On the distribution of formaldehyde in the western Po-Valley, Italy, during FORMAT 2002/2003

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Abstract

Formaldehyde was measured in the area of Milano, Italy, during the 2002 and 2003 FORMAT campaigns at three ground field sites and from an ultralight aircraft. The horizontal distributions show a strong impact of local emissions at a site in the centre of Milano and more photochemically driven diurnal patterns in the remote locations north and south of the city. The mixing ratios in the agricultural areas upwind of Milano were comparable to those downwind indicating the importance of biogenic emissions and anthropogenic agricultural activities. The vertical distributions were dominated by transport processes with advection of CH$_2$O above the planetary boundary layer by cloud venting. Comparison to model calculations show discrepancies in the diurnal patterns and regional distribution which allude to uncertainties in emission inventories.

1 Introduction

Formaldehyde, CH$_2$O, is one of the key substances in the photochemical production of radicals and of secondary photochemical compounds. CH$_2$O is a product within the oxidation chain of CH$_4$ in the atmosphere producing a background level of CH$_2$O in the order of about 0.5 ppb (Stockwell and Junkermann, 1996) but also a product of biogenic precursors or direct traffic or industrial emissions. In remote areas mixing ratios of CH$_2$O typically are below a few ppb and they are strongly correlated to local advection of polluted air masses (Stockwell et al., 1996; Slemr et al., 1993). In polluted environments mixing ratios may reach more than 30 ppb, most of these immissions are either directly from fossil fuel burning or from secondary reactions in the atmosphere during degradation of different VOC’s (Possanzini et al., 2002; Garcia et al., 2006). Under polluted conditions CH$_2$O serves as one of the main sources for radicals in the atmosphere, exceeding occasionally radical production from ozone photolysis up to an order of magnitude, (Kleinmann, 1996; Possanzini et al., 2002). Additional formaldehyde in the environment thus has a boosting effect on air chemistry. In higher concentrations
CH$_2$O is a toxic compound. Within the outdoor environment even in polluted situations the levels normally do not exceed the health critical values. Maximum values reported are about 50 ppb (Grosjean, et al., 1996; Eom et al., 2008). As formaldehyde is a very ubiquitous substance and has a strong impact on the photochemistry of polluted areas, the European Community Project FORMAT has been launched to investigate the three dimensional distribution and the diurnal patterns of formaldehyde mixing ratios in an area with high levels of pollution. The project also included a comparison of different in situ and remote sensing techniques for the measurement of formaldehyde under natural conditions in a moderate to highly polluted site. This comparison and its results are described in detail by Hak et al. (2005). A later instrument comparison was published by Wisthaler et al. (2008). Following the comparison exercise the participating instruments were distributed to sites upwind, downwind and in the center of the City of Milano and airborne measurements were performed using three instrumented aircraft, an ultralight research aircraft (Junkermann, 2001) and a motorized glider (METAIR) for measurements of vertical and horizontal distributions, both carrying an online measuring Hantzsch instrument (Junkermann and Burger, 2005) and a Partenavia PA68 equipped with a MAX-DOAS remote sensing system for the investigation of CH$_2$O, SO$_2$ and NO$_2$ (Wang et al., 2006). Within this paper only measurements from the Hantzsch technique installed on ground and microlight aircraft are presented.

2 Experimental

CH$_2$O measurements described in this paper were performed using the continuous Hantzsch technique with stripping of CH$_2$O into slightly acidic solution followed by liquid phase fluorimetric detection (Junkermann und Burger, 2005). The technique is also basis for a similar commercial instrument (AERO-LASER, Model 4001) used for the ground based investigations. Within the project three of these instruments, all running from the same batch of chemistry, were employed at the ground stations for continuous monitoring at an altitude of about two meters above ground. All instruments were op-
erated using internal gas phase calibration sources once per day, an internal zeroing cycle four times a day and were regularly calibrated using a liquid phase traveling standard. These additional liquid calibrations were performed at a minimum three times a week. All operating solutions were stored at 4°C in the field. Inlet lines for all instruments were made from 1/4″, 4 mm inner diameter, PFA tubing with a length of 10 m. At the inlet of these lines a 47 mm PFA in-line filter was installed to keep the inlet line clean. This filter was exchanged once a day. The procedure, adapted also for shipborne measurements (Stockwell and Junkermann, 1996) and highly polluted situations in Mexico City (de Gouw et al., 2009) avoids any losses in the inlet lines larger than 3%. The detection limit for the instruments was estimated in the laboratory to be below 30 ppt (3σ). Though stored in shelters the commercial instruments were subject to ambient temperature changes during the campaign and were not fully compensated for such variable field conditions. Thus for the field experiment a detection limit of <100 ppt (3σ) was estimated as calculated from the baseline and sensitivity drift within the 6 h zeroing intervals. All instruments were operated for more than three weeks in each of the two campaigns. While the northern station Alzate and the city station Bresso were installed at the same location during both campaigns the southern site was moved in 2003 by ~30 km from Cascina Casinazza at 45° 02′ 35″ N, 8° 58′ 45″ E in 2002 to the airfield of Spessa (45° 07′ 40″ N, 9° 21′ 35″ E) due to more simple logistics and more easy access. Figure 1 shows a map of the area including airspace signatures, motorways (double lines) and urban regions (yellow).

Airborne measurements of CH₂O were performed using a modified version of the Hantzsch instrument, described in detail in Junkermann and Burger (2005). The instrument was installed on a microlight aircraft (Junkermann, 2001). The instrument, stripped down in weight to 2.5 kg, has a slightly higher detection limit of 50 ppt compared to the commercial version, but several measures to increase the temperature stability resulted in the same 100 ppt field detection limit during the airborne application although the instrument was operated in a by far wider temperature range and was subject to temperature changes of >20°C within 15 min during vertical profile flights.
Zeroing was done manually dependent on the flight pattern, not to disturb data collection during vertical soundings, and liquid phase calibrations were preformed before and after each flight. Flights were operated from the airfield of Lecco Monte Marenzo in the northeast of Milano in 2002 and from the airfield of Spessa, south of Milano, in 2003. The choice of Spessa allowed the operation of the aircraft and one of the ground stations at one location and avoided the vicinity of the mountainous area of Lecco which is in the afternoon more often affected by local thunderstorms.

Within the whole western Po-Valley flights under visual flying rules (VFR) are allowed below a level of 2000 ft m.s.l. only. Above this level due to the high density of airports and commercial traffic the airspace is designated as an airspace category which is restricted solely to flights under instrumental flying rules. As the microlight aircraft is not allowed to operate within this airspace vertical profiles were limited to the northern and southern edges of the valley. In the area of Lecco and Como, approximately 10 km north of the ground station Alzate, it was possible to climb up to 9000 ft a.s.l. In the south the mountain slopes are less steep and the upper limit of the permitted airspace was 4500 ft a.s.l.

Although both campaigns were performed during the summer or early fall the weather patterns were quite different. The first campaign, running from the end of July until mid August, was characterized by more humid and hazy conditions with a high frequency of mid elevation cumulus clouds between ~1000 m and 3000 m above ground while in the second campaign in September to early October typically dry and cloud free conditions were encountered. Hence due to low visibility and high chance of thunderstorms in 2002 most of the flights were done in close vicinity of Lecco and Como and north of Milano. Only one flight lead to the south east of Milano. In 2003 due to the more favorable weather the typical flight pattern of the second campaign included a low elevation (~400–500 m) circle around Milano respectively the airport zone of the city airport of Linate (shaded airspace D, Fig. 1) with additional vertical profiles, ascents above Lecco up to 3000 m a.s.l. and descents close to Como back to about 300 m a.s.l. Occasional comparison flights also passed the ground site of Alzate at
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Introduction

The city location Bresso, which is situated on a small airfield just south of the northern motorway belt around Milano is the most affected one by direct emissions in the vicinity. Here local emissions by traffic, occasionally directly beneath the site is the main influence. The other stations were located in less traffic affected areas, at least 10 km from main motorways, Alzate at the edge of a glider airfield near a small village, Cascina Cassinazza in an agricultural area south of the river Po and Spessa also on a small airfield for sport aircraft situated in an agricultural rice growing area. In the northern part of the Po-Valley between Milano, Como and Lecco a larger fraction of the area is covered by mixed forests while in the southern half only small patches of forest are left. Here the main agricultural activity is rice production. As a difference to the north in the south several plantations of poplar might be important as local sources of CH$_2$O precursors. Population density and traffic is by far higher in the north than in the south. Along the northern rim of the valley and the motorway from Milano to Venezia and along the motorways from Milano to Como a belt of highly concentrated small to medium size industries is typical, also some chemical industry. Heavy industry (steel production) can be found 80 km to the east of Milano in Brescia. The closest airports are Malpensa, 30 km northwest, Bergamo, 30 km northeast, Linate, 5 km east and Piacenza, 50 km southeast. The center of the Po-Valley is mainly characterized by agriculture while another chain of midsize towns lines up on the southern rim from Alessandria to Bologna (Piacenza, Reggio Emilia etc). Several motorways are crossing the valley.

The different land use and population is also reflected in the regional emission pat-
terns. The main source of NO$_x$, VOC and ozone precursors is the core of the city of Milano with major extensions along the main motorways. The population of the inner city of Milano is shrinking since more than a decade with more people moving to the north into the prealpine hills. Thus, although decreasing in the center, overall the population in the greater Milano area is increasing.

After harvesting the remaining straw on the rice fields is burned to prevent from pests in the rice monoculture. The main visible sources for CH$_2$O and small particles are these numerous biomass burning fires. This fire activity is higher in the south than in the north.

3 Results

3.1 Ground based

All stations in both campaigns showed a pronounced diurnal variation of CH$_2$O on dry days without precipitation with maxima during the late morning and minima during the night hours. The complete data set is shown in Fig. 3a and b for 2002 and 2003, typical diurnal variations in Fig. 4. After the comparison week in 2002 CH$_2$O levels were rapidly decreasing in the city in early August due to the two weeks main holiday season and slightly increasing again after 12 August. These trends can be attributed to changes in local emissions. The northern and southern remote sites were by far less affected and showed more constant values throughout the campaign duration with the exception of three very clean days from 10 to 12 August during a föhn event. It is interesting to note that the diurnal maxima in 2002 were higher in the south than in the north. In 2003 the campaign began with variable conditions followed by a photochemical active period of about one week from 15 to 22 September with a pronounced increase of the nocturnal minima at the two northerly stations. Though the maxima in the south in this week also were the highest observed during the campaign the nocturnal minima remained at a low level.
As the emission situation in the south is very similar for both locations the two southern locations are believed to be comparable in this respect. There is no obvious reason for different emissions of CH$_2$O precursors or direct emissions in the vicinity of the two locations. Weather patterns and local anthropogenic emissions are reflected in the CH$_2$O daytime variability and nocturnal minimum levels. During episodes with high photochemical activity, temperatures, radiation intensity and emissions or pollution the diurnal variability can reach up to 4 ppb and the nighttime background values are increasing day by day within and in the vicinity of the densely populated areas up to 5 ppb. Other days (low and moderate polluted) show a variability of about 2–3 ppb and nighttime background values between 0.5 and 2 ppb. Nighttime minima were observed at all stations between 04:00 and 06:00 UTC in the morning. In 2002 with low and moderate pollution levels no significant differences between north and south in nighttime minima were observed.

To identify typical diurnal variations in different pollution levels three episodes without rainfall and frontal passages were selected from the whole data set and the average diurnal variability was calculated for at least five consecutive days. The cleanest conditions were found in the first week of August 2002, moderate conditions from August 12 to 19 and polluted conditions in 2003 from 15 to 22 September. The diurnal variations for three different scenarios, clean, moderate polluted and polluted, and the three locations are shown in Fig. 4a–i.

Within the diurnal variations some general features can be observed. The diurnal minimum was always observed between 04:00 and 06:00 UTC followed by a continuous ascent by 2–3 ppb within 4 h on all stations. Differences in the emission or pollution intensity are reflected in either enhanced background levels or the slope of morning CH$_2$O production rates. With additional traffic and anthropogenic emissions the rise rate of the morning peak increases. In the city the mixing ratio increased more than twice as fast, with 1.5–2 ppb/h, compared to ~0.7 ppb/h in the more remote locations north and south of the city. With increasing anthropogenic activity also the diurnal variability between maximum and minimum increases by about 0.5–1 ppb and secondary
afternoon or early evening peaks show up. In Bresso a midnight peak with a magnitude of \( \sim 1.5 \text{ ppb} \) was observed. The city location shows a similar pattern as it was observed in highly polluted conditions of Mexico City (De Gouw et al., 2009). After the main peak in the morning in the afternoon the CH\(_2\)O mixing ratios decrease rapidly and drop down to values close to the nighttime minima followed by a short secondary late evening or midnight maximum.

The diurnal patterns of CH\(_2\)O are dominated by local processes like vertical mixing or evolution of the planetary boundary layer as well as the temporal evolution of emissions. The rapid decline and the shape of the morning peak in Mexico (De Gouw et al., 2009) was attributed to dilution after breakup of the morning inversion layer concurrent with the development of the PBL from the nighttime inversion at \( \sim 200 \text{ m} \) up to \( >1500 \text{ m} \) above ground when additionally photolysis leads to a fast reduction of CH\(_2\)O levels. As CH\(_2\)O is rapidly photolysed during summer conditions with lifetimes of about 2 h (Behning and Wahner, 1998) high concentrations of formaldehyde during noon hours indicate strong sources in the vicinity. This is the case for the remote sites where during the day the production from biogenic precursors with a maximum during the noon hours is assumed to be the main source of CH\(_2\)O.

At the city location Bresso a direct impact of fresh emissions can be identified. The peaks are strongly dependent on wind direction and reflect the main emission pathways from traffic in the vicinity. In the Po-Valley the mixed layer is expected to be \( \sim 200 \text{ m} \) in the early morning and at \( \sim 800–1200 \text{ m} \) above ground at noon which would lead to a dilution of fresh morning emissions by a factor four to five. Probably the meteorology is less extreme as in Mexico and the break up of the morning inversion begins already before the morning rush hour in the city is terminated. Bresso had the highest mixing ratios during episodes with low wind speeds reaching up to about 15 ppb. The high variability and strong dependence from local sources is reflected in the smoothing and reduction of the maxima in a five day average to a level of \( \sim 9 \text{ ppb} \).

The two remote stations show a secondary maximum in the afternoon under moderate to polluted conditions at the time of the evening rush hour. The faster morning
increase due to traffic emissions is less significant compared to the city. A major difference between both sites was found in the most polluted week, when in Alzate the nighttime concentrations were comparable to those measured directly in the city.

Within previous campaigns (PIPAPO, Neftel et al., 2002) a strong transport system was observed between Milano and the mountain area north of Milano (Triangolo Lariano) which transported air from the flat polluted valley effectively into the mountains. Although sometimes visible in Alzate with regular changing wind directions in the diurnal cycle, during both FORMAT campaigns this wind system was not dominating. Winds were low to moderate and strong valley wind systems were not observed in the two main valleys of Lago di Como and Lago di Lecco, where the Monte Marenzo airfield is situated. The general trend during the high pressure episode (15 to 22 September) could be due to either an effective wind system, which was not observed from the airborne measurements, or from a similar anthropogenic emission in both, the city and the highly industrialized area north of the city, see also Fig. 2. Such emissions, increasing nighttime CH$_2$O levels are not visible in the agricultural dominated south.

3.2 Airborne

While in the first campaign flights were mostly performed north and east of Milano and typically aimed at the investigation of the vertical profile of CH$_2$O and at comparisons with the ground site at Alzate. Flights in the second campaign gave a more complete picture of the three dimensional distribution in the Po-Valley. On one day even a flight further east was performed for intercomparison with the Partenavia which was measuring power plant plumes in the eastern Po-Valley and for vertical profiles located more in the center of the valley. This is only possible in the airspace east of the line from Brescia to Cremona and requires to leave the direct vicinity of Milano.

The horizontal distributions in the well mixed boundary layer a few hundred m above ground during the day were generally in agreement with the ground based measurements and their diurnal variability. As special individual sources for CH$_2$O in the agricultural area in the south the frequent biomass burning fires were identified. Flying
directly through the fire plumes in low elevation, formaldehyde showed peak levels of up to 15 ppb on a background of ~4 ppm, though the residence time in the plume was only a few seconds, marked by the fast aerosol counter which indicated particle numbers >40,000/cm$^3$. As the instrument has a slow response time of 90 s this would correspond to peak levels of about 35 to 40 ppb in the plume. Injections of high concentrations of CH$_2$O into the well mixed planetary boundary layer by these agricultural activities increase the regional CH$_2$O mixing ratios. Their diurnal cycle is very similar to biogenic precursor emissions in otherwise remote areas and does not allow the discrimination between the two sources.

The meteorological conditions during the two campaigns resulted in different vertical distributions of CH$_2$O. During both campaigns the vertical distribution of CH$_2$O was controlled by vertical mixing processes with different time scales, the planetary boundary layer (PBL) during the noon hours was always well mixed which is a result of the fast mixing, within a few minutes, compared to the photochemical time constants for destruction reactions. Above the PBL significant formaldehyde levels were observed only in the presence of convective clouds which are pumping planetary boundary layer air into the free troposphere by cloud venting. During this process PBL air is transported through the cloud and is subject to wet chemical processes that are expected to remove CH$_2$O from the air to the liquid phase (Lelieveld and Crutzen, 1990). Part of the CH$_2$O reacts in the liquid phase to hydroxymethanesulfonate, HMS, a complex formed from CH$_2$O and S(IV) (Rao and Collet, 1995) or to formic acid, both reducing CH$_2$O gas phase levels within the presence of clouds (Lelieveld and Crutzen, 1990). Its not known how reversible these processes are in evaporating cloud droplets. In nonprecipitating clouds at least CH$_2$O, which survives conversion to HMS or formic acid, is released in higher elevations above the PBL and contributes to enhanced CH$_2$O concentrations in the cumulus cloud layer compared to the free troposphere. The result, a steady decline of CH$_2$O mixing ratios between cloud base, at the upper rim of the PBL and cloud tops starting at PBL concentrations at cloud base, indicates that the wet chemistry is probably not able to remove CH$_2$O significantly without precipitation. Above cloud
top level (~ 2500–3000 m) the CH$_2$O concentration drops to values below 1 ppb. An example is given in Fig. 5. The profiles were flown avoiding the clouds (VFR). Free tropospheric mixing ratios below 0.5 ppb (Kormann, 2005) were not observed within the altitude range, which extended just above cloud top.

Without convective clouds in the campaign 2003 the CH$_2$O mixing ratio drops more rapidly above the upper rim of the PBL to values of approximately 200 ppt concurrent to the drop in small particles and a drop in the absolute humidity. Figure 6 shows the results from vertical ascends and descends in the north and the south of the Po-Valley on 18 September 2003. Vertical mixing reaches higher altitudes in the north than in the south. The clear separation between planetary boundary layer and the free troposphere indicates that the main fraction of the CH$_2$O is located in the PBL as soon as transport processes are terminated.

A difference in the mixing height (Wiegner et al., 2006) can be due to a number of different processes. In case of a pronounced valley wind system ‘alpine pumping’ (Weissmann et al., 2005) a variability in the upper boundary of the PBL results from transport processes over tilted terrain, additional to these transport processes the thickness of the planetary boundary layer is a result of the shortwave energy conversion on the ground and thus on the albedo of the surface (Junkermann et al., 2009). Additionally the differences can be affected either by heat island effects of the city Milano (Weissmann et al., 2005) or by local thermal activity along the northern rim of the valley. A city plume would significantly increase the concentrations in the north of Milano. Given the variability and the uncertainties of the emissions from anthropogenic and natural emissions in the area and missing detailed characterization of the wind field from the experimental data neither from the ground measurements nor from the aircraft a city plume could be deduced although the model calculations and aircraft measurements from Liu et al. (2007a) indicate a plume like situation for 17 August 2002 above the main emission area northwest of Milano and within the high pollution episode the mixing ratios are higher in the north than in the south.
4 Model comparison

Comparing model calculations for the two format campaigns with the experimental data show pronounced differences. Model calculations for the FORMAT campaigns were performed by Liu et al. (2007a, b), using two different models, NILU RTCM (Regional Chemical Transport Model) (Flatoy and Hov, 1996) for 2002, and CAMx (Comprehensive Air Quality Model) (Environ, 2004) for the 2003 campaign. Both models were used and compared in Liu et al. (2007a, b) only for the city location Bresso and the northern site Alzate though the model domains include also the two southern sites. In the 2003 modeling activity a more easterly area was introduced which was considered to be free of local Milano pollution levels instead of the southerly site at the river Po. The model grid size for the NILU RTCM is $15 \times 15$ km with up to 30 vertical layers, CAMx was applied with a nested version and has $27 \times 27$ km for the coarse resolution and $9 \times 9$ km in the fine grid with ten vertical layers up to 4000 m above ground level.

In the calculations for 2002 we observed a reasonable correlation between measurement and model, both in the diurnal variability between maxima and minima as well as less precise in the timing of morning rise time. The model shows an additional late evening peak in the HCHO mixing ratio which is concurrent with a similar peak in the model CO. The duration of both late evening peaks is about two hour which is probably an artifact from the emission inventory. The horizontal distribution in the model gives higher mixing ratios in the north than in the south. The opposite trend with higher mixing ratios in the south, observed in the experimental data, could not be confirmed. From the model about 30–50% lower values would be expected for the southerly locations.

For 2003 calculations were done for three domains within the Po-Valley, the center of Milano, the northern station of Alzate and an area east of Milano (area 3) which was assumed to be not influenced by the emissions of Milano. This area is similar in agricultural land use to the southern location Spessa though the surroundings of Spessa have an even more pronounced rice monoculture. Although using a better spatial resolution the CAMx model performed similar in the diurnal variability but worse for the timing of
the diurnal patterns in the 2003 model exercise than the NILU RTCM. The timing of CH$_2$O maxima and minima is shifted by more than six hours to the evening although the model diurnal patterns of ozone and nitrogen oxides were in good agreement with the experiment. The CAMx model produced an even stronger evening peak than the NILU RTCM in formaldehyde and was not able to match the morning ascend in the mixing ratios properly. Also the patterns and again the maximum levels in more remote areas, not affected by Milano anthropogenic emissions (e.g. area 3 east of Milano, Liu et al., 2007b), are underestimated compared to the agricultural environment at Spessa.

For the vertical distributions model results are available only for the 2002 campaign. The agreement with the aircraft vertical distributions is better than the horizontal distributions. As the model strongly suppresses exchange between the planetary boundary layer the model profiles show a more pronounced step function of the mixing ratios at the upper rim of the PBL similar to what has been observed in the more stable conditions in 2003.

5 Summary and conclusions

Formaldehyde measurements have been performed in two campaigns in 2002 and 2003 during summer conditions in one of Europe’s most polluted areas at three different ground based sites “upwind”, in the center and “downwind” of the Milano metropolitan area and from a small aircraft operating on a regional scale and climbing up to the free troposphere. The conditions covered humid and cloudy conditions as well as dry high pressure situations and also a period with reduced anthropogenic emissions. Formaldehyde mixing ratios on the ground showed a pronounced diurnal variability on all three sites with a significant signature of local anthropogenic production only in the center of Milano where mixing ratios up to 15 ppb were occasionally observed. Both locations outside the city exhibited diurnal patterns typical for compounds generated by secondary photochemical reactions. The more remote southerly agricultural locations had surprisingly high CH$_2$O mixing ratios, which are up to a factor of two
higher than calculated by the two regional chemistry transport models which assumed a low wind speed situation with slow transport of pollution from Milano into the foothills of the Alps. These high formaldehyde levels would require either additional biogenic precursors or anthropogenic activities with a similar diurnal pattern. Biomass burning of rice straw at the end of the growing season could be identified as an important anthropogenic source of small particles and formaldehyde from frequent distributed local sources which has a similar diurnal pattern as biogenic emissions. Differences between model and experiment are most probably due to the uncertainties in the emission inventories, especially in the diurnal cycle and magnitude of direct anthropogenic emissions.

References


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Table 1. Aircraft instrumentation during the FORMAT campaign.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Instrument</th>
<th>Time-resolution</th>
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<tr>
<td>Ozone</td>
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</tr>
<tr>
<td>CH$_2$O</td>
<td>Fluorimeter</td>
<td>90 s</td>
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<tr>
<td>Act. Rad. 300 nm JO1D</td>
<td>2 Filterradiometers ‡↑</td>
<td>1 s</td>
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<tr>
<td>Act. Rad. 380 nm JNO$_2$</td>
<td>2 Filterradiometers ‡↑</td>
<td>1 s</td>
</tr>
<tr>
<td>Global radiation</td>
<td>2 LICOR Pyranom. ‡↑</td>
<td>2 s</td>
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<td>Aerosols/size distr.</td>
<td>GRIMM spectrometer</td>
<td>6 s&gt;0.3–20 µm</td>
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Fig. 1. The map shows the research area of Milano from the pilots view (with airspace information). Ground stations are marked with colored dots, airports/airfields with circles and landing strip indicator. Larger airports in the vicinity with extended control zones are Malpensa, Linate, Bergamo. The dotted lines in the north and the south indicate the boundaries of the 2000 ft (600 m above msl) allowed airspace for flights under visual flying rules. In the north up to 9000 ft maximum altitude are allowed, in the south 4500 ft above sea level. The reddish marked areas are the approach zones for the larger airports, Airspace D, with additional flying restrictions also in low altitudes.
Fig. 2. Ozone precursors and NO\textsubscript{x} emissions in the region Lombardia, the Milano area is the western half of the picture. The main motorways are clearly marked by the high NO\textsubscript{x} emissions. (http://www.arpalombardia.it/qaria/doc_MappeEmissione.asp).
Fig. 3. Half hour average concentrations of CH$_2$O at the three sites in the Po-Valley, Alzate in red (north) Bresso, green (Milano center) and Casinazza /Spessa, blue, (south). Note the different mixing ratio scales at Bresso.
Fig. 4. (a)–(i) Average diurnal variations of CH$_2$O at three different sites, for clean, moderate and polluted conditions, increasing pollution from left to right. A minimum of five consecutive days was used to calculate the diurnal patterns. The grey vertical bars give the variability of the underlying half hour averages. Note the larger mixing ratio scale under polluted conditions in Bresso (f).
Fig. 5. Vertical distribution of formaldehyde north of Milano under conditions with scattered convective clouds and low pollution levels in the PBL (~5000–8000 ultrafine particles/cm³), 15 August 2002. Clouds between 1500 and 2500 m. Colors indicate ascent and descent within ~30 km.
Fig. 6. Vertical profiles of formaldehyde in the north and south of the Po-Valley, 18 September 2003, under cloud free conditions, red and green profiles in the north (11:30–12:30), yellow and blue south of river Po (13:30–14:00). 20–40000 small particles/cm$^3$ > 10 nm, typical for moderate polluted conditions. Colors indicate ascents and descents.