

Volatile Organic Compounds in the Po Basin. Part B: Biogenic VOCs

M. STEINBACHER^{1,2}, J. DOMMEN¹, C. ORDONEZ¹, S. REIMANN²,
F. C. GRÜEBLER³, J. STAEHELIN³, S. ANDREANI-AKSOYOGLU¹
and A.S.H. PREVOT¹

¹Paul Scherrer Institut, Laboratory of Atmospheric Chemistry, CH – 5232 Villigen PSI, Switzerland,
e-mail: andre.prevot@psi.ch

²Swiss Federal Institute for Material Testing and Research (EMPA), Laboratory for Air
Pollution/Environmental Technology, CH – 8600 Dübendorf, Switzerland

³Swiss Federal Institute of Technology, Institute for Atmospheric and Climate Science, CH – 8093
Zurich, Switzerland

(Received 13 May 2004; Accepted 11 March 2005)

Abstract. Measurements of volatile organic compounds (VOCs) were performed in the Po Basin, northern Italy in early summer 1998, summer 2002, and autumn 2003. During the three campaigns, trace gases and meteorological parameters were measured at a semi-rural station, around 35 km north of the city center of Milan. Bimodal diurnal cycles of isoprene with highest concentrations in the morning and evening were found and could be explained by the interaction of emissions, chemical reactions, and vertical mixing. The diurnal cycle could be qualitatively reproduced by a three-dimensional Eulerian model. The nighttime decay of isoprene could be attributed mostly to reactions with NO₃, while the decay of the isoprene oxidation products could not be explained with the considered chemical reactions. Methanol reached very high mixing ratios, up to 150 ppb. High concentrations with considerable variability occurred during nights with high relative humidities and low wind speeds. The origin of these nighttime methanol concentrations is most likely local and biogenic but the specific source could not be identified.

Key words: isoprene, methanol, nighttime chemistry, oxidation products

1. Introduction

Volatile organic compounds (VOCs) play a central role in the photochemistry of the atmospheric boundary layer. VOCs, carbon monoxide (CO), and nitrogen oxides (NO_x) are the precursors of the tropospheric ozone (O₃) production. In the urban and semi-urban planetary boundary layer, O₃ production is usually limited by the availability of VOCs. Biogenic VOCs can play an important role in regional photochemistry and O₃ formation by reducing the OH concentration in clean air masses and increasing the peroxy radical concentration that results in an imbalance in the photostationary steady state (Fehsenfeld *et al.*, 1992; Trainer *et al.*, 1987). Even in some urban atmospheres in the United States, the biogenic emissions can

not be neglected in respect of photochemical smog formation (Chameides *et al.*, 1988). However, biogenic VOC species cannot be reduced through emission controls as other anthropogenic compounds. Therefore, rising attention was given to emissions of biogenic VOCs and their oxidation processes in the last years. Due to its high reactivity, especially isoprene ($\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}=\text{CH}_2$; 2-methyl-1,3-butadiene) and its oxidation products (methyl vinyl ketone and methacrolein) were in the focus of interest (Stroud *et al.*, 2001; Starn *et al.*, 1998; Curren *et al.*, 1998; Hurst *et al.*, 2001; Biesenthal *et al.*, 1997, 1998). Isoprene plays an important role in the production of O_3 not only in rural environments but also in anthropogenically influenced atmospheres (Biesenthal *et al.*, 1997). Measurements in Northern Italy over the whole year 2000 showed that the isoprene photooxidation contributed in summer 30 to 60% to the ambient formaldehyde concentrations and 50 to 75% to the local O_3 formation (Duane *et al.*, 2002). The general effect of biogenic VOCs on the tropospheric chemistry in Spain and for the Greater Paris Area was investigated by Thunis and Cuvelier (2000) and Derognat *et al.* (2003), respectively. While biogenic emissions contributed 10 ppb O_3 for the case study in Spain, the analysis in France showed up to 40 ppb O_3 produced due to biogenic VOC emissions for an extreme day. Airborne VOC measurements in the metropolitan area of Milan showed that isoprene contributes only less than 10% to the total VOC reactivity (Dommen *et al.*, 2002).

Apart from isoprene and methane, methanol (CH_3OH) is one of the species with the highest carbon turnovers in the atmosphere. Due to its high atmospheric concentrations, methanol can act at least locally as a substantial sink for hydroxyl radicals despite the slow reaction rate constant with OH. Via H-atom abstraction and subsequent reaction with O_2 , methanol is moreover a direct precursor of formaldehyde (Seinfeld and Pandis, 1998). The lifetime of methanol due to reaction with OH is 12 days (Atkinson, 2000). Because of the slow reactions of methanol in the gas phase, dry and wet deposition also become important sinks of this species.

The measurements discussed here were performed within the scope of the field experiment Pianura Padana Produzione di Ozono (PIPAPPO; ozone production in the Po Basin) in May and June 1998 (Nefel *et al.*, 2002) and during the FORMAT (Formaldehyde as a Tracer of Oxidation in the Troposphere) project in July/August 2002 and September/October 2003. In this paper, time series and diurnal cycles of isoprene, its main oxidation products, and methanol are presented and discussed. Especially the chemical and dynamical processes during the night were studied since they might significantly influence the starting conditions of the next day's photochemistry.

2. Sampling Site and Instruments

Biogenic VOC measurements were conducted during all three campaigns at Verzago-Alzate, around 35 km north of the city center of Milan. The measurement containers were placed at the border of a corn field. Corn is known to be a

non-isoprene emitter (Lamb *et al.*, 1993) or at most a very weak isoprene source (Plass-Dülmer *et al.*, 1998). A recent publication dealing with air-surface exchanges over corn showed that the majority (around 75%) of the VOC emissions can be related to methanol (Das *et al.*, 2003). No significant isoprene emission was detected in their study. The closest forest considering as an isoprene source was located approximately 200 to 300 m in southerly and westerly direction. As the forest consists of broad-leaved trees and monoterpenes are mostly emitted by conifers (Andreani-Aksoyoglu and Keller, 1995), no considerable monoterpene sources were expected at Verzago. A high-resolution emission inventory for a weekday in May 1998 for the Po Basin revealed that biogenic emissions are only significant during the sunlight hours and stationary anthropogenic sources dominate the VOC emissions whereas the traffic emissions contribute half as much (Dommen *et al.*, 2003).

An Airmotec HC1010 gas chromatograph (Konrad and Volz-Thomas, 2000) with flame ionization detector (GC-FID) (ChromatoSud, Saint Antoine, France) was used in 1998 and 2002 to measure hydrocarbons between C₄ and C₁₀. Laboratory test with added ozone indicated that ozone up to mixing ratios of 180 ppb do not cause sampling artifacts in the used analytical system (Grüebler, 1999). A proton transfer reaction mass spectrometer (PTR-MS) was used at Verzago in 2002 for measuring the most common atmospheric VOCs excluding the alkanes and small alkenes/alkynes (Lindinger *et al.*, 1998; Steinbacher *et al.*, 2004). With this measurement technique, VOCs are measured at their parent mass + 1, resulting in an isoprene signal at *m/z* 69, a signal of methyl vinyl ketone + methacrolein (both with a parent mass of 70 amu) at *m/z* 71, and methanol at *m/z* 33. Another GC-FID system (Varian 3400) was operated in 2003 to measure hydrocarbons from C₂ to C₇. Meteorological parameters like temperature, wind speed and direction, humidity, and radiation as well as inorganic species like ozone, carbon monoxide, and nitrogen oxides were also measured during the three campaigns. A more detailed description of the aims of the projects, the measurement sites, the instrumental equipment, meteorological conditions, and ozone concentrations is given in the companion paper (Steinbacher *et al.*, 2005).

3. Results and Discussion

3.1. ISOPRENE, METHYL VINYL KETONE, AND METHACROLEIN

3.1.1. Interpretation of Diurnal Cycles

Figure 1 shows a typical time series of isoprene (measured with PTR-MS as protonated mass 69), the estimated isoprene emissions according to the Guenther algorithm (Guenther *et al.*, 1993), and the sum of the main isoprene oxidation products methyl vinyl ketone and methacrolein (both measured at protonated mass 71) for a period in 2002. Similar diurnal variations of isoprene were found in the measurements during summer 1998 (Grüebler, 1999). The Guenther algorithm considers the isoprene emissions only as a function of light and temperature due to the light- and

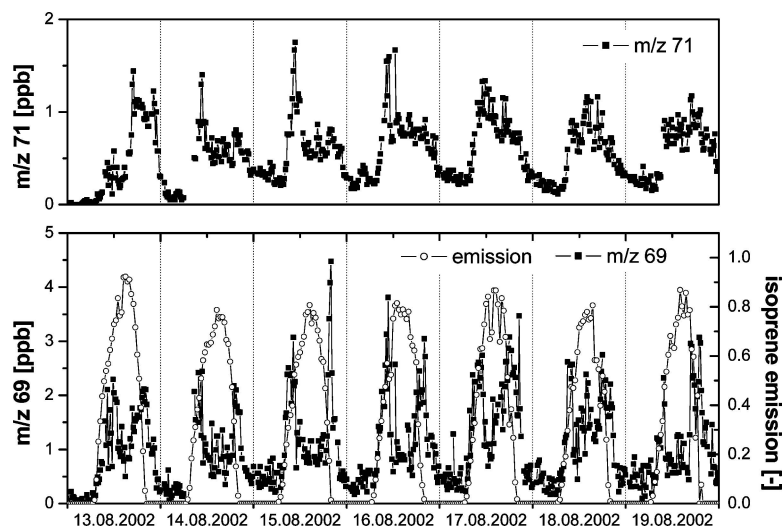


Figure 1. Isoprene mixing ratios (m/z 69), estimated isoprene emissions according to the Guenther algorithm (Guenther *et al.*, 1993), and methyl vinyl ketone + methacrolein mixing ratios (m/z 71) for a 7-day period in 2002.

temperature-dependent activity of the isoprene producing enzyme. Simpson *et al.* (1995) stated that the applicability of the algorithm to European conditions needs to be checked due to the different climatic conditions in the U.S. and in Europe. Steinbrecher *et al.* (1997) compared measured isoprene emissions with the simulated ones and concluded that the algorithm is able to predict the isoprene emissions for the Mediterranean area within an uncertainty of 50%.

Isoprene reacts rapidly with OH, O₃, and NO₃. The first generation products are methyl vinyl ketone (CH₂=CHCOCH₃; MVK) and methacrolein (CH₂=C(CH₃)CHO; MACR) in addition to formaldehyde. MVK is the favored oxidation product when isoprene reacts with OH radicals whereas MACR is produced more when isoprene reacts with O₃. The reported yields are summarized in Table I. Chemical lifetimes of isoprene, MVK, and MACR due to the reaction

Table I. Yields of MVK and MACR and the ratio of the yields from isoprene oxidation due to reactions with OH radicals, O₃, and NO₃ radicals (Kwok *et al.*, 1996 and references therein) and the rate constants k (in cm³ molecule⁻¹ s⁻¹ for isoprene with the reactants at 25 °C (Atkinson and Arey, 2003)

| Reactant | MVK | MACR | Ratio | k |
|-----------------|-------|-------|-------|---------|
| OH | 0.32 | 0.23 | 1.4 | 1.0E-10 |
| O ₃ | 0.16 | 0.39 | 0.4 | 1.3E-17 |
| NO ₃ | 0.035 | 0.035 | 1.0 | 6.8E-13 |

with OH radicals are 1.4 h, 6.8 h, and 4.1 h, respectively, assuming a 12-h daytime average OH radical concentration of 2.0×10^6 molecule cm^{-3} (Atkinson, 2000).

Recent studies have reported an anthropogenic fraction of isoprene attributed to traffic (Reimann *et al.*, 2000; Borbon *et al.*, 2001). From correlation analysis of field measurements at Bresso, a sub-urban site close the city center of Milan, Gruebler (1999) concluded that in summer approximately 50% of isoprene originated from road traffic at this site. The anthropogenic fraction of isoprene can be estimated from a usually good correlation with 1,3-butadiene. 1,3-butadiene measured with the GC-FID system in 2003 was on average below 100 ppt. Reimann *et al.* (2000) reported for measurements on the Swiss Plateau in winter an (anthropogenic) isoprene to 1,3-butadiene ratio of 0.4. A similar analysis in France resulted in an (anthropogenic) isoprene to 1,3-butadiene ratio of 0.3 (Borbon *et al.*, 2001). Therefore, the evening isoprene mixing ratios at Verzago with peaks of up to 3 ppb in 2003 (see Figure 3) are hardly attributable to vehicle emissions.

Figure 1 reveals that the measured isoprene mixing ratios cannot be explained when only considering the expected isoprene emissions. In the morning, the isoprene levels are rising with the start of the emissions but drop after 2 to 3 h and rise again in the late afternoon for a period of around 2 h. Thereafter, the isoprene concentrations suddenly decrease. Several other publications reported a similar bimodal diurnal cycle of isoprene with peaks in the morning and in the evening (Curren *et al.*, 1998; Starn *et al.*, 1998; Reimann *et al.*, 2000).

This characteristic pattern suggests an interplay between photochemical and dynamical processes. In the morning, the OH concentrations, the mixing height and the vertical mixing are low, and the isoprene mixing ratio first increases with increasing isoprene emissions. Later, OH production from ozone photolysis is enhanced, and the mixing height increases, incorporating residual layer air with lower isoprene concentrations into the boundary layer. Both effects lead to an isoprene decrease at around 11 AM. In the evening, isoprene is still emitted, and the lower OH radicals and the lower vertical mixing result in an increase in isoprene concentrations. As soon as the ground becomes colder than the air above, the stable nocturnal boundary layer arises and a distinct accumulation of isoprene occurs. The evening isoprene maxima at Verzago emerge when the estimated isoprene emissions nearly cease. This can only partially be explained by the distance of 200 to 300 m between the sampling site and the isoprene emitters and the time needed to advect the air masses from the forest to our instrument inlet. The mixing height in these evening hours must indeed be very low. After sunset, isoprene emissions vanish and isoprene mixing ratios decline due to chemical reactions with NO_3 , O_3 , and OH (OH could originate from alkene ozonolysis in the dark), and due to an increase of the wind speed (see Figure 2) resulting in a more efficient vertical and horizontal mixing. Typical OH concentrations during the night are up to 2 orders of magnitude smaller than during the day (e.g. Plass-Dülmer *et al.*, 1998). The oxidation products (MVK and MACR) are increasing shortly after the morning isoprene peak (Figure 1). This suggests that isoprene photooxidation is together with the enhanced vertical mixing

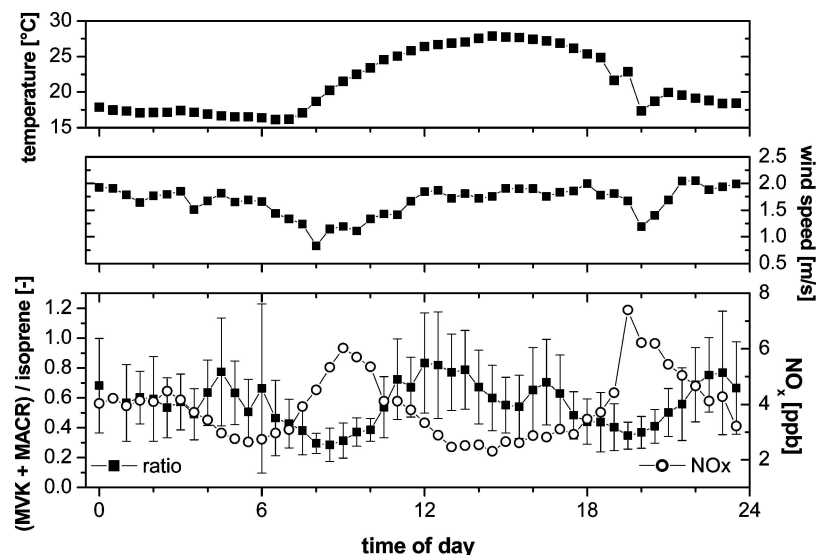


Figure 2. Mean daily cycles of the (MVK+MACR) to isoprene ratio, the NO_x mixing ratios, the wind speed and temperature at Verzago for August 12 to August 22, 2002. The bars denote the standard deviations of the mean.

and dilution responsible for the drop in the isoprene signal in the late morning. The concentration of the primary oxidation products also decrease around noon that again can be explained by further photooxidation and stronger vertical mixing. In contrast to the morning, the evening peak of isoprene is not followed by a peak of MVK + MACR indicating an isoprene decay due to the reaction with NO_3 or due to dynamic processes like vertical dispersion or horizontal advection of isoprene-depleted air masses. The relevant nighttime processes will be discussed in detail later in Section 3.1.3.

3.1.2. MVK + MACR to Isoprene Ratio

Figure 2 illustrates the diurnal cycles of the ratio of the oxidation products MVK + MACR to isoprene, nitrogen oxides, wind speed, and temperature at Verzago for the fair weather period from August 12 to 22, 2002. We detected low ratios around 8.30 AM and 7.30 PM, and higher values during the day and during nighttime. The MVK + MACR to isoprene ratio is partly driven by the OH chemistry that decomposes isoprene, and generates and destroys MVK and MACR at the same time. Photolysis of MVK and MACR is 6 to 7 times slower than the oxidation due to the reaction with OH. Besides the oxidant chemistry, the ratio depends also on the isoprene emission strengths (and therefore on temperature and radiation), dynamic processes and the proximity of the sampling inlet to the isoprene source (Biesenthal *et al.*, 1998; Montzka *et al.*, 1995). Most of the diurnal cycles of this ratio

published in the previous literature showed a different pattern with low ratios during the day and increased ratios in the night reflecting the diurnal isoprene emissions profiles (Biesenthal *et al.*, 1997, 1998; Apel *et al.*, 2002). In contrast to that and in agreement with our data, Montzka *et al.* (1993, 1995) reported the highest isoprene concentrations in the early evening and the lowest (MVK+MACR)/isoprene ratios in the early morning and the evening.

Yokouchi (1994) and Biesenthal *et al.* (1998) suggested a relationship between the (MVK+MACR)/isoprene ratio and the NO_x concentration in the atmosphere. Since MVK and MACR are produced by the reaction of isoprene peroxy radicals with NO whereas the competing reaction of isoprene peroxy radicals with another (hydro or organic) peroxy radicals produces organic hydroperoxides, enhanced NO_x levels up to 2–3 ppb could result in higher MVK and MACR yields. At higher NO_x mixing ratios, the (MVK+MACR)/isoprene ratio decreases again with increasing NO_x due to a limitation of OH by the reaction of OH with NO₂ forming (stable) HNO₃ molecules. The NO_x mixing ratios at our sampling site were between 2 and 6 ppb, slightly above the suggested NO_x optimum for the highest (MVK+MACR)/isoprene ratios. In agreement with Biesenthal *et al.* (1998), elevated NO_x concentrations coincide with low (MVK+MACR)/isoprene ratios. This relation should be only important during the photoactive periods, i.e. during daytime. However, the most distinct anti-correlation was found in the morning and the evening hours when photochemistry is less important. During these hours, the isoprene and NO_x mixing ratios show similar profiles with elevated values due to the accumulation of the emissions in a shallow boundary layer. Most of all emissions and reduced vertical mixing determine the concentrations during this time. An analysis restricted to afternoon periods showed no relation between the (MVK+MACR)/isoprene ratio and the NO_x concentrations possibly due to the small variability range of the NO_x mixing ratios. It is therefore difficult to evaluate the validity of the suggestion of Yokouchi (1994) and Biesenthal *et al.* (1998).

The wind speed is low in the early morning and late evening hours suggesting a reduced mixing when the mixing layer and the stable nocturnal boundary layer, respectively, start to develop. Low wind speeds cause less efficient horizontal mixing and also less turbulent conditions with reduced vertical mixing. But most of all, the vertical mixing is driven by convection. As the convection is strongest when the temperature at the ground is high, the temperature can be used as a rough measure for thermal convection. Lowest (MVK+MACR)/isoprene ratios, and highest NO_x mixing ratios were measured when the lowest temperatures at the ground were observed.

At our sampling site the nearest major isoprene sources are approximately 200–300 m away, and therefore the (MVK+MACR)/isoprene ratio is driven by photochemistry (as seen in Figure 1 with the highest MVK+MACR ratios slightly after the morning isoprene peak) as well as by dynamic processes (as seen in Figure 2 with the lowest (MVK+MACR)/isoprene ratios in the morning and evening hours with low wind speed and temperature).

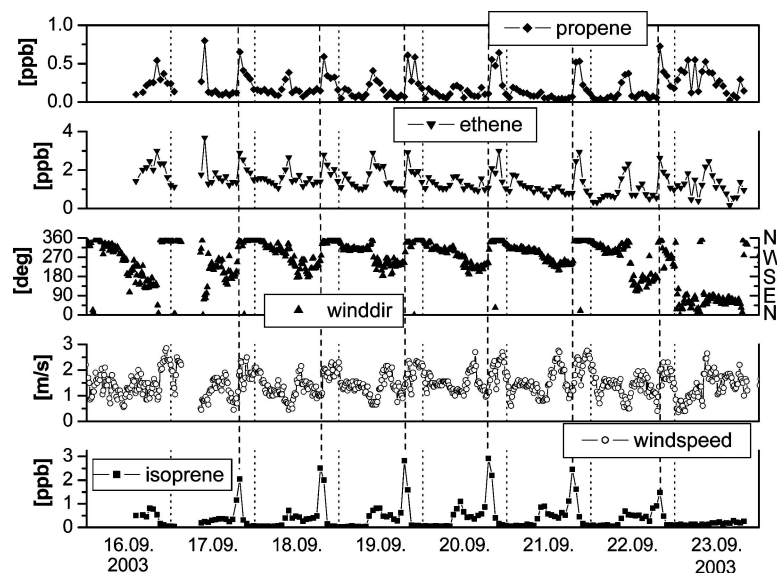


Figure 3. Time series of isoprene, wind speed, wind direction, ethene, and propene during the 2003 campaign. The dashed lines denote the isoprene maxima to aid visual inspection of the data.

3.1.3. Isoprene Nighttime Chemistry and Dynamics

Figure 3 shows an 8-day time series of isoprene, wind speed and direction, and two alkenes at Verzagò in September 2003. The morning peaks were less pronounced and the evening peaks were shorter compared to 2002, but the diurnal bimodal isoprene cycle was similar to 2002 and 1998 (not shown) despite reduced isoprene emissions in fall compared to summer. Stable meteorological conditions led to a recurrent daily pattern of isoprene, wind, and other VOCs between September 17 and 21. Usually, the wind speed was reduced in the afternoon simultaneously with a stable wind direction from SSW and in coincidence with elevated isoprene levels. Between 6 and 7 PM, the wind direction switched abruptly from SSW to N followed by a sudden decrease of the isoprene signal and an increase of ethene and propene. Isoprene-depleted and more polluted air from the vicinity north of the sampling site suggested a change of the air mass. During the night, the wind direction remained north and the alkene mixing ratios decreased again due to cleaner air advection from the Alpine foothills located around 5 km north of Verzagò. Based on this case study, a dominant dynamic influence on isoprene decrease seems to be likely.

Figure 4 demonstrates typical decays of isoprene mixing ratios for the 2002 campaign at Verzagò. In the majority of cases, an exponential decay (illustrated by a linear decay using a logarithmic scale) points to a (pseudo-)first order decay mechanism. The isoprene lifetime can be calculated from the negative slope on a logarithmic scale. For the presented days, lifetimes vary between 1.7 and 2.9 h. A

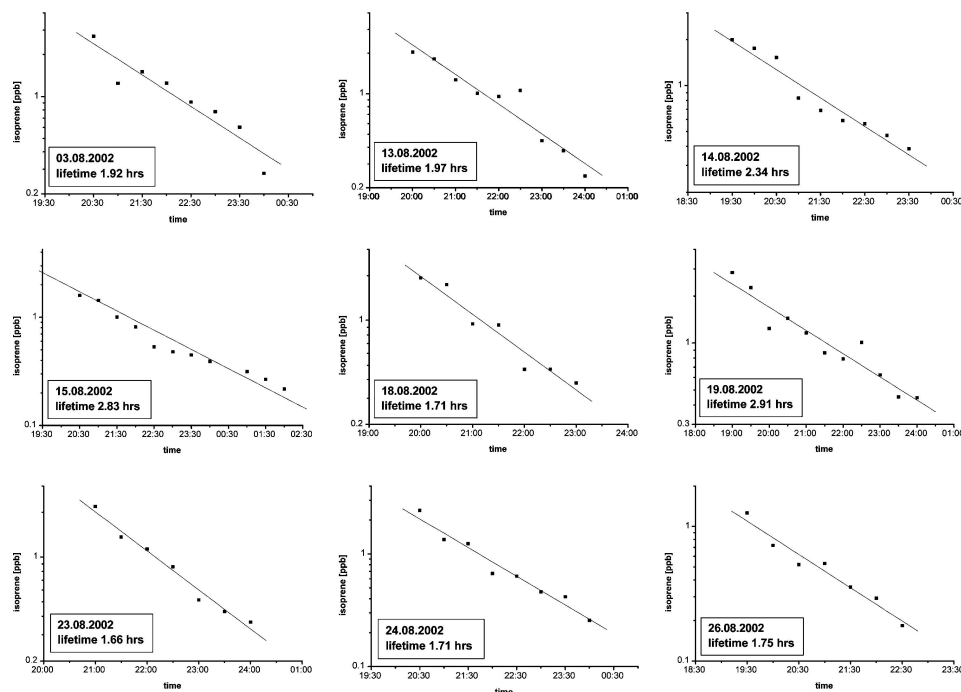


Figure 4. Typical nighttime isoprene decays at Verzago in summer 2002.

summary of all isoprene lifetimes calculated from the exponential decay is given in Table II. The number of representative decays is smaller in 2003, due to both the lower time resolution of the VOC measurements and the selection criteria of more than 4 data points and a R^2 higher than 0.85 for the considered nights. In total, lifetimes are between 0.8 and 3.3 h, in a good agreement with published data of Biesenthal *et al.* (1998) (1–3 h), Hurst *et al.* (2001) (2–5 h), and Apel *et al.* (2002) who distinguished between nighttime data before (lifetime of ca. 0.75 h) and after 9.30 PM (lifetime around 3.6 h).

In the next step of our analysis, we assumed that the decrease in isoprene concentration is entirely caused by the reaction with NO_3 . We considered a reaction

Table II. Mean isoprene lifetimes (in hours), standard deviations, and minimum and maximum lifetimes for selected days with a representative isoprene decay (# of data points ≥ 5 , $R^2 \geq 0.85$)

| Year | # of days | Average | Stdev | Min | Max |
|------|-----------|---------|-------|-----|-----|
| 1998 | 17 | 1.70 | 0.44 | 0.9 | 2.5 |
| 2002 | 12 | 2.04 | 0.64 | 0.8 | 3.0 |
| 2003 | 7 | 1.92 | 0.83 | 1.0 | 3.3 |

rate constant of $6.54 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at $18 \text{ }^\circ\text{C}$, and calculated the hypothetical constant NO_3 mixing ratio needed to fit the measurements. For the mean lifetimes in 1998, 2002, and 2003, we received mean NO_3 mixing ratios of 10.9 ppt, 9.6 ppt, and 10.5 ppt, respectively. In total, the mixing ratios ranged from 23.0 ppt (lifetime of 0.8 h) to 5.2 ppt (3.3 h). Similar values are reported in the literature (e.g. Biesenthal *et al.*, 1998, Ciccioli *et al.*, 1999).

No NO_3 measurements were performed during the three campaigns. As the sink mechanisms of NO_3 could not be properly estimated due to the unknown loss terms like hydrolysis and deposition of N_2O_5 as well as gas phase reactions of NO_3 with not measured VOC species (e.g. monoterpenes) (Geyer *et al.*, 2001), an estimation of NO_3 assuming equilibrium conditions is highly uncertain. However, we analyzed the variability of NO_3 in view of the NO_3 production rate due to the reaction of NO_2 with O_3 . Figure 5 shows a scatter plot of the NO_3 mixing ratios derived from the nighttime isoprene slopes versus the mean NO_3 production rates during the same periods. A correlation between the NO_3 production rate and the NO_3 mixing ratios that were indirectly derived by fitting the isoprene measurements is present. Estimated enhanced production rates in common with higher NO_3 mixing ratios and subsequently shorter isoprene lifetimes are visible despite of large uncertainties of both variables. The scatter might be related to other influencing processes such as horizontal advection of air masses with other isoprene contents or vertical dispersion of the measured air masses with isoprene depleted air. Lowest NO_3 values were derived for the 2002 campaign due to less polluted boundary layer conditions and

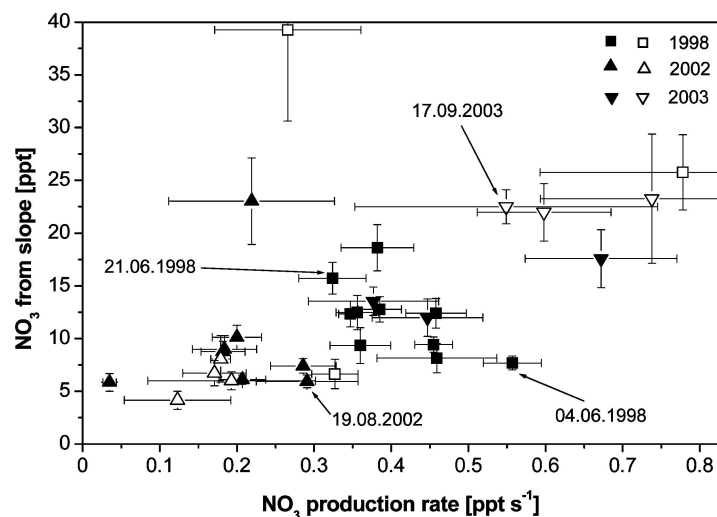


Figure 5. NO_3 mixing ratio derived from the isoprene slopes vs. the estimated NO_3 production rates for 1998, 2002, and 2003. Open symbols represent data that are based on slopes with less than 5 data points or a R^2 of <0.85 . Vertical and horizontal bars represent the errors of the slope and the standard errors of the average NO_3 production rate, respectively. Labeled data are also illustrated in Figure 7.

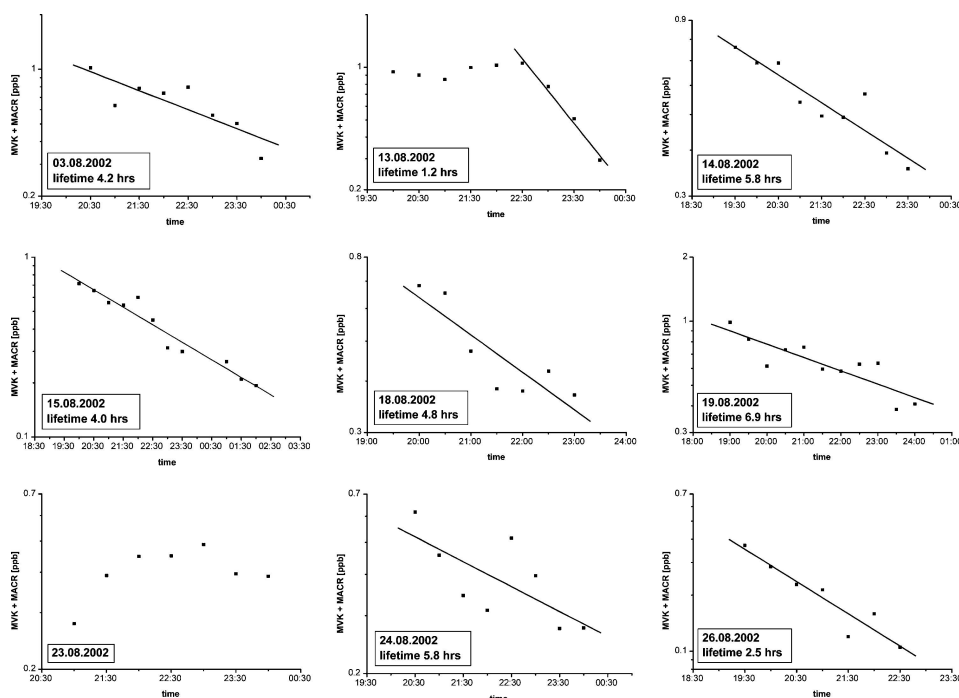


Figure 6. Typical nighttime MVK+MACR decays at Verzagò in summer 2002.

thus lower NO_2 and O_3 concentrations as a consequence of reduced anthropogenic activities during August as described in the companion paper (Steinbacher *et al.*, 2005). The isoprene decay that led to the data point with nearly 40 ppt of NO_3 was at least partly influenced by a change of the air mass. This was corroborated by an O_3 mixing ratio increase from 40 to 60 ppb between 8 and 9 PM. Excluding this data point, the correlation coefficient R is 0.69, suggesting an important influence of NO_3 chemistry on the isoprene decay at this semi-rural site.

Figure 6 presents the corresponding plots to Figure 4 for the sum of the two oxidation products. An exponential decay could not be detected every night, but was still frequently observed. Assuming chemical reactions as the dominant pathway of the observed decrease in MVK+MACR (in a similar way as described above), the calculated concentrations of OH and NO_3 would be unrealistically high, much higher than required to explain the isoprene decrease. Apart from that, such high OH concentrations would result in a considerable isoprene degradation leading again to a formation of these oxidation products. Therefore, a chemical explanation for the nighttime decay of MVK+MACR could not be found.

Additionally, we performed a sensitivity analysis with a box model to gain further insight into the nocturnal behavior of isoprene and the oxidation products. For this purpose, the Master Chemical Mechanism (MCM), version3, a freely downloadable model (<http://chmlin9.leeds.ac.uk/>) (Jenkin *et al.*, 1997, 2003; Saunders *et al.*, 2003)

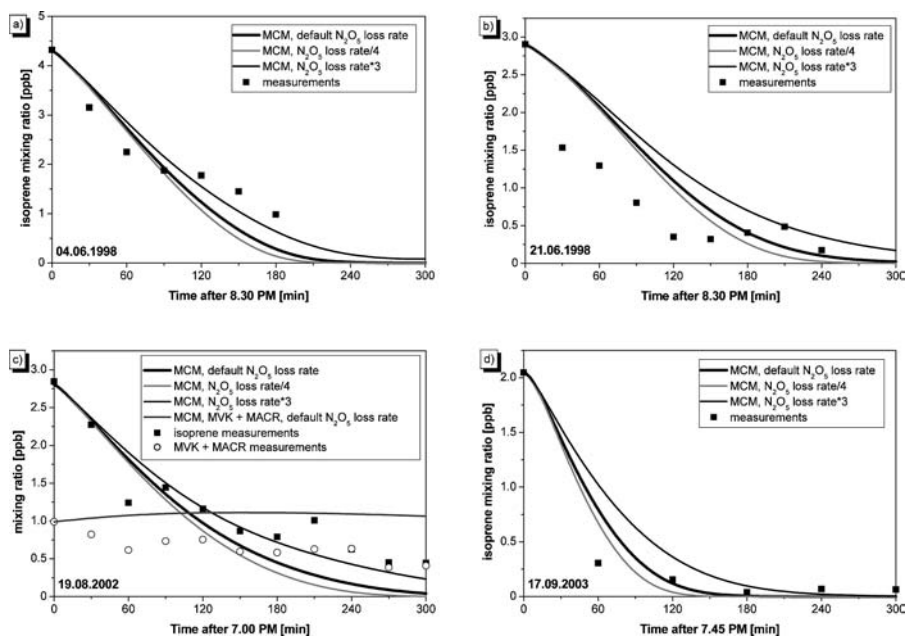


Figure 7. Measured and modeled decay of isoprene on four nights. Measured and model decay of MVK + MACR are included for 2002. Modeled data are based on a box model with different N_2O_5 loss rates.

was used. It is a nearly explicit mechanism with more than 12 600 reactions and more than 4 300 species. Here, only a reduced mechanism for the isoprene degradation including the whole set of inorganic reactions was taken into account. Two reactions representing the homogeneous hydrolysis of N_2O_5 with one and two H_2O molecules were added to the mechanism (Finlayson-Pitts and Pitts Jr., 2000). Figure 7 shows the results of the box model simulations and the corresponding measurements of isoprene for four nights. MVK+MACR model results and measurements were included when available. The measured mixing ratios of isoprene, NO, NO_2 , O_3 (and MVK+MACR when available) at the beginning of the isoprene drop were used as the starting conditions of the model. NO_2 and O_3 were constrained to the measurements during the whole simulation. The heterogeneous formation of nitrous acid on surfaces in the presence of water and nitrogen oxides is not included in the model. If the heterogeneous formation of nitrous acid was a considerable sink of NO_2 , which could subsequently lead to a reduced isoprene loss by reaction with NO_3 , this process would be taken into account in the model by constraining the modeled NO_2 to the measurements. Three different loss frequencies were used in the model to account for the uncertainty of the reaction of N_2O_5 on aerosol surfaces. Geyer *et al.* (2001) estimated from measurements near Berlin a variability of loss rates between $0.3 \times 10^{-4} s^{-1}$ and $22 \times 10^{-4} s^{-1}$. Three different loss frequencies were used in our model simulations to account for the uncertainty of the reaction of

N_2O_5 on aerosol surfaces. These were the default loss rate of the MCM ($4 \times 10^{-4} \text{ s}^{-1}$), as well as a lower (1×10^{-4} ; 'loss rate/4') and a higher ($12 \times 10^{-4} \text{ s}^{-1}$; 'loss rate* 3') rate. Figure 7a shows the night of June 4, 1998, a case with a high aerosol loading in the atmosphere. In agreement to that, the model fits best with the results when using the highest N_2O_5 loss rate, whereas on June 21, 1998 (panel b), the model can not reproduce the strong isoprene decay at all. This points to a significant dynamic influence (e.g. due to the advection of less biogenically influenced air masses) that can not be considered by the box model. In contrast to other nights, wind speed higher than 3 m/s occurred during this period. For the case in 2002 (Figure 7c), the model run with the highest loss rate can again nicely reproduce the isoprene decay, whereas the decay of the oxidation products can not be reproduced in accordance with the analysis already undertaken when discussing the exponential MVK+MACR decays. In disagreement to the measurements, the MVK+MACR level even increased due to a slight generation of the oxidation products during the isoprene degradation. For the last case (Figure 7d), the model run with the default loss rate can explain the measured isoprene profile with concentrations close to the detection limit already 120 min after the start of the isoprene drop. It is possible to reproduce the decay chemically even if the low isoprene concentration after already 60 min might be due to a dynamic effect. These four cases reveal that the chemistry can often explain the isoprene decay when adapting the highly variable N_2O_5 loss rate. Geyer *et al.* (2001) attributed 42% of the NO_3 loss to the reaction of N_2O_5 with aerosols. These simulations support the simple approach presented in Figure 5. It seems that the main driving factor of the isoprene decay is chemistry. Only in selected cases, the dynamic processes might play a dominating role.

The contribution of vertical dispersion could only be estimated. During several nights in August 2002, the ozone levels as well as temperatures stayed nearly constant beginning between 8.30 and 9.30 PM (indicated with arrows in Figure 8) and lasting several hours, whereas a substantial drop of both parameters could be observed before and after. It is known that O_3 concentrations considerably decrease during the night close to the ground due to dry deposition resulting in a vertical O_3 gradient. This 'step' in our temperature and ozone data could be explained by vertical mixing and downward transport of warmer and less O_3 -depleted air. This mechanism could also explain the decay of both isoprene and MVK+MACR at night. Similar to the observations, one would also expect a shorter lifetime of isoprene compared to MVK+MACR since the vertical gradient of isoprene, with its sources only at the ground, is usually more pronounced than that of the oxidation products, which can be produced in the whole boundary layer. But a weakness of this hypothesis concerns the good agreement of the measured and modeled isoprene series. The decay due to vertical dispersion has to be as strong as the expected chemical degradation so that the agreement of the model-measurement comparison would be fortuitous. Furthermore, assuming typical isoprene and O_3 gradients in the atmospheric boundary layer, it can be shown that the effect of the

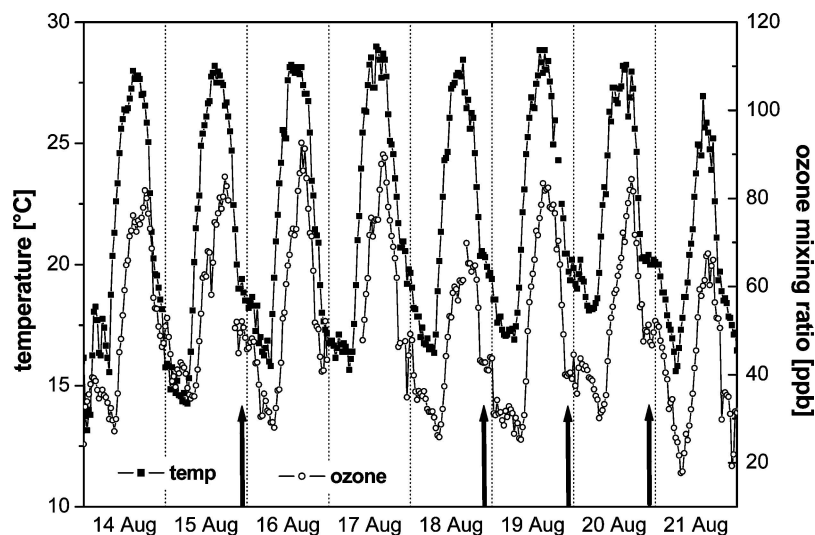


Figure 8. 8-day time series of ozone and temperature in 2002. The arrows mark situations with stable temperature and ozone mixing ratios at night.

vertical mixing that is needed to maintain constant O_3 levels can only partly explain the observed isoprene decay.

The role that deposition plays at the sampling site is difficult to evaluate. O_3 is known for its potential to be substantially depleted due to dry deposition at night. As constant O_3 levels are often observed during the nighttime periods when the isoprene decays take place, the vertical mixing compensates the O_3 loss due to dry deposition. Deposition should be negligible for isoprene as it is a nonpolar compound. For the oxidation products MVK and MACR, deposition is a possible candidate for the decrease, because vertical mixing as well as chemistry failed. The MVK+MACR loss rate is in the same range as the estimated vertical mixing rate derived from the O_3 measurements and assumptions concerning mixing height (100 to 300 m) and O_3 deposition rate (0.5 cm/s). But consequently, negligible concentrations of MVK+MACR have to be assumed in the residual layer to attribute the whole decay to the vertical mixing.

The nighttime isoprene chemistry and dynamics were mostly studied in the United States (Biesenthal *et al.*, 1998; Starn *et al.*, 1998; Hurst *et al.*, 2001; Faloon *et al.*, 2001; Stroud *et al.*, 2002; Sillman *et al.*, 2002; Apel *et al.*, 2002). As the sampling sites were in different environments, no consistent interpretation could be found within these publications. Measurements at remote-forested sampling sites led to the conclusion that OH was the most important oxidizing agent, whereas NO_3 played an unimportant role due to the low NO_x levels (Biesenthal *et al.*, 1998; Hurst *et al.*, 2001; Faloon *et al.*, 2001; Sillman *et al.*, 2002). At sub-urban, semi-rural sites, or locations that are impacted by anthropogenic emissions, NO_3 dominates as the main chemical isoprene sink (Starn *et al.*, 1998; Stroud *et al.*, 2002; this study).

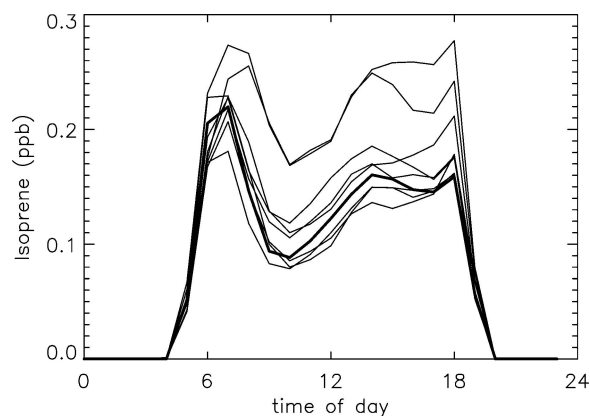


Figure 9. Diurnal cycle of isoprene for Verzago (bold line) and 8 adjacent grid cells for 13 May 1998, modeled with a 3-D Eulerian model.

Dynamics like horizontal advection and vertical dispersion have to be considered at every individual sampling site but can not be generalized as it was done for the chemical processes.

3.1.4. 3-Dimensional Modeling of Diurnal Cycles of Isoprene

A three-dimensional Eulerian model CAMx (Comprehensive Air Quality Model with Extensions) was used to simulate the diurnal cycle of isoprene. Figure 9 shows the results for May 13, 1998, an already well described case during the first intensive period of the PIPAPO campaign (Baertsch-Ritter *et al.*, 2003, 2004; Andreani-Aksoyoglu *et al.*, 2004). CAMx (Version 4), including the Carbon Bond Mechanism IV with an aerosol chemistry module, was used (Andreani-Aksoyoglu *et al.*, 2004). The meteorology was preprocessed with the SAI Mesoscale Model (Baertsch-Ritter *et al.*, 2004). The measured mixing ratios were lower in 1998 than in 2002 and 2003 due to still reduced emissions in May. However, the model slightly under-predicts the measurements. But the model nicely reproduced the measured bimodal diurnal isoprene cycle for 9 grid cells of 3×3 km size around Verzago. The highest isoprene levels shown here were simulated for the 3 grid cells north of Verzago, in agreement with the emission inventory that showed larger isoprene sources within the Alpine foothills region.

3.2. METHANOL

We measured methanol mixing ratios with the PTR-MS during the 2002 campaign. The results from a 10-day period are presented in Figure 10 and show spike-like methanol plumes. Like isoprene, tropospheric methanol (CH_3OH) can be of anthropogenic and biogenic origin. The global main sources are biogenic emissions,

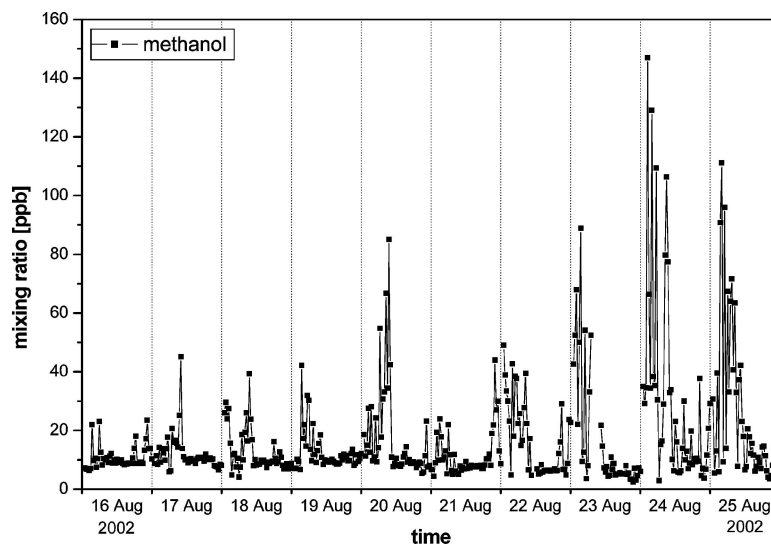


Figure 10. 10-day time series of methanol measured with PTR-MS in summer 2002.

chemical production in the atmosphere (Galbally and Kirstine, 2002), biomass burning (Holzinger *et al.*, 1999), emissions from dead plant material (Warneke *et al.*, 1999), and primary anthropogenic sources (Goldan *et al.*, 1995; Holzinger *et al.*, 2001). Especially in summer, biogenic processes are by far the dominating sources (Holzinger *et al.*, 2001). The emissions are affected by leaf temperature and stomatal conductance (MacDonald and Fall, 1993) as well as by solar radiation (Das *et al.*, 2003). Warneke *et al.* (1999) reported enhanced methanol emissions of dead plant material after humidification in the laboratory. After getting wet, the VOCs attached to the cell structures dissolve in the water and are subsequently released to the atmosphere according to Henry's law.

With a total average mixing ratio of 13.2 ppb the measurements at Verzago are in good agreement with data recently published by Das *et al.* (2003). They measured over a maize field in North Carolina and obtained averaged methanol mixing ratios of 16.4 and 11.0 ppb in 0.5 and 2.5 m height above the tops of the plants, respectively. No spikes were reported like in our measurements. This might be partly due to the low time resolution as hourly integrated air samples were collected. Warneke *et al.* (2002) measured approximately 2 m above an alfalfa field highly time resolved methanol mixing ratios between 10 and 50 ppb with some peaks up to 100 ppb. Both of these studies observed the highest methanol emissions during the day or after cutting the grass in accordance with laboratory studies. In contrast to that, our results show exceedingly enhanced mixing ratios in the late night.

Only measurements with sweet gum saplings in Alabama also revealed enhanced predawn methanol emissions (MacDonald and Fall, 1993). Explanations of the responsible processes are still speculative. MacDonald and Fall (1993) proposed a

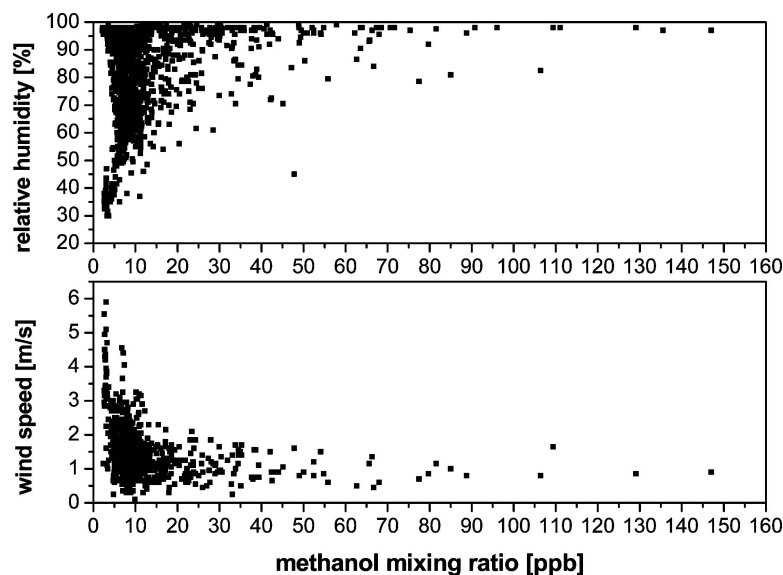


Figure 11. Scatterplot of relative humidity and wind speed versus the methanol mixing ratio at Verzago in summer 2002.

combination of improved nighttime leaf water status influencing the cell expansion rate, a methanol enrichment in the condensed water on the plant surface or a methanol accumulation inside the plant due to a reduced stomatal conductance. Holzinger *et al.* (2001) observed increased methanol concentrations after rainfall in a semi-rural environment in Austria and related this effect to the process already reported by Warneke *et al.* (1999).

At Verzago, the methanol levels are most probably of local origin as suggested by Figure 11. Elevated methanol mixing ratios appeared with low wind speed and relative humidities higher than 95%. Therefore, the methanol bursts might be ascribed to a condensation process and a similar process as reported by Warneke *et al.* (1999) and MacDonald and Fall (1993). Our findings show other characteristics than those reported by Holzinger *et al.* (2001). They observed decreased mixing ratios after condensation and suggested enhanced methanol removal due to wet deposition on dew-wetted surfaces. We suppose that the condensed water could dissolve the methanol on the plant surface and release it afterwards in the atmosphere. The low wind speed possibly promotes the accumulation in the vicinity of the sampling site as it favors the condensation due to reduced vertical and horizontal mixing. A small part of the field was cut at the beginning of the campaign (mid to end of July) to enable an undisturbed light path from the DOAS instruments to the reflector, but the peaks appeared several weeks after the cut. Therefore a direct effect of the cut can be excluded and only an effect due to fermentation of the cut corn could be conceivable.

3.3. POTENTIAL IMPACT TO LOCAL OZONE FORMATION

We used the approach of Carter (1994) to estimate the potential impact on ozone formation from isoprene and the anthropogenic VOCs presented in the companion paper (Steinbacher *et al.*, 2005). We considered mean trace gas concentrations and the maximum ozone incremental reactivities to calculate mean ozone formation potentials. The results reflect the different conditions of the three campaigns and show that isoprene contributes 1.6 times more to the ozone local formation than toluene in 1998, even 5.6 times more in summer 2002 due to the reduced anthropogenic emissions, and only 0.7 times in autumn 2003. Benzene contributions range between 6 and 7% compared to the contribution by toluene. In Bresso, the ozone formation due to toluene dominates the contribution from isoprene. In 1998, it is 1.6 times, in 2003 even 4.8 times more. Benzene is also in Bresso only a minor contributor (4 to 5% compared to toluene). It is worth mentioning again that about 50% of the isoprene at Bresso was related to road traffic.

As alkenes were only measured at Verzago in 2003, a more extended set of VOCs could be analyzed with respect to ozone formation during this campaign. It showed that ethene was by far the most dominant contributor followed by toluene and propene. A similar result was found for Bresso in 2003. Ethene contributed to 35% of the ozone formation when taking into account all 29 compounds that were measured during this campaign (see Latella *et al.*, 2005). There, higher aromatics also played an important role. This is also in common with potential contribution to ozone formation based on source contribution estimates from chemical mass balance and positive matrix factorization for the Bresso 2003 dataset (Latella *et al.*, 2005). This analysis shows that gasoline and diesel exhaust are the major contributors to ozone formation (38% and 24%, respectively).

4. Conclusions

Three measurement campaigns within a period of 5 years were performed in the Po Basin in early summer 1998, summer 2002, and autumn 2003. Bimodal diurnal isoprene cycles were observed at the semi-rural site during each campaign and were qualitatively reproduced by a 3-dimensional Eulerian model which cannot account for local phenomena at the sampling site. The bimodal structure was most pronounced during fair weather periods due to enhanced isoprene emissions. Time series of methyl vinyl ketone (MVK) + methacrolein (MACR) showed rising concentrations shortly after the isoprene morning peak and supported the interpretation of the photochemical influence that was at least partly responsible for the isoprene decay during noontime. The second isoprene peak in the late afternoon was not followed by an increase of MVK + MACR that would be expected if the isoprene + OH reaction was the dominant process of the nighttime isoprene decay. Further analyses revealed that the reaction with NO₃ seemed to be most likely the dominating process for the nighttime isoprene decay whereas dynamic processes i.e.

advection of air masses and vertical dispersion seemed to be more important for the decay of the isoprene oxidation products.

Considerable methanol peaks were observed at the semi-rural sampling site during several nights at the end of August 2002. In contrast to most of the previous publications that reported methanol emissions driven by temperature, light, stomatal conductance, or due to cutting, the enhanced methanol levels at Verzago were found during the night with low wind speed and high relative humidities. Condensation processes either on the plant surfaces or inside the plant and/or a fermentation of cut corn close to the sampling site that was promoted under humid conditions, might be responsible for the high methanol mixing ratios measured in the late night. Low wind speed could favor the enhanced levels due to reduced mixing and more favorable conditions for high humidities.

A simple approach to estimate the local ozone formation potentials of the different VOCs showed that isoprene contributed at the semi-rural site 1.6, 5.6 and 0.7 times compared to toluene to the ozone formation in 1998, 2002, and 2003, respectively. Small alkenes (especially ethene) were the most dominant contributors at the urban as well as at the semi-rural site. The interpretation of the VOC patterns at Verzago in this and the companion paper (Steinbacher *et al.*, 2005) forms an important basis and provides knowledge for the further interpretation of formaldehyde as an intermediate of the VOC oxidation in the boundary layer.

Acknowledgments

We thank the PIPAPO and FORMAT crews. This work was supported by the Swiss National Science Foundation under Grant No. 21-61573.00. The FORMAT project was funded by the Research Directorate of the European Commission under Grant No. EVK2-CT-2001-00120 and by the Federal Office for Education and Science in Switzerland, BBW nr. 01.0233.

References

- Andreani-Aksoyoglu, S. and Keller, J., 1995: Estimates of monoterpene and isoprene emissions from the forests in Switzerland, *Journal of Atmospheric Chemistry* **20**, 71–87.
- Andreani-Aksoyoglu, S., Prévôt, A. S. H., Baltensperger, U., Keller, J., and Dommen, J., 2004: Modeling of formation and distribution of secondary aerosols in the Milan area (Italy), *Journal of Geophysical Research* **109**, art.-nr.: D05306, 10.1029/2003JD004231.
- Apel, E. C., Riemer, D. D., Hills, A., Baugh, W., Orlando, J. J., Faloona, I., Tan, D., Brune, W. H., Lamb, B. K., Westberg, H., Carroll, M. A., Thornberry, T., and Geron, C. D., 2002: Measurement and interpretation of isoprene fluxes and isoprene, methacrolein, methyl vinyl ketone mixing ratios at the PROPHET site during the 1998 intensive, *Journal of Geophysical Research* **107**(D3), art.-nr.: 4034, 10.1029/2000JD000225.
- Atkinson, R., 2000: Atmospheric Chemistry of VOCs and NO_x, *Atmospheric Environment* **34**, 2063–2101.
- Atkinson, R. and Arey, J., 2003: Atmospheric degradation of volatile organic compounds, *Chemical Reviews* **103**, 4605–4638.

- Baertsch-Ritter, N., Keller, J., Dommen, J., and Prévôt, A. S. H., 2004: Effects of various meteorological conditions and spatial emission resolutions on the ozone concentration and ROG/NO_x limitation in the Milan area (I), *Atmospheric Chemistry and Physics* **4**, 423–438.
- Baertsch-Ritter, N., Prévôt, A. S. H., Dommen, J., Andreani-Aksoyoglu, S., and Keller, J., 2003: Model study with UAM-V in the Milan area (I) during PIPAPO: Simulations with changed emissions compared to ground and airborne measurements, *Atmospheric Environment* **37**, 4133–4147.
- Biesenthal, T. A., Bottenheim, J. W., Shepson, P. B., Li, S.-M., and Brickell, P. C., 1998: The chemistry of biogenic hydrocarbons at a rural site in eastern Canada, *Journal of Geophysical Research* **103**(D19), 25487–25498.
- Biesenthal, T. A., Wu, Q., Shepson, P. B., Wiebe, H. A., Anlauf, K. G., and Mackay, G. I., 1997: A study of relationships between isoprene, its oxidation products, and ozone, in the Lower Fraser Valley, BC, *Atmospheric Environment* **31**(14), 2049–2058.
- Borbon, A., Fontaine, H., Veillerot, M., Locoge, N., Galloo, J. C., and Guillermo, R., 2001: An investigation into the traffic-related fraction of isoprene at an urban location, *Atmospheric Environment* **35**, 3749–3760.
- Carter, W.P.L., 1994: Development of ozone reactivity scales for volatile organic compounds, *Journal of the Air & Waste Management Association* **44**, 881–899.
- Chameides, W. L., Lindsay, R. W., Richardson, J., and Kiang, C. S., 1988: The role of biogenic hydrocarbons in urban photochemical smog: Atlanta as a case study, *Science* **241**, 1473–1475.
- Ciccioli, P., Brancaleoni, E., and Frattoni, M., 1999: Reactive hydrocarbons in the atmosphere at urban and regional scales, in *Reactive Hydrocarbons in the Atmosphere*, edited by C.N. Hewitt, pp. 159–207, Academic Press, San Diego.
- Curren, K., Gillespie, T., Steyn, D., Dann, T., and Wang, D., 1998: Biogenic isoprene at the Lower Fraser Valley, British Columbia, *Journal of Geophysical Research* **103**(D19), 25467–25477.
- Das, M., Kang, D., Aneja, V. P., Lonneman, W., Cook, D. R., and Wesely, M. L., 2003: Measurements of hydrocarbon air-surface exchange rates over maize, *Atmospheric Environment* **37**, 2269–2277.
- Derognat, C., Beekmann, M., Baeumle, M., Martin, D., and Schmidt, H., 2003: Effect of biogenic volatile organic compound emissions on tropospheric chemistry during the Atmospheric Pollution Over the Paris Area (ESQUIF) campaign in the Ile-de-France region, *Journal of Geophysical Research* **108**(D17), art.-nr.: 8560, 10.1029/2001JD001421.
- Dommen, J., Prévôt, A. S. H., Baertsch-Ritter, N., Maffei, G., Longoni, M. G., Grüebler, F. C., and Thielmann, A., 2003: High-resolution emission inventory of the Lombardy region: Development and comparison with measurements, *Atmospheric Environment* **37**, 4149–4161.
- Dommen, J., Prévôt, A. S. H., Neining, B., and Bäumle, M., 2002: Characterization of the photooxidant formation in the metropolitan area of Milan from aircraft measurements, *Journal of Geophysical Research* **107**(D22), art.-nr.: 8197, 10.1029/2000JD000283.
- Duane, M., Poma, B., Rembges, D., Astorga, C., and Larsen, B. R., 2002: Isoprene and its degradation products as strong ozone precursors in Insubria, northern Italy, *Atmospheric Environment* **36**(24), 3867–3879.
- Faloona, I., Tan, D., Brune, W. H., Hurst, J. M., Barkley Jr. D. J., Couch, T. L., Shepson, P. B., Apel, E., Riemer, D., Thornberry, T., Carroll, M. A., Sillman, S., Keeler, G. J., Sagady, J., Hooper, D., and Paterson, K., 2001: Nighttime observations of anomalously high levels of hydroxyl radicals above a deciduous forest canopy, *Journal of Geophysical Research* **106**(D20), 24315–24333.
- Fehsenfeld, F. C., Calvert, J. G., Fall, R., Goldan, P. D., Guenther, A. B., Hewitt, C. N., Lamb, B. K., Liu, S. C., Trainer, M., Westberg, H., and Zimmerman, P. R., 1992: Emissions of volatile organic compounds from vegetation and their implications for atmospheric chemistry, *Global Biogeochemical Cycles* **6**(4), 389–430.
- Finlayson-Pitts, B. J. and Pitts Jr. J. N., 2000: *Chemistry of the Upper and Lower Atmosphere*, Academic Press, San Diego, pp. 969.

- Galbally, I. E. and Kirstine, W., 2002: The production of methanol by flowering plants and the global cycle of methanol, *Journal of Atmospheric Chemistry* **43**, 195–229.
- Geyer, A., Alicke, B., Konrad, S., Schmitz, T., Stutz, J., and Platt, U., 2001: Chemistry and oxidation capacity of the nitrate radical in the continental boundary layer near Berlin, *Journal of Geophysical Research* **106**(D8), 8013–8025.
- Goldan, P. D., Trainer, M., Kuster, W. C., Parrish, D. D., Carpenter, J., Roberts, J. M., Yee, J. E., and Fehsenfeld, F. C., 1995: Measurements of hydrocarbons, oxygenated hydrocarbons, carbon monoxide and nitrogen oxides in an urban basin in Colorado: Implications for Emission Inventories, *Journal of Geophysical Research* **100**(D11), 22771–22783.
- Grüebler, F. C., 1999: Reactive hydrocarbons in the Milan area: Results from the PIPAPO campaign. PhD thesis. Institute for Atmospheric Science, Swiss Federal Institute of Technology Zurich.
- Guenther, A. B., Zimmerman, P. R., Harley, P. C., Monson, R. K., and Fall, R., 1993: Isoprene and monoterpene emission rate variability: Model evaluation and sensitivity analyses, *Journal of Geophysical Research* **98**(D7), 12609–12617.
- Holzinger, R., Jordan, A., Hansel, A., and Lindinger, W., 2001: Methanol measurements in the lower troposphere near Innsbruck (47°16'N, 11°24'E), Austria, *Atmospheric Environment* **35**, 2525–2532.
- Holzinger, R., Warneke, C., Hansel, A., Jordan, A., Lindinger, W., Scharffe, D. H., Schade, G., and Crutzen, P. J., 1999: Biomass burning as a source of formaldehyde, acetaldehyde, methanol, acetone, acetonitrile, and hydrogen cyanide, *Geophysical Research Letters* **26**(8), 1161–1164.
- Hurst, J. M., Barket Jr. D. J., Herrera-Gomez, O., Couch, T. L., Shepson, P. B., Faloona, I., Tan, D., Brune, W. H., Westberg, H., Lamb, B. K., Biesenthal, T. A., Young, V., Goldstein, A., Munger, J. W., Thornberry, T., and Carroll, M. A., 2001: Investigation of the nighttime decay of isoprene, *Journal of Geophysical Research* **106**(D20), 24335–24346.
- Jenkin, M. E., Saunders, S. M., and Pilling, M. J., 1997: The tropospheric degradation of volatile organic compounds: A protocol for mechanism development, *Atmospheric Environment* **31**(1), 81–104.
- Jenkin, M. E., Saunders, S. M., Wagner, V., and Pilling, M. J., 2003: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part B): Tropospheric degradation of aromatic volatile organic compounds, *Atmospheric Chemistry and Physics* **3**, 181–193.
- Konrad, S. and Volz-Thomas, A., 2000: Characterization of a commercial gas chromatography-flame ionization detection system for the in situ determination of C₅-C₁₀ hydrocarbons in ambient air, *Journal of Chromatography A* **878**, 215–234.
- Kwok, E. S. C., Aschmann, S. M., Arey, J., and Atkinson, R., 1996: Product formation from the reaction of the NO₃ radical with isoprene and rate constants for the reactions of methacrolein and methyl vinyl ketone with the NO₃ radical, *International Journal of Chemical Kinetics* **28**, 925–934.
- Lamb, B. K., Gay, D., Westberg, H., and Pierce, T., 1993: A biogenic hydrocarbon emission inventory for the U.S.A. using a simple forest canopy model, *Atmospheric Environment* **27A**(11), 1673–1690.
- Latella, A., Stani, G., Cobelli, L., Duane, M., Junninen, H., Astorga, C., and Larsen, B.R., 2005: Semicontinuous GC analysis and receptor modelling for source apportionment of ozone precursor hydrocarbons in Bresso, Milan 2003, *Journal of Chromatography A*, **107**, 29–39.
- Lindinger, W., Hansel, A., and Jordan, A., 1998: On-line monitoring of volatile organic compounds at pptv levels by means of Proton-Transfer-Reaction Mass Spectrometry (PTR-MS). Medical applications, food control and environmental research, *International Journal of Mass Spectrometry and Ion Processes* **173**, 191–241.
- MacDonald, R. C. and Fall, R., 1993: Detection of substantial emissions of methanol from plants to the atmosphere, *Atmospheric Environment* **27A**(11), 1709–1713.

- Montzka, S. A., Trainer, M., Angevine, W. M., and Fehsenfeld, F. C., 1995: Measurements of 3-methyl furan, methyl vinyl ketone, and methacrolein at a rural site in the southeastern United States, *Journal of Geophysical Research* **100**(D6), 11393–11401.
- Montzka, S. A., Trainer, M., Goldan, P. D., Kuster, W. C., and Fehsenfeld, F. C., 1993: Isoprene and its oxidation products, methyl vinyl ketone and methacrolein, in the rural troposphere, *Journal of Geophysical Research* **98**(D1), 1101–1111.
- Neftel, A., Spirig, C., Prévôt, A. S. H., Furger, M., Stutz, J., Vogel, B., and Hjorth, J., 2002: Sensitivity of photooxidant production in the Milan Basin: An overview of results from a EUROTRAC-2 Limitation of Oxidant Production field experiment, *Journal of Geophysical Research* **107**(D22), art.-nr.: 8188, 10.1029/2001JD001263.
- Plass-Dülmer, C., Brauers, T., and Rudolph, J., 1998: POPCORN: A field study of photochemistry in north-eastern Germany, *Journal of Atmospheric Chemistry* **31**, 5–31.
- Reimann, S., Calanca, P., and Hofer, P., 2000: The anthropogenic contribution to isoprene concentrations in a rural atmosphere, *Atmospheric Environment* **34**, 109–115.
- Saunders, S. M., Jenkin, M. E., Derwent, R. G., and Pilling, M. J., 2003: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): Tropospheric degradation of non-aromatic volatile organic compounds, *Atmospheric Chemistry and Physics* **3**, 161–180.
- Seinfeld, J. H. and Pandis, S. N., 1998: *Atmospheric chemistry and physics: From air pollution to climate change*, John Wiley & Sons, Inc., New York, pp. 1326.
- Sillman, S., Carroll, M. A., Thornberry, T., Lamb, B. K., Westberg, H., Brune, W. H., Faloona, I., Tan, D., Shepson, P. B., Sumner, A. L., Hastie, D. R., Mihele, C. M., Apel, E. C., Riemer, D. D., and Zika, R. G., 2002: Loss of isoprene and sources of nighttime OH radicals at a rural site in the United States: results from photochemical models, *Journal of Geophysical Research* **107**(D5), art.-nr.: 4043, 10.1029/2001JD000449.
- Simpson, D., Guenther, A. B., Hewitt, C. N., and Steinbrecher, R., 1995: Biogenic emissions in Europe. 1. Estimates and uncertainties, *Journal of Geophysical Research* **100**(D11), 22875–22890.
- Starn, T. K., Shepson, P. B., Bertman, S. B., Riemer, D. D., Zika, R. G., and Olyszyna, K., 1998: Nighttime isoprene chemistry at an urban-impacted forest site, *Journal of Geophysical Research* **103**(D17), 22437–22447.
- Steinbacher, M., Dommen, J., Ordóñez, C., Reimann, S., Staehelin, J., and Prévôt, A. S. H., 2005: Volatile organic compounds in the Po Basin. Part A: anthropogenic VOCs, *Journal of Atmospheric Chemistry*, **51**, 271–291.
- Steinbacher, M., Dommen, J., Ammann, C., Spirig, C., Neftel, A., and Prévôt, A. S. H., 2004: Performance Characteristics of a Proton-Transfer-Reaction Mass Spectrometer (PTR-MS) derived from laboratory and field measurements, *International Journal of Mass Spectrometry*, **239**, 117–128.
- Steinbrecher, R., Hauff, K., Rabong, R., and Steinbrecher, J., 1997: Isoprenoid emission of oak species typical for the Mediterranean area: source strength and controlling variables, *Atmospheric Environment* **31**(SI), 79–88.
- Stroud, C. A., Roberts, J. M., Goldan, P. D., Kuster, W. C., Murphy, P. C., Williams, E. J., Hereid, D., Parrish, D. D., Sueper, D. T., Trainer, M., Fehsenfeld, F. C., Apel, E. C., Riemer, D. D., Wert, B. P., Henry, B. E., Fried, A., Martinez-Harder, M., Harder, H., Brune, W. H., Li, G., Xie, H., and Young, V. L., 2001: Isoprene and its oxidation products, methacrolein and methyl vinyl ketone, at an urban forested site during the 1999 Southern Oxidants Study, *Journal of Geophysical Research* **106**(D8), 8035–8046.
- Stroud, C. A., Roberts, J. M., Williams, E. J., Hereid, D., Angevine, W. M., Fehsenfeld, F. C., Wisthaler, A., Hansel, A., Martinez-Harder, M., Harder, H., Brune, W. H., Hoenninger, G., Stutz, J., and White, A. B., 2002: Nighttime isoprene trends at an urban forested site during the 1999 Southern Oxidant Study, *Journal of Geophysical Research* **107**(D16), art.-nr.: 4291, 10.1029/2001JD000959.

- Thunis, P. and Cuvelier, C., 2000: Impact of biogenic emissions on ozone formation in the Mediterranean area – a BEMA modelling study, *Atmospheric Environment* **34**, 467–481.
- Trainer, M., Hsie, E. Y., McKeen, S. A., Tallamraju, R., Parrish, D. D., Fehsenfeld, F. C., and Liu, S. C., 1987: Impact of natural hydrocarbons on hydroxyl and peroxy radicals at a remote site, *Journal of Geophysical Research* **92**(D10), 11879–11894.
- Warneke, C., Karl, T., Judmaier, H., Hansel, A., Jordan, A., Lindinger, W., and Crutzen, P. J., 1999: Acetone, methanol and other partially oxidized volatile organic emissions from dead plant matter by abiological processes: Significance for atmospheric HO_x chemistry, *Global Biogeochemical Cycles* **13**(1), 9–17.
- Warneke, C., Luxembourg, S., de Gouw, J. A., Rinne, H. J. I., Guenther, A. B., and Fall, R., 2002: Disjunct eddy covariance measurements of oxygenated volatile organic compounds fluxes from an alfalfa field before and after cutting, *Journal of Geophysical Research* **107**(D8), art.-nr.: 4067, 10.1029/2001JD000594.
- Yokouchi, Y., 1994: Seasonal and diurnal variation of isoprene and its reaction products in a semi-rural area, *Atmospheric Environment* **28**(16), 2651–2658.