene	0.32	2.50	0.01	
Other VOCs	other	16.00	0-1	0.00	0.16
			FAC	**0.05**	**0.31**

A19 Source profile of emissions from gas combustion

Hewitt (1999)

Compound class	Specific compound	% of emissions (f*100)	FAC (%)	f*FAC
Alkanes				
	Ethane	48	0	0
	Propane	16	0	0
	Butane	16	0	0
Alkenes				
	Ethene	7.2	0	0
	Propene	2.4	0	0
	Butene	2.4	0	0
Aldehydes				
	Formaldehyde	7.2	0	0
	Acetaldehyde	0.48	0	0
	Propionaldehyde	0.16	0	0
	other aldehydes	0.16	0	0
			FAC	**0**