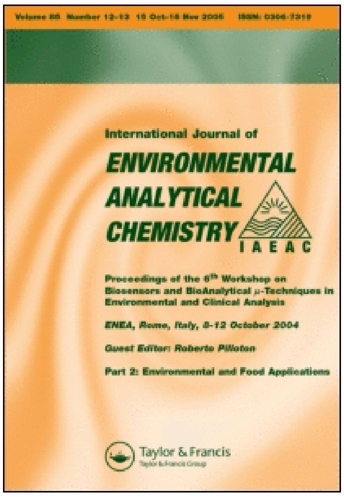

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MEASUREMENT OF VOLATILE ORGANIC COMPOUND (VOC) CONCENTRATION PROFILES IN THE ATMOSPHERE OF A REMOTE FOREST REGION

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The immission situation for volatile organic compounds (VOCs) in an alpine forest area at Achenkirch, Tyrol, was assessed by carrying out sampling campaigns with parallel sampling at the three sampling sites at 1030, 1220 and 1686 m a.s.l., respectively. More than 80 different non-methane hydrocarbon compounds were identified and quantitatively determined. It was thus possible to record temporal and altitude profiles of the individual VOCs which allows first to make a source discrimination between the different compounds and second an assessment of their relevance for the photochemical ozone formation in the troposphere. These data is used to assess the potential threat of the alpine forest vegetation due to direct (toxic) or indirect effects (as ozone precursors) by VOCs. Results are presented for the sampling campaign of the 14.06.1996 that illustrate the extraction of information from and the interpretation of the observed VOC mixing ratio patterns. The VOC mixing ratios are comparatively low on a daily average at the two higher located sampling stations (14 and 16 ppbC, respectively), but significantly higher in the valley (40 ppbC daily average and 71 ppbC peak concentration). Ethene is the most abundant single compound. Although no emission source could be identified explicitly, it is very probable that these high peak concentrations are due to long range transport from stronger polluted areas in South Germany as can be deduced from the specific VOC pattern.

Keywords: Volatile organic compounds; non-methane hydrocarbons; ozone precursors; air quality; temporal variability

INTRODUCTION

Despite the trace concentration (µg or ng/m^3) levels at which volatile organic compounds (VOCs) occur, they play a significant role in the chemistry of the

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troposphere [1]. They are of both anthropogenic and biogenic origin and fuel the formation of tropospheric (ground level) ozone [1, 2]. Nitrous oxides, NO_x, act as catalysts in this reaction cycle, making it most efficient in areas where either traffic or major point sources contribute to the emission of both VOCs and NO_x [3,4]. In the presence of VOCs and NO_x, the formation of tropospheric ozone correlates with the intensity of sunshine, giving thus rise to the so-called summer smog events [1–4].

The measurement of VOC mixing ratios (= immission concentrations) is important since it allows through interpretation of the concentration patterns and the correlation between the individual VOCs to discriminate between different sources of VOCs and to distinguish whether they have been brought by long-range transport to the sampling area or they have been emitted locally. Only the knowledge of the sources and the concentration patterns allows to develop suitable strategies for the reduction of the VOCs and the associated adverse effects.

In the present case, the assessment of the VOC immission situation was undertaken in a forest area near Achenkirch, Tyrol as part of a multi-disciplinary project initiated in 1990 by the Austrian Forest Research Center [5]. The overall aim of the project was to identify biological, chemical, physical, geological and meteorological factors that contribute to the menace or damage of forests in high alpine areas. This is of particular importance for Austria where due to its geographical situation a large fraction of its forested area is at elevated levels. The project is expected to bring some insight into the reasons for the so-called "new forest decline" which in contrast to the previously investigated examples of forest damage cannot be attributed to a single reason, e.g. acid rain, or high concentrations of SO_2, NO_x or ozone. In the case of this new forest decline, the mixing ratios of single noxious substances are too low to provide a satisfactory explanation for the observed forest damage [6]. Thus, synergistic effects of the various chemical substances, but also of chemical, biological and other potential stress factors have to be considered in order to better understand the complex reasons for the observed situation of particularly the Austrian alpine forests.

The data presented here origins from a sampling campaign at the Schulterberg mountain near Achenkirch, Tyrol carried out on the 14.06.1996. Samples were taken at three sampling points at different altitude and in ca. 1.5 hour-intervals during daytime, starting before sunrise and finishing after sunset. This procedure allowed to follow the variation of individual VOC's immission concentrations with time and altitude. The recorded data, although remaining only exemplary, may be interpreted in terms of emission sources and potential correlation between individual substances.

EXPERIMENTAL

Sampling

VOC concentration profiles were recorded along the altitude profile of the Schulterberg mountain near Achenkirch/Tyrol as a function of both the time and the altitude by collecting 12 samples in intervals of approximately 1.5 h, starting before sunrise and taking the last sample after sunset simultaneously at the three sampling points at different altitudes (valley station: 1030 m a.s.l., middle station: 1220 m a.s.l., peak station: 1686 m a.s.l.).

The sampling campaign was carried out in June 1996 and was the last of in total 3 measuring campaigns in the years 1995 and 1996, each campaign of two days duration. Only results obtained from the sampling date of 14.06.1996 are presented in this report. The sampling area has been described and characterized earlier [7].

Meteorological data (temperature, solar radiation, humidity and wind velocity) were measured continuously near the sampling location through the whole year. Data of O_3 and NO_x mixing ratios were measured continuously at the Christlum profile, situated near the Schulterberg profile with measuring stations in comparable heights [7] and allowing to use these data for our interpretation. All meteorological data and data for O_3 and NO_x were provided by the Austrian Forest Research Center, Vienna.

Sampling and analysis was previously optimized to allow the separation and detection of more than 80 different VOCs as described elsewhere [8, 9]. Basically, sampling was carried out by sampling a defined air volume onto adsorption tubes with self-designed sampling units. Two different adsorption tubes were used in series, the first one filled with Tenax TA for the collection of the less volatile compounds ($\geq C_6$) and the second one filled with a combination of Molsieve 5A and Cabosieve S-III for the more volatile compounds (C_2-C_6). The adsorbent tubes (18 cm length, 6 mm o.d., 4 mm i.d. glass tubes) were filled in house with the solid adsorbents. A Nafion dryer was used between the two adsorption tubes to remove the water vapor. Air samples of 4.5 L volume were taken at a flow rate of 150 $mL.min^{-1}$ during a 30 min interval. One of the sampling units allowed to cool the second adsorption tube to –30 °C by means of Peltier-elements which enabled the quantitative sampling and analysis even of the C_2-hydrocarbons.

While at this sampling station (which was used at the peak only) the trapping efficiency of the C_2-hydrocarbons may be assumed to be complete due to the sub-ambient sampling step, it is less than 100% at the two other stations (in the middle and in the valley) since sampling is carried out at ambient temperature. This however is only important for the direct comparison of the C_2-hydrocarbon mixing ratios between the three different sampling points. The trapping efficiencies of all other VOCs may be assumed equal under the applied sampling conditions and thus are comparable. Also, the diurnal trends obtained at every sampling station are consistent and allow the unconstrained interpretation of the C_2-hydrocarbon profiles.

Sampling was carried out without an ozone scrubber. Although it is known that particularly biogenic compounds (e.g. terpenes and isoprene) are sensitive to oxidants like ozone [10, 11 12], we renounced to use an ozone scrubber during sampling to avoid losses of the more polar substances like alcohols and aldehydes in which we were also interested in this study. Therefore, underestimation of some terpenes due to reactions with oxidants during sampling cannot be excluded but was critically checked by evaluating the oxygenated compounds suspected to be their reaction products..

The loaded adsorption tubes were stored in stainless steel containers pressurized with N_2 (purity $\geq$99.999%) to avoid contamination prior to analysis.

Analysis

Since the samples were automatically split into two fractions by sampling onto the two differently filled adsorption tubes, the use of optimized conditions for separation and analysis of each fraction was possible. Generally, the samples were analyzed by thermal desorption (with two-step cryofocusing), followed by gas chromatographic separation of the analytes and parallel detection by a flame ionization and a mass spectrometric detector. This analysis strategy, that is described in detail elsewhere [8, 9], allowed to obtain qualitative information for identification of unknown compounds and reliable quantitative data.

All concentrations are given in the ppbC unit which enables the calculation of mass balances since it takes account of the number of carbon atoms per molecule. It is defined as: $1 \text{ ppbC} = 10^{-9} \text{ mol/mol} * 12 \text{ g/mol} = 1.2 * 10^{-8} \text{ g C/mol}$.

Using the molar volume at standard conditions ($p = 101325$ Pa, $T = 273$ °K), $V = 0.0224 \text{ m}^3$, one obtains: $1 \text{ ppbC} = 1.2 * 10^{-8} \text{g C/mol} / (0.0224 \text{ m}^3\text{/mol}) = 5.36 * 10^{-7} \text{ g C/m}^3 = 0.536 \text{ µg C/m}^3$.

RESULTS AND DISCUSSION

Since the full data collected during the sampling campaign are reported elsewhere [13], only selected data of the second measuring day (14.06.1996) are presented here in the following. Although this data cannot provide a comprehensive evaluation of the VOC immission situation in the Achenkirch valley, it may still serve as a snapshot and reflect a typical situation, thus allowing to draw valid conclusions. These are based on the variation of the concentration profiles with the altitude and during the day and the correlation of the different compounds in samples from the same sampling point.

Total VOC immission concentrations

In the samples collected in this area, compounds from various substance classes could be identified: Ethene and ethyne were in all samples the by far most abundant compounds (thus stressing again the importance of quantitative sampling of the C_2-compounds). Apart from these, higher alkenes (mainly C_3-C_5, up to C_9), several alkanes (C_2-C_{11}) and iso-alkanes (C_4-C_8), aromatic compounds (BTX, C_3-benzenes), isoprene and terpenes, halogenated compounds (C_1-C_2) and oxygenated compounds like alcohols (C_2-C_8), aldehydes and ketones (C_4-C_8), esters of acetic acid (C_2-C_4) and furanes were detected. The total VOC immission concentrations (mean value calculated as daily average, standard deviation, highest and lowest value) as well as the contribution of the individual substance classes to the total VOC immission concentrations at the three sampling sites of the Schulterberg profile are given in Table I.

TABLE I Total VOC immission concentrations (in ppbC) and contribution of the individual substance classes to the total VOC immission concentration (in %) measured at the Schulterberg profile on the 14.06.1996 (calculated as daily average on a ppbC basis)

in ppbC	*Valley Station (1030 m a.s.l.)*	*Middle Station (1220 m a.s.l.)*	*Peak Station (1686 m a.s.l.)*
Mean	40	16	14
Minimum	17	10	9
Maximum	71	25	27
Standard deviation	20	4	6
	in %		
Ethene	59	19	44
Higher alkenes and ethyne	10	11	6
Alkanes	8	24	24
Isoprene and terpenes	6	9	9
Aromatic compounds	7	16	9
Oxygenated compounds	9	19	6
Halogenated compounds	1	2	2

The VOC mixing ratios ranged between 9 and 71 ppbC, with the highest concentrations being observed at the lowest sampling station. Comparing the mean values of the VOC immission concentration of the three different stations, a significant decrease between the valley station and the middle station was observed, whereas no further decrease between the upper two stations could be found. This indicates that the air masses in the valley station have a stronger input by nearby sources while the two sampling stations in the middle and at the peak of the Schulterberg mountain are more detached from the local immission situation and there seems to be a stronger exchange of the air masses between these two. This results in more similar and generally lower VOC concentration levels than in the valley. The high standard deviation at the valley station indicates a strong variation of the total VOC mixing ratios during the day which can actually be seen in Figure 1, showing a very pronounced concentration maximum for ethene during the day which first is responsible for the high daily average concentration in the valley and second again supports the interpretation that there is a strong local emission source that influences the immission profiles in a very distinct way.

The diurnal variation of the total VOC immission concentration, presented as the sum of contributions of the individual substance classes, is shown in Figure 1. While a pronounced concentration maximum (mainly caused by very high ethene mixing ratios in the early afternoon) can be observed at the valley station, the total VOC mixing ratios at the other two stations remained nearly constant.

Ethene is of particular interest, since it is a phytotoxic substance which is emitted anthropogenically by combustion processes. It may however also be of biogenic origin since it is emitted by plants during stress or maturation, acting as a phytohormone and controlling the plant growth [14]. An elevated ethene mixing ratio above 10 ppb can lead to plant damage and, therefore, the threshold value for ethene was fixed to an 8h-average of 10 ppb [15]. The Austrian Academy of Sciences has even suggested a stricter value, allowing to exceed the threshold value of 10 ppb ethene only for 30 min during an 8 hour-interval [16]. This threshold value is generally exceeded in urban areas where ethene concentrations of more than 100 ppb can be observed. In rural areas, however, ethene concentrations are normally found to be lower than 10 ppb, but under similar conditions ethene concentrations up to 30 ppb were reported by König who investigated VOC immission concentrations in an other valley in the Tyrolean alps, the Zillertal [17].

During former sampling campaigns in the same area at the Schulterberg profile in summer 1995, Haunold and Rosenberg [8, 18] reported also a pronounced ethene maximum in the early afternoon, but the concentrations observed then were 6 times lower (around 10 ppb). However, there is no doubt on the consist-

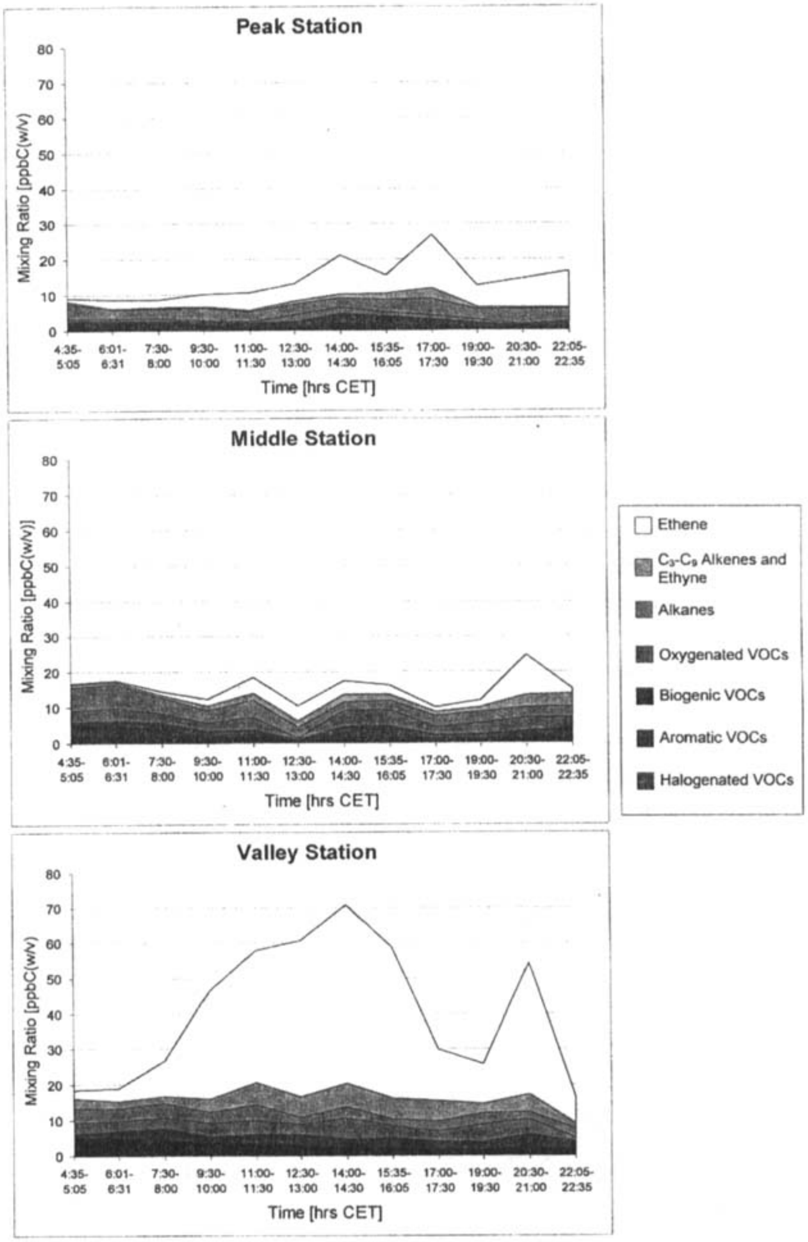

FIGURE 1 Cumulative diurnal concentration profiles of the individual substance classes at the Schulterberg profile on the 14.06.1996 (CET = Central European Time)

ency of these data, since even higher ethene concentrations (up to 120 ppbC) were measured on the first sampling day of this campaign (11.06.1998) at the valley station. Since the valley station was only equipped with an ambient temperature sampling unit, the values are definitely not over- but they may rather be underestimated.

It is important to mention that VOC immission concentrations strongly depend on season, micro-and macroclimatic conditions and the meteorological situation. Therefore it is not the single result but rather the exemplary nature of the data that shall be presented here to demonstrate which general conclusions can be drawn of these data.

Diurnal concentration profiles of individual substance classes

Halogenated compounds

Halogenated compounds are well-known examples for ubiquitous atmospheric pollutants. Consequently, they also occur in the Achenkirch valley, where dichloromethane, tetrachloromethane, trichlorofluoromethane, 1,1,1-trichloroethane, 1,1,2-trichloro-1,2,2-trifluoroethane and tetrachloroethene were actually found in nearly all samples. Due to the relatively low response of the FID for halogenated compounds, only four of them, namely dichloromethane, tetrachloromethane, 1,1,1-trichloroethane and tetrachloroethene, could be determined quantitatively. Their diurnal concentration profiles showed no significant variation neither with the time of the day nor with the height of the sampling point, resulting in nearly constant immission concentrations of these compounds at all stations of the Schulterberg profile. In Table II the total mixing ratios of the halogenated compounds as well as the contributions of the individual substances to the total immission concentration are listed. Only very low immission concentrations of the halogenated compounds between 0.08 and 0.44 ppbC were observed. The most abundant halogenated VOC found at the Schulterberg profile was 1,1,1-trichloroethane with a relative contribution to the sum of the halogenated compounds ranging from 52 to 71%.

The halogenated compounds investigated in this study are emitted exclusively by anthropogenic sources such as vaporization losses during their application as solvent, propellant or cooling agent. Most halogenated compounds have atmospheric lifetimes ranging from some days up to several years which favors their long-range transport from industrial regions to rural and remote areas [19], allowing their fairly uniform distribution throughout the northern hemisphere. The 48h-backward trajectories [20] (showing the way that the air masses had taken during the previous two days before they arrived at the Achenkirch valley) indicated clearly that a very stable meteorological situation with constant winds from the north east was dominating during the observation period, transporting air masses from the North Sea across the Federal Republic of Germany to the sampling area in the Achenkirch valley.

TABLE II Total immission concentration of the halogenated compounds (in ppbC) and contribution of the individual substances to the total immission concentration (in %) measured at the Schulterberg profile on the 14.06.1996 (calculated as daily average on a ppbC basis)

in ppbC	*Valley Station (1030 m a.s.l.)*	*Middle Station (1220 m a.s.l.)*	*Peak Station (1686 m a.s.l.)*
Mean	0.32	0.30	0.25
Minimum	0.24	0.08	0.21
Maximum	0.45	0.44	0.36
Standard deviation	0.05	0.09	0.05
in %			
Dichloromethane	13	1	8
1,1,1-Trichloroethane	52	64	71
Tetrachloromethane	35	21	15
Tetrachloroethene	0	4	6

Biogenic compounds

Isoprene and the terpenes are the best studied biogenic compounds [10, 11, 21]. Beside isoprene and α– and β-pinene, a number of other terpenes like camphene, sabinene, δ-3-carene, *l*-limonene and 1,8-cineol were found in nearly all samples. Since *l*-limonene and 1,8-cineol could not be separated under the applied gas chromatographic conditions, the sum of these two compounds was evaluated.

The terpenes and isoprene are locally emitted by the vegetation surrounding the sampling points and therefore show strong concentration variations during the day and with the altitude (Figure 2). The total immission concentrations of the biogenic compounds ranged from 0.5 to 3.6 ppbC (Table III). Isoprene and α–pinene were the most abundant biogenic compounds, contributing 11–24% and 26–33%, respectively, to the total immission concentration of the biogenic compounds. β-pinene, which showed a diurnal concentration profile very similar to α-pinene (see also results of the cross correlation), contributed 7–17% to the total immission concentration of the biogenic compounds.

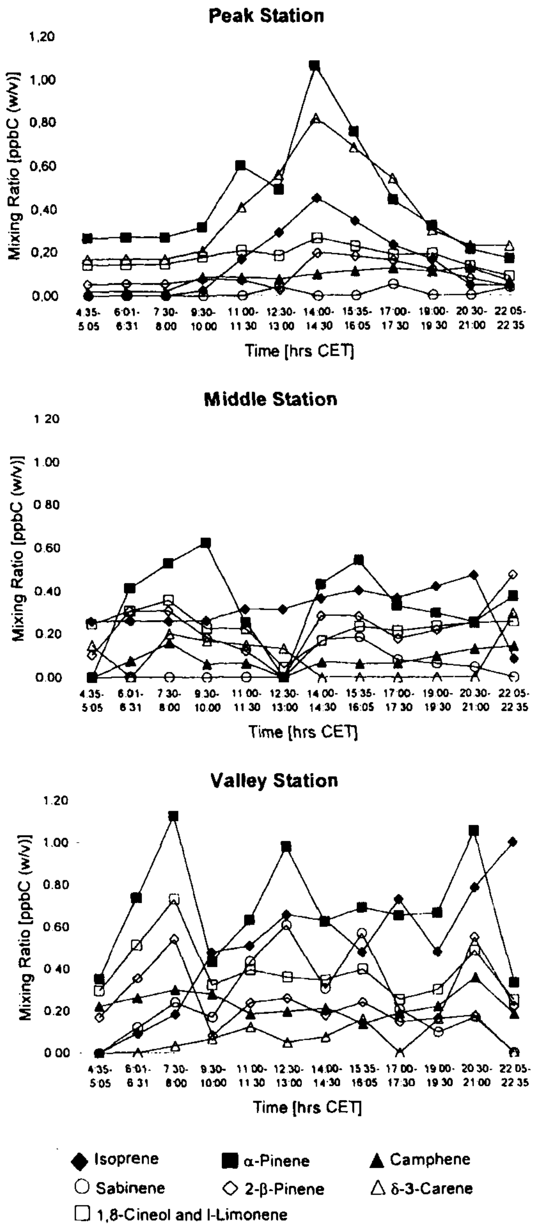

FIGURE 2 Diurnal concentration profiles of the biogenic compounds at the Schulterberg profile on the 14.06.1996

TABLE III Total immission concentration of the biogenic compounds (in ppbC) and contribution of the individual substances to the total immission concentration (in %) measured at the Schulterberg profile on the 14.06.1996 (calculated as daily average on ppbC basis)

in ppbC	*Valley Station (1030 m a.s.l.)*	*Middle Station (1220 m a.s.l.)*	*Peak Station (1686 m a.s.l.)*
Mean	2,4	1,4	1,3
Minimum	1,0	0,5	0,7
Maximum	3,6	1,8	2,9
Standard deviation	0,7	0,4	0,7
in %			
Isoprene	21	24	11
α-Pinene	29	26	33
β-Pinene	11	17	7
Camphene	10	6	6
δ-3-Carene	3	7	26
Sabinene	10	3	1
1,8-Cineol and 1-Limonene	16	17	16

At the middle and the valley station, which both are situated in the middle of a forest, similar, rather non-uniform concentrations profiles were found, but the variations at the middle station were less pronounced as compared to those at the valley station. At the peak station, where alpine pasture and meadows are predominant, the biogenic compounds showed completely different diurnal profiles compared to the other two stations, exhibiting a concentration maximum in the early afternoon.

The explanation for the observed behavior can only be given by considering the meteorological situation in the Achenkirch valley: This area is known to often exhibit inversion situations before sunrise and after sunset where the temperature is higher in an intermediate altitude and lower below and above this air layer. This results in two relatively well separated air basins in which also different atmospheric chemical process can take place. During daytime, the temperature generally increases which leads to an increased exchange of the air masses and thus to a significant rise of the mixing ratios of biogenic compounds in the early afternoon, producing the high concentrations at the peak.

It was mentioned earlier that sampling was carried out without an ozone scrubber. This bears the risk of decomposition for the more reactive unsaturated compounds, particularly isoprene and the terpenes [10, 11]. During the decomposition of isoprene and the terpenes by the reaction with ozone or the highly reactive NO_2- and OH-radicals, mainly low molecular weight aldehydes and ketones are formed. With the sampling technique used in this campaign, formaldehyde could not be measured, but several other compounds, attributed as decomposition products in the literature, like methacroleine (2-methylpropenal), methylvinylketone (3-butene-2-one) [22, 23] and 6-methyl-5-heptene-2-one [12], were identified in most of the samples. Some of the oxygenated compounds, particularly 6-methyl-5-heptene-2-one were also proposed to be emitted biogenically by flowers, fruits and trees [17, 24]. Whether methacroleine, methylvinylketone and 6-methyl-5-heptene-2-one have already been present in the original air samples or whether they are artifacts due to the applied sampling strategy cannot be decided with certainty. This has to be kept in mind when interpreting the data of the biogenic compounds, since an underestimation of the concentrations of isoprene and the terpenes due to decomposition by oxidants cannot be excluded. But even in the case that a part of the biogenic compounds is lost due to oxidative decomposition, the trend of the diurnal profile of the biogenic compounds can still be evaluated under the assumption that the fraction lost is more or less constant. Particularly at the highest sampling station, the ozone concentrations does not vary strongly and there is no observable (inverse) correlation between ozone and terpene concentrations (compare Figure 2 and 3).

Other substance classes

The diurnal concentration profiles of the different VOC substance classes investigated at the Schulterberg showed great differences, which can be interpreted by attributing them to different sources of origin and chemical reactivity in the atmosphere. The diurnal concentration profiles of the alkenes (including ethyne, but without ethene), the aromatic and the oxygenated VOCs observed at the valley station can be seen in Figure 4.

Total immission concentrations of the *alkenes* (including ethyne, excluding ethene) at the valley station ranged from 1.4 to 7.1 ppbC. Besides ethene, propene and the butene isomers were the most abundant alkenes found at the valley station of the Schulterberg profile with contributions to the total alkene mixing ratios of 44% and 30%, respectively (calculated as daily average). Ethene, the main component of the VOCs found at the Schulterberg profile, was eveluated separately since its mixing ratio exceeded that of all other substances by at least one order of magnitude. At the other two sampling sites lower concentrations (0.3–3.6 ppbC) and no characteristic diurnal profile for the alkenes (and ethyne) were found. Comparing the diurnal profiles of ethene, propene and the butenes, a

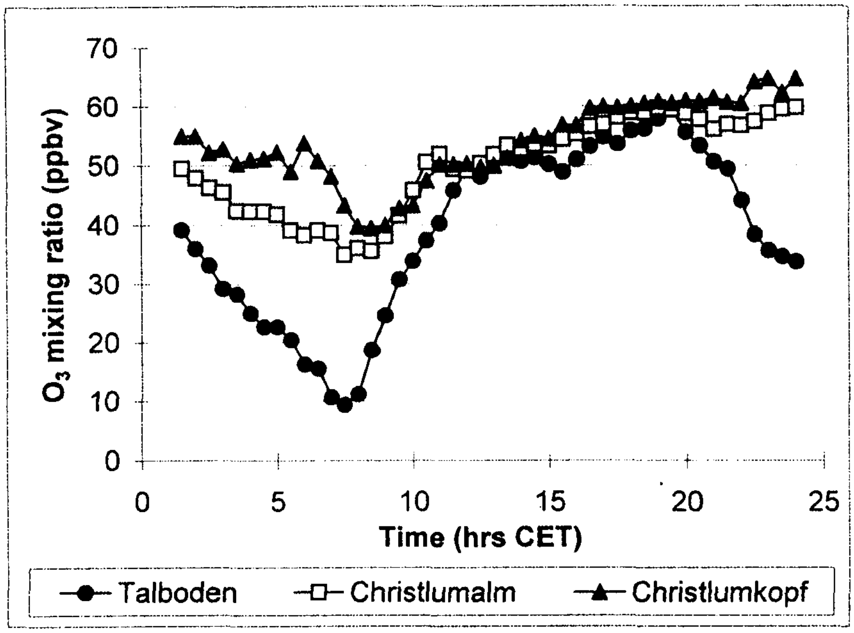

FIGURE 3 Ozone profiles at the near-by Christlum profile (Valley Station: 930 m a.s.l., "Christlumalm": 1280 m a.s.l., "Christlumkopf": 1758 m a.s.l.) from the 14.06.96

high similarity between these compounds with a pronounced concentration maximum in the early afternoon was observed (compare Figure 1 and Figure 4).

The fact that ethene and the C_3- and C_4-alkenes show a high degree of correlation is remarkable, considering that the atmospheric lifetime is significantly higher for ethene (36 hrs) than for the higher alkenes (4–10 hrs) [25]. A high correlation between different VOCs with relatively high and largely different reactivity can thus be interpreted in the way that these substances are emitted by the same source and that this source is near the sampling sites, so that both the high correlation and the pronounced concentration profile can be observed. The actual sources of these high alkene concentrations however are not unraveled yet. Main sources of alkenes are combustion processes like traffic exhaust or domestic heating, but in the particular situation of this sampling campaign in the Achenkirch valley, these emittents are unlikely to sufficiently explain the observed diurnal profile of the alkenes. Pollution of the Achenkirch valley by traffic exhaust was negligible during the period of observation and the temperatures ranged between 15 and 20°C, indicating no need for extensive heating. An indisputable explanation for the concentration maximum of the alkenes with particularly high ethene values in the early afternoon cannot be given.

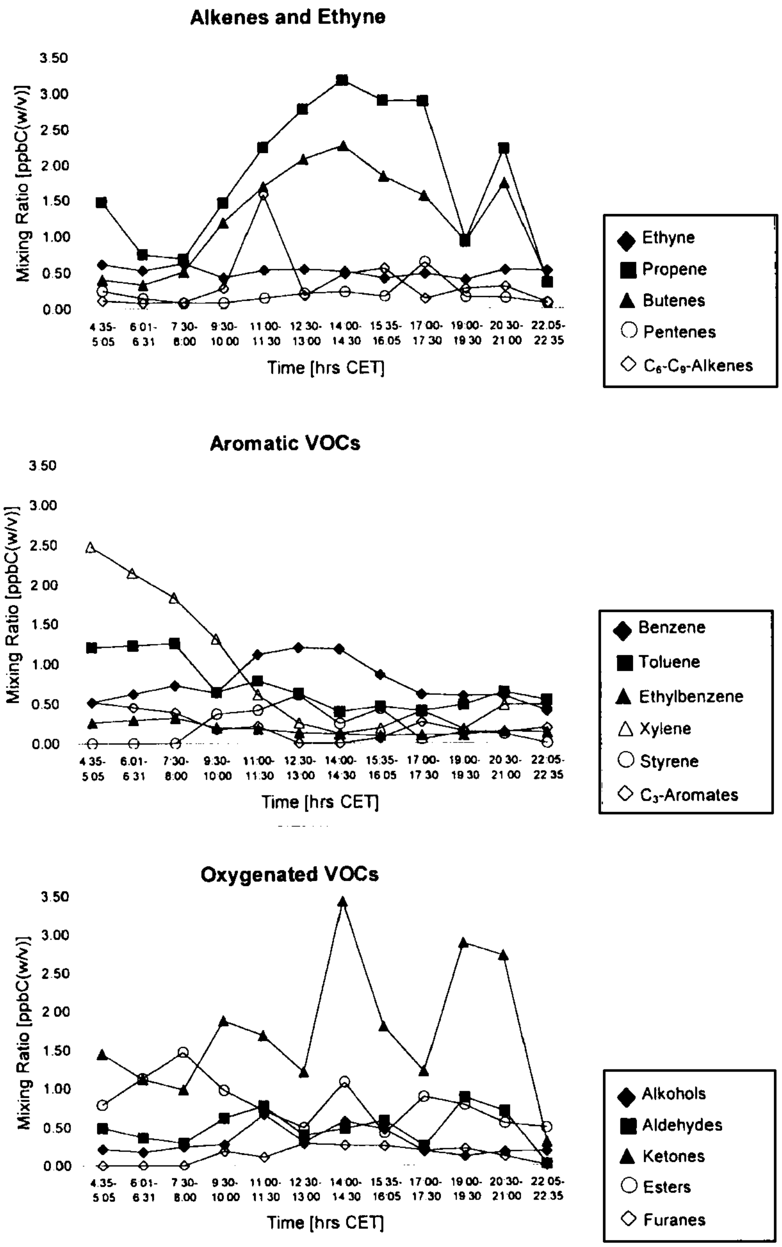

FIGURE 4 Diurnal concentration profiles of the alkenes and ethyne, aromatic and oxygenated VOCs at the valley station of the Schulterberg profile on the 14.06.1996

Ethyne is also emitted by combustion processes like the alkenes, but showed completely different concetration profiles with only little variations during the day at all three stations of the Schulterberg profile. Its concentrations ranged from below the detection limit to 0.8 ppbC. Since ethyne has an atmospheric lifetime of 13.5 days which by far exceeds the atmospheric lifetime of the alkenes it may have reached the sampling area after long range transport from a remote source resulting in nearly constant concentrations at all three stations.

The group of the *aromatic VOCs* shows a different behavior from the previously discussed classes of compounds: They reach their highest concentrations during the early morning hours, in contrast to the alkenes (which peak in the early afternoon). The total immission concentration of the aromatic compounds at the valley station ranged between 1.6 and 5.0 ppbC. Nearly identical diurnal profiles of the aromatic compounds with a similar concentration range (0.6–6.4 ppbC) were found at the middle station. At the peak station, lower concentrations (between 0.2 and 2.0 ppbC) and less pronounced diurnal profiles were observed. The distribution of the BTX-compounds was very similar at the different stations of the Schulterberg profile each contributing approximately a quarter (benzene: 14–26%, toluene: 25–30%, xylenes: 25–40%) to the total immission concentration of the aromatic VOCs (the rest being further C_2- and C_3-alkylbenzenes). While toluene, the xylenes and some C_3-aromates show a similar behavior with a maximum in the early morning (before sunrise), benzene behaves different in that it reaches its maximum concentration in the early afternoon (similar to ethene). This is surprising, since benzene and the alkylbenzenes are believed to be emitted by the same, exclusively anthropogenic sources like traffic exhaust, incomplete combustion processes and vaporization losses (e.g. at petrol stations). However, their atmospheric reactivity differs largely, with the atmospheric lifetime of the alkylbenzenes (2–19 hrs) being ca. 5 to 50 times lower compared to that of benzene (93 hrs) [26].

Alkylbenzenes are easily decomposed by reaction with OH-radicals, while reactions with ozone or photolysis only accounts for ca. 1% of their decomposition processes [26]. The ratio of toluene and benzene concentration is usually a very sensitive indicator for long range transport of VOCs: When the measurement is made close to the emission source (traffic exhausts), a benzene/toluene ratio close to 0.5 is encountered [27]. Due to the higher atmospheric lifetime of benzene than of toluene, this ratio approaches unity when the compounds are transported over a greater distance. This indicates that also in this case, the emission of aromatic compounds from traffic or other local combustion sources in the Achenkirch valley is of secondary importance as compared to long-range transport.

A variety of *oxygenated compounds* like alcohols (C_2-C_8), aldehydes (C_4-C_{12}), ketones (C_3-C_8), esters of acetic acid and some substituted furanes were detected and exhibited distinct diurnal profiles. Similar concentrations of the oxygenated compounds were observed at the valley and the middle station, covering the ranges of 1.0–5.8 and 0.4–4.6 ppbC, respectively. As had also been noticed for other compounds, a significant decrease of the immission concentration was observed between the middle station and the peak station with mixing ratios between 0.3 and 1.8 ppbC found at the peak station. The ketones were the most abundant oxygenated compounds found at the Schulterberg profile, contributing 38–59% to the total immission concentration of the oxygenated VOCs (see Table IV).

TABLE IV Contribution of the individual substances to the total immission concentration (in %) of alkenes, aromatic and oxygenated compounds measured at the valley station of the Schulterberg profile on the 14.06.1996 (calculated as daily average on ppbC basis)

Alkenes and Ethyne	*[%]*	*Aromatic VOCs*	*[%]*	*Oxygenated VOCs*	*[%]*
Propene	45	Benzene	25	Ketones	50
Butenes	30	Toluene	25	Esters	25
Pentenes	5	Xylenes	30	Alcohols	9
C_6-C_9-Alkenes	8	Ethylbenzene	6	Aldehydes	14
Ethyne	12	Styrene	7	Furanes	4
		C_3-Benzenes	7		

It has already been mentioned before that it is not possible to determine to which extent the oxygenated compounds have already been present in the air samples in the form and the concentration in which they are analyzed and what is an analytical artifact, stemming from the reaction with ozone which was still present in the samples due to the fact that no ozone scrubber was used. It may be estimated that the artifacts due to the reaction with ozone are of only minor importance since they neither do correlate with the diurnal profile of ozone nor with that of the terpenes.

Cross Correlation

Environmental sampling campaigns in which a variety of individual substances are determined with temporal and spatial resolution inevitably produce a large amount of data. To reveal the underlying structure and the potential connections between the data and to make these relations visible in an adequate way, the sta-

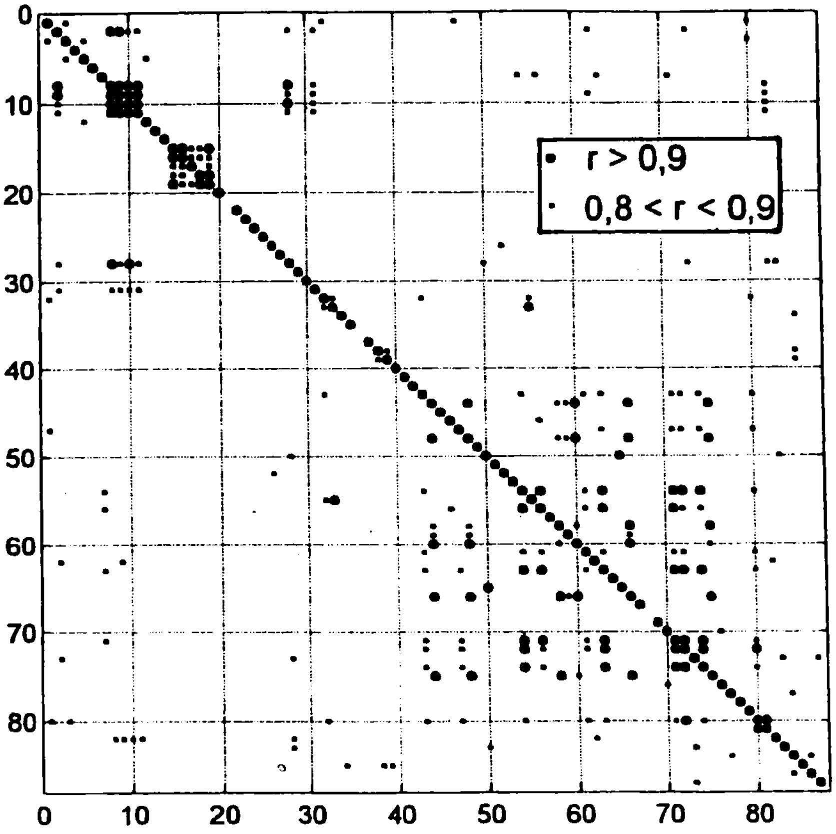

FIGURE 5 Results of the cross correlation between the diurnal profiles of each individual VOC monitored at the valley station of the Schulterberg profile on the 14.06.1996

tistical tool of a cross correlation was chosen. For this aim, the diurnal concentration profiles for each individual compound were considered as a set of data (a data vector) for which the correlation was calculated with every other compound (data vector) for each station and each sampling day. The results of this cross correlation for the valley station of the 14.06.1996 are shown in Figure 5. Each number on the axes of the graph represents an individual compound (see Table V) and the size of the points indicates the value of the respective correlation coefficient. A high correlation coefficient between the diurnal concentration profiles of different compounds may be interpreted in the way that these substances are emitted by the same source (provided that they have similar atmospheric reactivities). The cross correlation can thus be used as a tool for source assignment.

TABLE V List of the quantitatively determined VOCs during the sampling campaign. The number is the same that was assigned to the individual compounds for the cross correlation presented in Figure 5

No.	*substance*	*No.*	*substance*	*No.*	*substance*
1	ethane	30	isoprene	59	propanoic acid
2	ethene	31	unknown	60	heptane
3	propane	32	acetic acid methyl ester	61	methylcyclohexane
4	propene	33	2-methylpropanal	62	3-methyl-1,4-heptadiene
5	*i*-butane	34	2-butenal	63	toluene
6	ethyne	35	dihydrofurane	64	cyclopentanone
7	n-butane	36	2-methylpentane	65	*i*-octane
8	trans-2-butene	37	3-butene-2-one	66	1-octene
9	1-butene	38	butanal	67	butanoic acid
10	*i*-butene	39	2-butanone	68	tetrachloroethene
11	cis-2-butene	40	3-methylpentane	69	acetic acid, butyl ester
12	*i*-pentane	41	1-hexene	70	octane
13	pentane	42	2-methylfurane	71	ethylbenzene
14	3-methylpentane	43	hexane	72	m-, p-xylene
15	trans-2-pentene	44	2-methyl-3-butene-2-ol	73	styrene
16	2-methyl-2-butene	45	acetic acid ethyl ester	74	o-xylene
17	1-pentene	46	2-methyl-1-propanol	75	1-nonene
18	2-methyl-1-butene	47	methylcyclopentane	76	nonane
19	cis-2-pentene	48	acetic acid	77	α-pinene
20	methylcyclopentane	49	1,1,1-trichloroethane	78	propylbenzene
21	cyclohexane	50	benzene	79	camphene
22	hexane	51	tetrachloromethane	80	3-ethyltoluene
23	2-methyl-1-propene	52	cyclohexane	81	4-ethyltoluene
24	butane	53	1-butanol	82	6-methyl-5-heptene-2-one
25	ethanol	54	2-methylhexane	83	sabinene
26	2-methylbutane	55	2-pentanone	84	β-pinene
27	acetone	56	3-methylhexane	85	δ-3-carene
28	furane	57	pentanal	86	1,8-cineol & 1-limonene
29	pentane	58	1-heptene	87	1-octanol

Three main groups showing a high degree of correlation could be identified:

(1) alkenes: ethene (#2), four butene isomers (#8-#11) and 5 pentene isomers (#15-#19)

(2) traffic exhaust: *i*-heptanes (#54 and #56), toluene (#63), the xylenes (#72 and #74) and some C_3-substituted aromates (#80 and #81), no correlation with benzene (#50)

(3) biogenically emitted compounds: α-pinene (#77), β-pinene (#84) and 1,8-Cineol and *l*-limonene (#86).

Some other correlations can be observed in the diagram in Figure 5 which however cannot be explained easily. They may either indicate more complex emission patterns and sources or be due to coincidence.

However, even if the cross correlation calculation gives the possibility of revealing that different compounds are originating from the same source, it does certainly not have the potential of identifying this source. The actual source apportionment still remains a point of further research.

CONCLUSION

The identification and quantitative measurement of more than eighty individual VOCs along an altitude profile in the Tyrolean alps at Achenkirch revealed that there are large differences both in concentration levels and diurnal profiles of the individual compounds. This makes a time- (and potentially also altitude-) resolved measurement necessary in order to obtain additional information on the possible sources and environmental fate of the VOCs. In the particular case of the measurements at the Schulterberg altitude profile, it was observed that the largest contributions to the observed VOC levels were due to long-range transport from sources located in South and Central Germany rather than due to local emissions in the Achenkirch valley.

However, a such measuring campaign represents an enormous workload, both in its preparation and in the actual sampling, analysis and data evaluation which limits its practicability for extended sampling periods that would be able to produce more comprehensive data. It is thus necessary for further alike projects to reduce the number of compounds evaluated (and thus the workload for the evaluation) by choosing those compounds which are the most relevant from the point of view of photochemical reactivity. A suitable indicator is the photochemical ozone creation potential (POCP, [28]) which allows the classification of the VOCs into different groups. One possible classification is that suggested by Solberg, Schmidbauer et al. used during the EMEP Programme [29]. They distinguish five different groups of compounds with decreasing atmospheric reactivity from group 1 to group 5 (see Table VI). Limiting the determination of VOCs in air samples to the few lead (indicator) compounds of groups 1–3 would significantly reduce the effort for analysis and evaluation of the data and thus make even extended measuring campaigns feasible. The reduction of the number of evaluated compounds to those that are relevant and the knowledge of the inherent data structure (as obtained e.g. by cross correlation of the full data set) would still allow to draw valid conclusions from these data.

TABLE VI Classification of some indicator VOCs according to their atmospheric reactivity (Group 1 = highest reactivity, Group 5 = lowest reactivity) according to [29]

Group 1	*Group 2*	*Group 3*	*Group 4*	*Group 5*
propenes	ethene	cyclopentane	butanes	ethane
sum pentenes	heptanes	hexanes	pentanes	propane
isoprene	xylenes	toluene		ethyne
		ethylbenzene		benzene

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