A New Portable Instrument for Continuous Measurement of Formaldehyde in Ambient Air

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ABSTRACT

A new instrument for the in situ measurement of formaldehyde with online concentration output was built on the base of the Hantzsch chemistry fluorimetric detection of formaldehyde in liquid phase. The instrument was specially designed for applications in a fast-changing environment, for example, in airborne research. Individual instrument components were optimized to reduce size, weight, and power consumption and to improve response time. The small size, battery-operated system was shown to reach good performance, stable sensitivity, and detection limits of <100 ppt for temperatures between 0° and 35°C during aircraft flight missions in field campaigns in the Italian Po Valley. The instrument proved its performance with formaldehyde mixing ratios ranging from 0.5 to 25 ppb.

1. Introduction

Formaldehyde in the atmosphere is one of the important compounds for photochemical reactions leading to production of radicals and secondary photooxidants. Its photolysis products are significant radical sources, especially in fall and winter months when the radical production from ozone photolysis becomes less important due to low ultraviolet radiation levels (Kleinmann 1991). Formaldehyde is produced naturally by oxidation of methane and many other nonmethane hydrocarbons and photochemical decomposition of isoprene, but it is also directly emitted in biomass burning events. In anthropogenic polluted areas it was found in peak values of up to 70 ppb in Los Angeles, California, street canyons, indicating an emission from traffic exhaust (Grosjean et al. 1983); up to 40 ppb in downtown Mexico City, Mexico (Grutter et al. 2005); and 60 ppb inside a Rio de Janeiro, Brazil, street tunnel (Grosjean et al. 1990). It is a widely used solvent for a variety of chemical products. In remote areas mixing ratios were found between 2.5 ppb and below 0.5 ppb (Slemr et al.

1996; Junkermann and Stockwell 1999). From satellites it can be detected worldwide, with high concentrations in areas downwind of huge forest areas (southern United States, Amazon basin, central Africa) and in areas with heavy pollution like Belgium, northern Italy, and industrial areas in Southeast Asia (Chance et al. 2000; Wittrock et al. 2000). Formaldehyde can thus be used also as an indicator for anthropogenic activity. The database about the distribution of formaldehyde in the atmosphere is still very limited despite its importance in environmental chemistry. This is mainly due to the lack of suitable instrumentation for monitoring.

Measurement techniques for formaldehyde in ambient air are available utilizing either spectral absorption [differential optical absorption spectroscopy (DOAS), also from satellite or Fourier transform infrared (FTIR) spectrometry] or chemical reaction in the liquid phase [2,4-dinitrophenylhydrazine (DNPH), fluorimetry]. For an overview and a recent comparison of the most common techniques see Hak et al. (2005). The spectroscopic methods need light paths in the range of kilometers to reach the required detection limits for remote atmospheric measurements and are thus mainly used for specific research projects. Multipath optical cells are required to fold the light path for local applications (Hak et al. 2005). DNPH cartridge sampling is the technique used in most monitoring programs. It has a poor time resolution and requires after-sampling analysis at

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an analytical laboratory. For continuous in situ monitoring with online concentration output, within the last decade instruments based on liquid phase fluorimetry were developed. These instruments, developed by the Institute for Meteorology and Climate Research (IMK-IFU, Garmisch-Partenkirchen, Germany), are based on the technique using fluorimetric instruments in Lazrus et al. (1988) and Kelly and Fortune (1994). The first reported sensitive technique with detection limits below 200 ppt, the enzyme chemistry of Lazrus et al. (1988) has the disadvantage that the chemicals used are extremely expensive, sensitive, and unstable during storage. This technique was used for several years for measurements in remote continental areas by Slemr et al. (1996), airborne applications by Heikes et al. (1996), and in maritime environments by Junkermann and Stockwell (1999). The Hantzsch chemistry based on the reaction of formaldehyde with acetylacetone (Schneider et al. 1903; Nash 1953) introduced by Kelly and Fortune (1994) promised to be cheaper for routine operation, more simple in instrumental design, and faster although the original data presented by Kelly and Fortune (1994) still show high zero drift and noise not suitable for fast measurements at low mixing ratios. Similar instruments, further improved and built as a commercial version within the IMK-IFU, with current detection limits under laboratory conditions below 30 ppt are now widely used for research, even in very clean environments in the Antarctic and on board aircraft (Riedel et al. 1999; Kormann et al. 2003). They are designed for use within a laboratory or similar temperature-stable environment. Operation of such an instrument on board an open research aircraft (Junkermann 2001) required a significant redesign of the components to obtain a rugged, simple, temperature-independent, and dc-voltage operated system. The instrument described here was built for outdoor use under rapidly changing environmental conditions.

2. Design of the formaldehyde monitor

The technique for the measurement of gas phase formaldehyde using the fluorimetric Hantzsch chemistry in the liquid phase requires the transfer of formaldehyde quantitatively from the gas phase into the liquid phase. Then, within the liquid phase, the sensitive analysis can be done. The stripping of water-soluble formaldehyde from air occurs in a stainless steel, temperature controlled, stripping coil with well-known surface area and gas and liquid flows. Steel is used as it is simpler to maintain at a stable temperature than glass. Gas and liquid flow are separated downstream of the

coil, and the liquid is subsequently analyzed. The operating parameters of the stripper are similar to the original design of Lazrus et al. (1988). Settings are gas flow 1 L min^{-1} at 20°C, 1013 hPa and liquid flow 0.42 mL min^{-1}. A mixing ration of 10 ppb of formaldehyde in the gas phase leads to 10^{-6} mol L^{-1} solution at the exit of the stripping coil, assuming all molecules of the water-soluble gas are transferred into the liquid phase. The collection efficiency was measured with two instruments in series. The technique is calibrated using liquid standards and calculating the gas phase concentration from the enrichment factor between gas and liquid flows in the stripper. With a liquid phase detection limit of 3×10^{-9} mol L^{-1} ($3\,\sigma$), the resulting gas phase detection limit with the afore mentioned settings is 30 ppt. This is the performance currently reached in the laboratory for zeroing intervals of 6 h. Reduction of the liquid flow improves the detection limit (the same number of molecules is transferred into a smaller liquid volume) but has, at the same time, the disadvantage of increasing the residence time and the time lag between sampling and signal output. This is especially critical for aircraft measurements as the time lag is slightly pressure dependent and the mobile platform requires a minimum time resolution of about 90 s for a reasonable vertical resolution at climbing rates of about 3 m s^{-1}. The minimum liquid flow rate with a stable liquid flow is 0.25 mL min^{-1}. Below this flow rate, with the current dimensions of the stripping coils, the signal gets noisy as a result of incomplete wetting of the coil walls by the 0.1N H$_2$SO$_4$ scrubbing solution. As a compromise between sensitivity and detection speed the new instrument was designed for 0.35 mL min^{-1} stripper flow. For a constant and stable sampling efficiency the air and liquid flows must be stabilized and known as well as possible, and the stripper has to be kept at a fixed temperature (10°C for the current instrument). To control the airflow a Honeywell mass flow sensor with ±1.5% accuracy and precision better than 0.5% is used. Its flow signal controls a small dc pump to maintain the airflow. The liquid flow is stabilized by a peristaltic pump, also within ±0.5%. To obtain a maximum of time resolution and detection limit the individual components of the instrument have to be optimized as detailed in the following section.

3. Optimization of the stripper

The length of the stripping coil is one factor that determines sampling efficiency and time resolution. Too long a stripping coil increases the time constant of the technique, preventing rapid changes upon changing

atmospheric mixing ratios and uncertainties due to variable water vapor mixing ratios in ambient air. Additionally, the stripping efficiency is pressure dependent. Reduction of the pressure reduces the stripping efficiency. The stripping coil was thus optimized to be as short as possible while still obtaining a minimum of 98% sampling efficiency at 600-hPa pressure. This is about the maximum altitude for an nonpressurized aircraft, the first application for the instrument. At every altitude below this level, the sampling efficiency would be greater than 98% due to the longer residence time of the formaldehyde in the stripping coil. The coil inner diameter is 2 mm; its total length 120 cm. Variable water vapor concentrations affect slightly the amount of stripping solution at the end of the stripper. The air leaving the stripper contains 100% relative humidity at $10°C$, or ~ 0.016 g L^{-1}. Sampled air with 100% relative humidity at $20°$ contains about twice this amount of water and the excess water (~ 0.015 mL) is trapped in the stripper, diluting the stripping solution with 3.4% additional water. At lower temperatures the stripping solution will be concentrated by a maximum of 2%. The effect can easily be corrected when additional humidity measurements are available. The rate of liquid lost or gained, D_w, (mL min^{-1}) is given by Magnus formula

$$D_w(\text{mL min}^{-1}) = 0.0778 \times \text{rh} \times \exp[17.5t/(241.2 + t)]$$
$$- 0.015\,62,$$

where rh is relative humidity (%) and t is temperature (°C).

Lower temperatures in the stripping coil would be favorable for sampling efficiency but will increase condensation problems and cooler requirements. The stripping coil is kept at constant temperature ($10°C$) by means of a small thermoelectric cooler. The unit is designed for temperature differences of up to $25°C$ at a maximum ambient temperature of $35°C$.

4. Reactor design

After separation of gas and liquid, 0.15 mL min^{-1} of the "Hantzsch" reagent is added to the liquid flow and the mixture is subsequently passed through a stainless steel reactor kept at $65°C$. The Hantzsch reagent consists of 1 mol L^{-1} ammonium acetate, 0.04 mol L^{-1} acetic acid, and 0.02 mol L^{-1} 2,4-pentanedione (acetylacetone). The formaldehyde signal, as well as the background signal, is strongly dependent on the temperature and residence time in the reactor. Long residence times result in a more complete chemical reaction but

increase dramatically the background signal. The optimum signal to noise ratio is obtained with $\sim 85\%$ chemical conversion within ~ 60 s residence time. This is achieved with a reactor length of 80 cm and 1-mm inner diameter. At higher residence times the background signal increases more rapidly than the signal.

5. Fluorimeter layout

A specially designed one-channel $90°$ fluorimeter with a 3 mm $\times$ 3 mm $\times$ 10 mm quartz fluorescence cell (Hellma) is used for continuous-flow fluorimetric detection. As already pointed out by Kelly and Fortune (1994), the fluorescence can be excited by two wavelengths, either 254 or 410 nm, with better fluorescence yield but higher background signal for the shorter wavelength. The first prototype of the instrument and the current commercial version, thus, are all equipped with mercury lamps, either with or without phosphor coatings. The main problems with these lamps are their temperature dependence of the radiation output and their own heat production. To stabilize the lamps a complex active regulator circuit with thermally decoupled sensing diodes was necessary. With the first light-emitting diodes (LEDs) appearing in the mid-UV range this problem was solved. The new fluorimeter was built with a 5-mm blue LED (383UBC, Roithner Lasertechnik, Vienna) with peak wavelength at 430 nm. Some other advantageous properties of the LED could be used to shrink the size of the unit. The mercury lamp design requires two lenses within a 60-mm optical arm to feed light into the fluorescence cell with the excitation filter mounted between the lenses. Compared to the mercury lamp, the LED has a narrower angle ($12°$) of light emission. The window of the fluorescence cell is 3 mm wide and 10 mm high. The LED thus could be mounted 7 mm in front of the cell window directly on top of the wavelength selection interference filter (400FS70–12.5, Andover Corp., 6.2 mm thick) without any further optical components and significant loss of light. The slight angular variation of the light path for a fraction of the light does not disturb the desired wavelength selectivity.

Also, the fluorescence detection side could also be appreciably reduced in size for this instrument. The fluorescent light at 500 nm is filtered with a long-pass glass filter (GG495, Schott, 4 mm). Compared to the original design with two lenses within the 60-mm detection arm, the glass filter is now directly mounted in the housing of the photomultiplier window of a small-size hybrid photomultiplier unit (R7711–05, Hamamatsu). The effective surface of the 13-mm side on
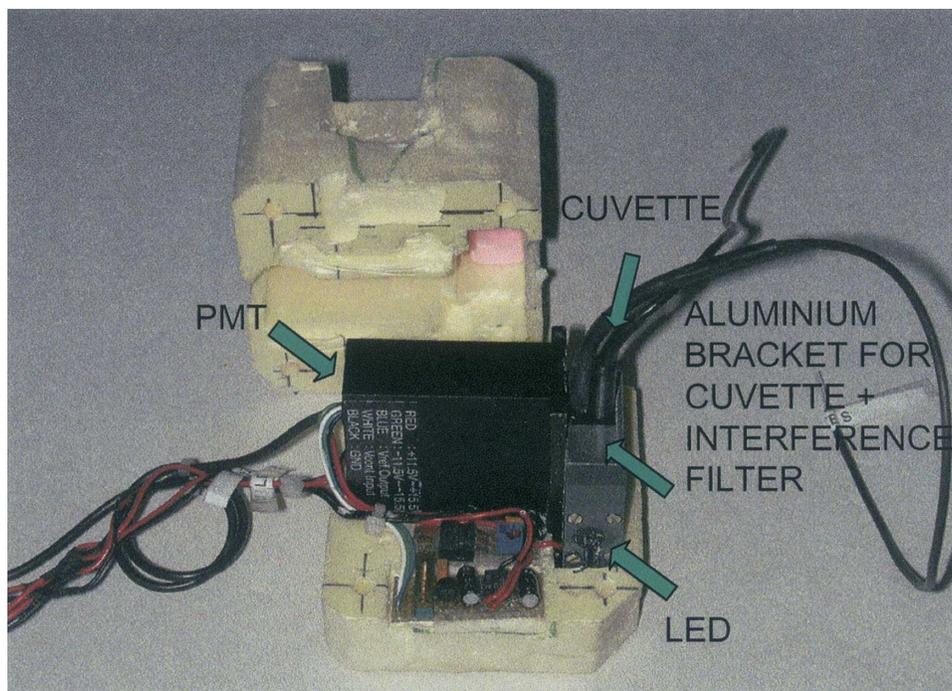
FIG. 1. The LED fluorimeter with temperature control, constant current supply, and photomultiplier sensor module in its temperature shield. LED, interference filter, and cuvette are mounted together on a small aluminium bracket connected directly to the photomultiplier module housing.

multiplier within this unit is twice as large as the fluorescence cell window and thus receives a very high fraction of the emitted light without the need of any focusing optics. The new hybrid photomultiplier tube (PMT) assembly additionally is only 51 mm $\times$ 53 mm $\times$ 19 mm in size. Omission of most of the optical components and the use of smaller components allowed us to built a very small size unit (Fig. 1). The reduction in size also allowed the whole fluorimeter unit to be enclosed with insulating material and to be temperature stabilized at 35°.

The new fluorimeter was the main improvement for a rugged space- and energy-saving instrument. Although the wavelength is less favorable, the better temperature stabilization compensates for this disadvantage. The new fluorimeter achieved a detection limit in the liquid phase for 6-h zeroing intervals of 4×10^{-9} mol L^{-1}.

6. Liquid flow

The last problem to be solved was a liquid flow system that was small in size, had long-term stability, and could tolerate bubbles within the flow lines. The commercial version uses an eight-channel peristaltic pump (Ismatec CH, Glattbrugg, Switerland), of which six channels are used. New small-size piezoelectric pumps have appeared on the market but, up to now, none are able to handle the chemicals used in the Hantzsch formaldehyde chemistry and to cope with bubbles in the liquid flow. Thus, the current solution still works with a peristaltic pump, but the number of tubings was reduced to four. The original large pump motor was replaced by a new small-size stepper motor. The peristaltic pump is stable for about 4–6 weeks of operation after an initial conditioning phase of about 3 hours after replacement of the tubing. The critical stripping-solution flow can be simply checked from the consumption of stripping solution using a volumetric storage container.

Finally, the whole instrument was built into a small box of 18 cm $\times$ 18 cm $\times$ 25 cm size, including the liquids for operating up to six hours. The total weight is below 2.5 kg, exclusive of batteries and data acquisition, a suitable starting point to build a portable, battery-operated instrument.

The instrument consists of separate stripper, reactor, and fluorimeter modules. Each module runs from any unstabilized 12–14-V dc supply and contains a separate temperature control unit, providing a 5-V signal as a control whether the operating temperatures are

reached and are within 0.2° of their set points. The fluorimeter unit delivers the measurement response signal and the temperature digit, which significantly reduces the requirements for data acquisition.

7. Calibration

Zeroing signals are obtained by passing the ambient air through a filter cartridge containing a Hopkalit catalyst (Dräger, Lübeck, Germany). For the span signal liquid standards with 10^{-6} mol L^{-1} are applied to the stripping-solution line. The preparation of this standard is done by dilution of a long-term stable 10^{-2} mol L^{-1} working standard using stripping solution for dilution. For gas phase standards a small stand-alone permeation unit is available, delivering about 8 ng min^{-1} of formaldehyde from a Kintek wafer; 8 ng min^{-1} within 1 L of air at 20°C corresponds to a mixing ratio of 6 ppb. For a stable output this calibration source needs to be operated continuously 24 hours a day. It is the preferred system for automatic calibration for long-term monitoring since diluted formaldehyde solutions are not stable for long term. To reduce the weight as far as possible in aircraft applications it is used only for ground-based checks of the air inlet and the efficiency of the zero trap.

8. Data acquisition and instrument control

In the aircraft application, the instrument is controlled by a commercial datalogger from Vaisala, Finland (QLC50). This datalogger is able to read the signals, to switch valves with TTL signals, and to calculate directly online mixing ratios (in parts per billion) and distribute these data via RS232 or CAN two-wire data network.

9. Interferences

Kelly and Fortune (1994) presented a list of possible interfering compounds that were tested as negative. Among those are acetaldehyde, benzaldehyde, propionaldehyde, butyraldehyde, acrolein, acetone, methyl ethyl ketone, methyl isobutyl ketone, formic acid, and methanol. No interferences were found. A good correlation between the Hantzsch technique and the spectroscopic DOAS technique was found also in smog chamber experiments up to 120 ppb (R. Volkamer 2002, personal communication) with significantly higher mixing ratios of other organic compounds than present in the ambient, even a heavily polluted atmosphere. Ozone, one of the main components of atmospheric trace gases, affects similar techniques for other compounds, for example, the technique for the detection of hydrogen peroxide (Lazrus et al. 1986). We therefore investigated a possible ozone interference. A positive interference of 200-ppt formaldehyde signal for 100 ppb of ozone was found that was linear and independent of changes in the relative humidity. This has to be taken into account for measurements at very low levels of formaldehyde, as, for example, found in the southern Atlantic and in the free troposphere. Sulphur dioxide was also found to have no measurable effect at mixing ratios below 100 ppb.

10. Performance of the new formaldehyde monitor

The small-size formaldehyde monitor was used successfully during field campaigns of the European Community Formaldehyde as a Tracer of Oxidation in the Troposphere (FORMAT) project (information available online at www.nilu.no/format) onboard the small research aircraft D-MIFU. Figure 2 shows the instrument installed in an aircraft instrument pod. Flights were performed within the Po Valley in the area of Milan, Italy, and extended from ground level up to about 3000 m. Instrument temperatures during these flights varied by more than 20°. Although a detection limit of 4×10^{-9} mol L^{-1}, corresponding to a gas phase mixing ratio of 40 ppt, was obtained in the laboratory during the field campaign, the performance was slightly worse. Nevertheless, a detection limit of 100 ppt was still achievable. One critical point in previous applications was the stability of the zero baseline. This zero baseline now is stable within less than 50 ppt for all conditions and was measured every two hours during the flights and every time maximum altitude was reached. Further, we checked the repeatability of the response on a liquid standard solution. The precision of repeated measurements of the same liquid standard was better than 5% over the whole temperature range 0°–35°C. Stability of the operating solutions is another issue for ambient measurements. It is recommended that the Hantzsch reagent be stored at temperatures below 5°C to prevent zero-baseline drifts and possible sensitivity changes. On our small aircraft the liquids were not refrigerated but were simply kept in Nalgene high-density polyethylene (HDPE) bottles inside the instrument pod. Within four hours of a typical flight mission the zero background did not increase by more than 150 ppt. With several zero baselines taken during the flight, this effect was taken into account in the final data analysis. The sensitivity proved to be stable within less than 5%. It should be noted that during the FORMAT field campaign (see also Fig. 3), in a second instrument with the same modular design and similar
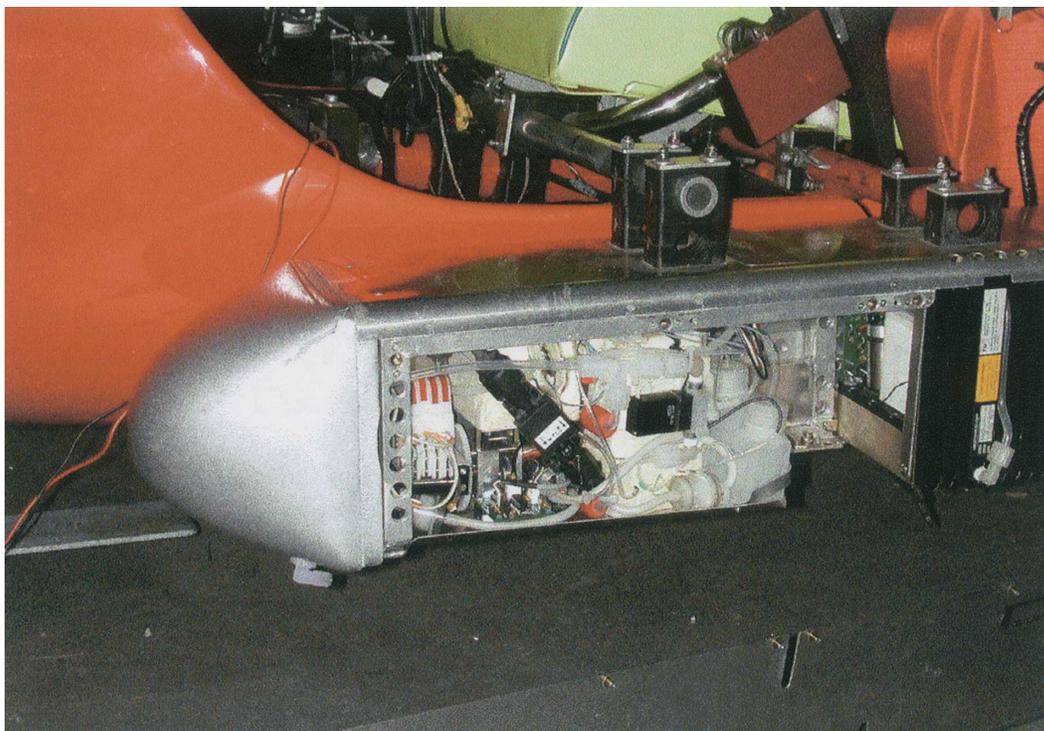
FIG. 2. Formaldehyde monitor mounted inside the instrument pod of the microlight research aircraft D-MIFU, including reservoir bottles for operating liquids and waste. The PFA inlet line is protected by an inline aerosol filter. For flight missions the pod is closed with an aluminium cover without any further thermal isolation.

but different setup and not temperature stabilized liquid storage, more serious problems with a drifting zero baseline were encountered (J. Dommen 2003, personal communication). In addition to storage temperature, contamination of the reagents by trace compounds in the ambient air may cause a zero drift. In critical applications and long-term measurements we thus add small zero traps to the venting lines of the reagent bottles, filled with the catalyst Hopkalit.

Time resolution depends on the flow-rate settings. With 0.40 mL min^{-1} liquid and 1 SLPM gas flow, the time to reach 90% of the final value is 90 s. The total delay between sampling and display of the formaldehyde concentration is less than 3 min. With the stripping-solution flow reduced to 0.35 mL min^{-1}, the delay time is close to 4.5 min. Figure 3 shows the results of a flight on September 2003 around Milan at low altitude with an ascent into the clean atmosphere up to 2700 m AGL north of Milan and a passage of a small biomass-burning plume in the agricultural area to the south. Within the planetary boundary layer formaldehyde mixing ratios were between 5 and 8 ppb with higher values to the north of Milan. Above the boundary layer the mixing ratios rapidly decreased to less than 500 ppt. In the rice straw fire plume the formaldehyde signal increased up to 12 ppb despite the short aircraft transit time of only 12 s within the plume indicated by the fast (1 s) particle counter signal. Due to the slow instrument response of the formaldehyde monitor to a short spike of a few seconds of enhanced formaldehyde in the sample air, this spike is smeared out over the next 3 min. Recalculation of the short-time formaldehyde variation from the slow signal results in an in-plume mixing ratio of about 25–30 ppb, assuming that formaldehyde is distributed in the rice straw plume in a pattern similar to that for small particles.

11. Summary

A new rugged portable instrument for the measurement of ambient air concentrations of formaldehyde was designed specifically for use under rapidly changing environmental conditions during aircraft campaigns. Special emphasis was put on the stabilization of the instrument components to overcome an apparent drift of span and zero baselines observed in previous instrument versions. This is a basic requirement for stable online calculation of formaldehyde concentration. The instrument proved to fulfill the requirements for pressure and temperature stability during measurements on
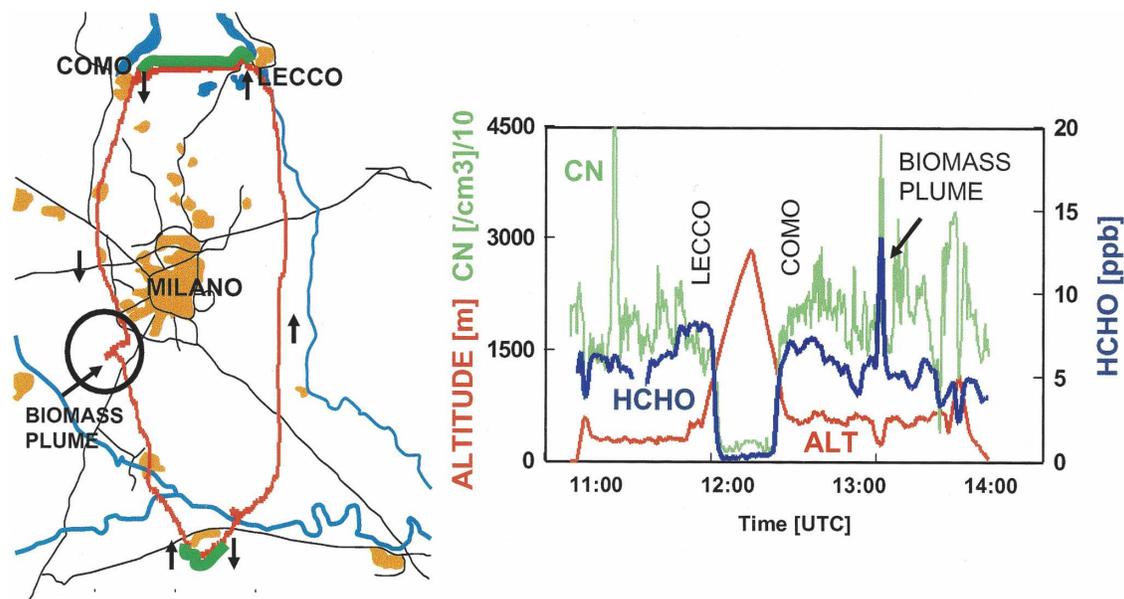
FIG. 3. (a) Research area and flight track in the Po Valley. (b) Formaldehyde mixing ratio (blue), flight altitude above ground (red), and small particles >10 nm and <1000 nm (green, divided by 10) along the flight track. Marked in black: passage through the plume (<20 s) of a rice straw biomass fire with more than doubling of the signal despite poor time resolution. Thick green lines parallel to the flight track indicate the parts of the track above 600 m AGL. The fast aerosol signal is used during the flight to separate different air masses.

board an open research aircraft to calculate online mixing ratios of formaldehyde with a zeroing interval of 2 h. In field use of this instrument, the detection limit was about 100 ppt, somewhat worse than the 40 ppt observed under controlled laboratory conditions. The 100-ppt detection limit still allowed quantitative measurements under remote conditions. The instrument was used successfully during an international field campaign in the Italian Po Valley, measuring a range of formaldehyde mixing ratios from 500 ppt to more than 25 ppb.

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