Formaldehyde record from Lys Glacier firn core (Monte Rosa massif, Italy) and agreement of its profile with corresponding meteorological conditions

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Introduction

FORMALDEHYDE IS A VERY TOXIC URBAN POLLUTANT (EYE-IRRITATING EFFECT AND IRRITATION OF THE RESPIRATORY TRACT RESULTING IN ASTHMA-LIKE SYMPTOMS) AND HAVE A CARCINOGENIC EFFECT

Thus this compound in anthropic environments recently have received more attention (WHO, 1987)

FOR THE REASONS ABOVE, THE FORMALDEHYDE HAS BEEN DETECTED:

in the atmosphere
in aerosol phase (Grosjean 1982) and
in gas phase (Báez et al., 2001; Largiuni et al. 2002a)

In the literature concentrations of formaldehyde in air as high as 24.8 or 32.7 µg m^{-3} in very polluted areas are reported (Báez et al., 1989; de Andrade et al., 1995) In Florence (Italy) mean/maximum formaldehyde concentrations of 3.3/23.4 µg m^{-3} were measured (Largiuni et al., 2002a)

in rain water collected in urban areas (Kieber et al., 1999; Largiuni et al., 2002a)

Because of the high formaldehyde solubility in water, its rain concentration often is very high; the mean/maximum formaldehyde content in rain collected in Florence was 98/443 µg l^{-1} (Largiuni et al., 2002a)

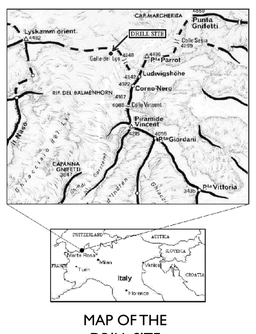
ONLY A FEW DATA IN SNOW OR ICE INSTEAD ARE AVAILABLE.

Formaldehyde is involved in relevant photochemical processes: it is an important component in the control of the oxidizing capacity of the troposphere and its concentration in firn and ice cores provides information about the oxidation capacity of the past troposphere (Fuhrer et al., 1996; Hutterli et al., 1999). At present, few data from alpine ice core are available in literature (Houdier et al., 2000) in spite of the ability of these archives to give high resolution records back to pre-industrial period.

High elevated cold glaciers in the Alps contain in fact a record of precipitation chemistry over many centuries. Due to their location close to the densely populated and industrialised areas of western Europe they provide important information of human's impact on the environment and may offer the opportunity to study the atmospheric long-range transport and local patterns of formaldehyde distribution.

DATA ON FORMALDEHYDE CONCENTRATION WITHIN FIRST 16 M OF LYS GLACIER FIRN CORE (MONTE ROSA MASSIF – ITALY) ARE PRESENTED HERE.

Experimental phases



MAP OF THE DRILL SITE

The study area is characterized by high-altitude conditions: the air temperatures are practically persistent sub-zero throughout the year, the precipitation rates and the wind speed are very high (Suter and Hoelzle, 2002).
Because its high altitude (4248 m a.s.l.), with temperature at 10 m depth of –10.2°C indicating the mean annual temperature below the melting point (Smiraglia et al., 2000), the Colle del Lys glacier can be considered a "cold glacier" in according to Harberli & Alean (1985) conditions.

The dating of the ice core was established by annual layer counting using the strong seasonal pattern of NH_4^+ concentrations and $\delta^{18}O$ values, revealing that the core covers a period of two years and a half, from June 2000 to the beginning of 1998, with a mean annual accumulation rate of 3.79 m w.eq. The use of several seasonal parameters allowed us to reduce the uncertainty in the core dating.

Wind crusts along all the firn core are absent and the pattern of the seasonal markers is regular, with winter signals well preserved, indicating that the wind scouring effects do not disturb significantly the entire record. Moreover, no melt-layers were found in the top 18m of the core; the absence of melt guarantees a continuous record of the climate and environmental history in the firn and ice.

COLLE DEL LYS
Sampling of firn core

The 23.75 m depth firn core was drilled in June 2000 on the Colle del Lys (Monte Rosa, Italy), at 4248 m a.s.l., but only the upper 18 m was used because the quality of the core.
The drilling system, already used during the PNRA (Italian National Research Antarctic Programme), is able to reach a maximum depth of 150 m to obtain cores measuring 50-80 cm in length and 98 mm in diameter.
Before storing for the transport, the logging of length and weight was done, and the density of the firn was calculated on site.

UNIVERSITY OF MILANO-BICOCCA
Sub-sampling

After logging, individuals cores were sealed into polyethylene plastic bags and transported frozen to the Laboratory of Glaciology of Environmental Sciences Department, University of Milano-Bicocca, Italy, for sub-sampling. In a cold room at –25°C the external 1-1.5 cm of the core was removed in a mechanical lathe with a stainless-steel tool.
The inner part (80-70 mm diameter) was cut into 16 cm sub-samples for analysis of chemical species, stable isotope and atmospheric dust. The sub-samples were immediately put in the pre-cleaned polyethylene 250 ml containers placed in double polyethylene bags to minimize contamination risks.

UNIVERSITY OF FLORENCE - *Chemical analysis*

The sub-samples were transported frozen to the Analytical Laboratory of the Chemical Department of the University of Florence where they were kept frozen at –20°C and preserved until the time of analysis.
Formaldehyde content was determined in 100 samples with a mean resolution of 16 cm. Formaldehyde determination was performed with a spectro-fluorimetric method based on the formation of diacetyldihydrolutidine, a fluorescent compound, by the Hantzsch reaction between formaldehyde and acetylacetone, acetic acid and ammonium acetate.

A detailed description of the analytical apparatus and of the method performances is reported in Largiuni et al., 2002b. Control blanks were tested for the sampling and analysis procedures and for the cleanliness of the containers, which showed contamination values below 0.11 µg l^{-1} for formaldehyde, about two orders lower than the concentration values determined in the samples. On the same samples also ionic content was determined by Ion Chromatography methods elsewhere described (Udisti et al., 1991; Udisti et al., 1994; Piccardi et al., 1994).

CHEMICAL PROFILES AND THEIR SEASONAL BEHAVIOUR

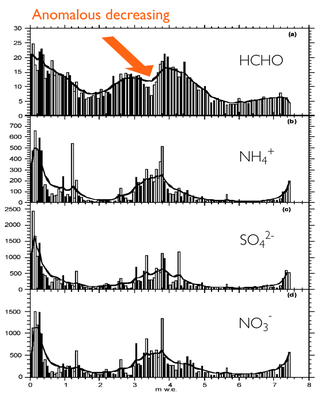


Figure 2 – Concentration versus depth profiles of HCHO (a), NH_4^+ (b), SO_4^{2-} (c) and NO_3^- (d). Depth is expressed as m of water equivalent (m w. eq.). Bars mark the samples concentration; the bold lines represent the order 10 smoothed profiles. One the left side of the diagrams concentrations are reported in micrograms per liter

Figure 2a shows the formaldehyde concentration/depth profile for the depth range analyzed (16 m) in the firn core. Bars mark the samples concentration, expressed as µg l^{-1}; the bold line shows the smoothed profile (10-samples moving average). The depth scale is reported as meters of water equivalent (m w.eq.). A waving pattern ranging from minimum values around 4 µg l^{-1} and maximum values around 25 µg l^{-1} is evidenced by the formaldehyde profile; the highest peaks are recorded at the surface and at 3.8 m depth but another slightly lower peak is detectable at 3.6 m depth.
For a seasonal characterisation, the same figure reports the ammonium (Figure 2b), sulphate (Figure 2c) and nitrate (Figure 2d) concentration/depth profiles. Indeed, these components are usually employed as seasonal tracers (summer maximum) in alpine ice cores (Preunkert et al., 2001). These profiles are similar to the formaldehyde profile, even though they seem to reveal a much higher variability in summer as expected from aerosol-associated species (more sporadic) respect to the relatively constant gas-phase formaldehyde. Comparing the four smoothed profiles we can find three summer peaks: in the most superficial layers (sampling was performed in summer), at 3.6 m depth and one at the firn core bottom.

The formaldehyde presents a double summer peak around 3.6 m could, showing a more complex seasonal pattern with respect the ammonium, sulphate and nitrate patterns. Anyway, a seasonal character can be suggested for formaldehyde.

Formaldehyde in glaciers and polar areas

SITE	SAMPLE	CONC. RANGE (µg l^{-1})	REFERENCES
Northern Victoria Land (Antarctic coastal areas)	Snowpits	7.7 mean value	Largiuni et al. accepted
Neumayer (Antarctic coastal areas)	Superficial fresh snow	58.6	Riedel et al. 1999
Law Dome (Antarctic coastal station)	Ice core	2.0-14.3	Gillett et al. 2000
Dome C (East Antarctic plateau)	Ice core	0-10	Röthlisberger et al. 2000
South Pole, Siple Dome, Dome C (Antarctica)	Superficial snow Shallow firn	~ 6 0.3-1.1	Hutterli et al. 2002
New Grip Ice Core (Central Greenland)	Ice core	0-12	Fuhrer et al. 1993
Summit (Central Greenland)	Snowpits fresh snow	1-6.5	Hutterli et al. 1999
Canadian Forces Station Alert (Canada)	Snow samples	~1-24 0-21	Sumner and Shepson 1999
Canadian Forces Station Alert (Canada)	Surface hoar	Winter 12.1 Spring 6.9	Perrier et al. 2002
Col du Dome (Mont Blanc Massif-France)	Superficial fresh snow	Summer 29.5 Winter 9.8	Houdier et al. 2000
Col du Dome (Mont Blanc Massif-France)	Ice core	7.1-10.1 at 110 m depth	Houdier et al. 2000
Lys Glacier (Monte Rosa Massif-Italy)	Ice core	3.8-24.8	This study

Table 1 - HCHO concentration values determined in snow samples collected in some Antarctic, Greenland, Canadian and Alpine sites.

The formaldehyde concentrations determined in the firn core were compared to other measurements on snow and ice samples from medium and high latitude glaciers (Table 1) to evaluate the reliability of the presented data.

For the lower anthropic contribution, the formaldehyde content in polar areas is generally lower than that found at mid-latitude sites. The formaldehyde background values, mainly coming from natural sources such as in-cloud methane photooxidation in Antarctica (Legrand and De Angelis, 1995) and continental biospheric emissions in northern high latitude regions (Legrand and De Angelis, 1996), is not negligible. Formaldehyde arctic concentrations are higher than antarctic levels because the higher anthropogenic inputs; Antarctica continent provides the cleanest atmospheric environment because of its remoteness from industrialized countries. It can state also that the fresh snow concentrations in Greenland are comparable to the ones measured on Lys glacier (Hutterli et al., 2003).

In temperate areas the anthropogenic contribution causes higher values in the formaldehyde atmospheric content. At Col du Dome, the only other alpine site at this time sampled for formaldehyde measurements (Houdier et al., 2000), superficial snow samples show formaldehyde summer values about three times as winter values, confirming the formaldehyde content and the seasonal pattern found at the Colle del Lys.

Conclusions

The first high resolution formaldehyde record in an alpine site is presented. A very sensitive and reproducible spectrofluorimetric method in flow injection analysis allowed to obtain the analysis of the 16 m ice core drilled at Lys Glacier (Monte Rosa massif, Italy).
The formaldehyde concentration/depth profile was compared with the seasonal markers (ammonium, sulphate and nitrate) profiles. A seasonal trend also for formaldehyde content was evidenced by the higher values in summer (13.5 µg l^{-1} mean value) and lower values in winter (7.0 µg l^{-1} mean value).
The obtained formaldehyde data set was compared with other formaldehyde determination in snow and ice samples from remote and continental areas such as Antarctica, Greenland and Alps. The data here presented appeared to be consistent with those determined in the other examined sites taking into account the different contribution of natural and anthropic input in each area.
To explain a particular summer behaviour in the formaldehyde concentration/depth profile, meteorological conditions have been considered to obtain reliable informations about the atmospheric circulation during the snowfall events. In particular, some atmospheric phenomena are responsible for the anomalous decreasing in formaldehyde concentration recorded during the 1999 summer.
The study on these preliminary data suggests that long-term formaldehyde record from alpine ice cores could provide reliable information about the past formaldehyde atmospheric content back to the pre-industrial period, leading to an assessment of the changes in the oxidizing capacity of the atmosphere related to the different anthropic contribution.

Meteorological parameters

METEOROLOGICAL OBSERVATORY OF MILANO DUOMO - *Meteorological analysis*

DATES OF THE EVENTS	CHARACTERISTICS OF THE ATMOSPHERIC CIRCULATION
3-4 May 1999	Low pressure centre at surface over Balearic Islands Warm air stream from Tunisia to the Alps Mean temperature: -7°C; positive anomaly: +4°C Wind speed: about 50 km h^{-1}
4-5 July 1999	Low pressure centre at surface between Catalonia and Balearic Islands Warm air stream from Algeria to the Alps Mean temperature: -2.5°C; positive anomaly: +1°C Wind speed: about 60 km h^{-1}
14 July 1999	North-westerly cold winds at surface (foehn in the lee of the Alps) Upper cold front over the Alps Mean temperature: -3°C; negative anomaly: -1°C Wind speed: about 40 km h^{-1}
22-23 July 1999	North-westerly cold winds at surface Cold front close to the western side of the Alps Mean temperature: -4°C; negative anomaly: -3°C Wind speed: about 40 km h^{-1}
30-31 July 1999	North-westerly cold winds at surface Cold front close to the western side of the Alps Mean temperature: -5°C; positive anomaly: -4°C Wind speed: about 20 km h^{-1}
8-10 August 1999	Low pressure at surface over Brittany; high pressure over Ionian Sea Warm air stream from Algeria to the Alps Mean temperature: +1°C; positive anomaly: +2°C Wind speed: about100 km h^{-1}

Table 2 – List of the six snowfall episodes occurred in the investigated area between May and August 1999. Fundamental characteristics of the atmospheric circulation are shown for each episode.

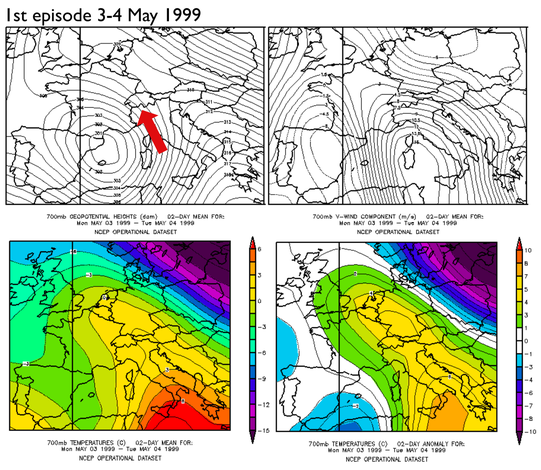
To better explain the behaviour of formaldehyde depositions along the investigated period, meteorological conditions have been considered, mainly for what is concerning the atmospheric circulation during the snowfall events. Through this investigation, six snowfall episodes have been singled out: their characteristics are synthetically reported in Table 2.

The first two episodes and the last one are characterised in the lower atmosphere by a warm air stream which develops over the Mediterranean Sea from Africa coastal areas to the Western Alps.
The three remaining snowfall episodes, on the contrary, are connected to atmospheric conditions characterised by a flux of cold air, directed from Northern Europe to the Alps.

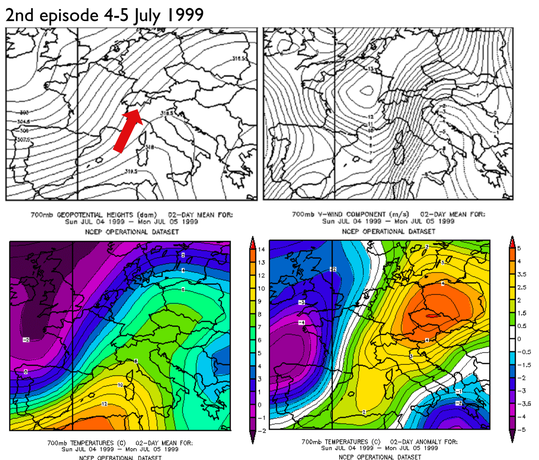
To have a description of the six episodes, some mean meteorological maps have been considered by an interactive procedure available at NOAA-NCEP via internet (see web site in bibliography), as shown in the six figures which describe the different meteorological situations. In each one of these figures the following mean maps are represented:

a) the topography of the 700 hPa isobaric surface, by the isocontouring of the geopotential height (dam);
b) the meridional component of the wind (m/s), which is positive if the wind is directed northwards;
c) the air temperature (C);
d) the air temperature anomaly (C) with respect to the normal.

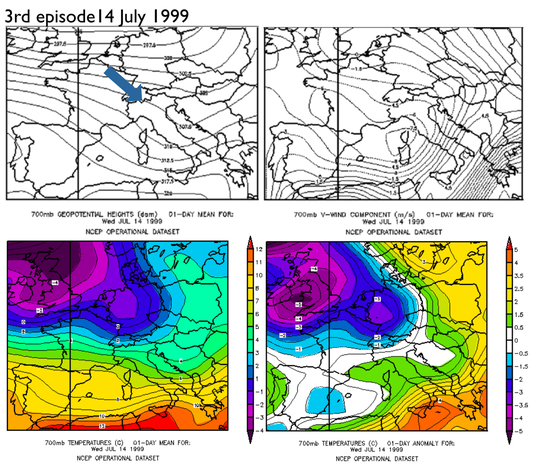
1st episode 3-4 May 1999



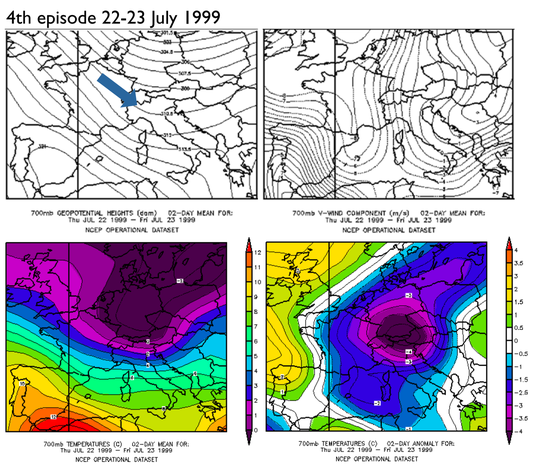
2nd episode 4-5 July 1999



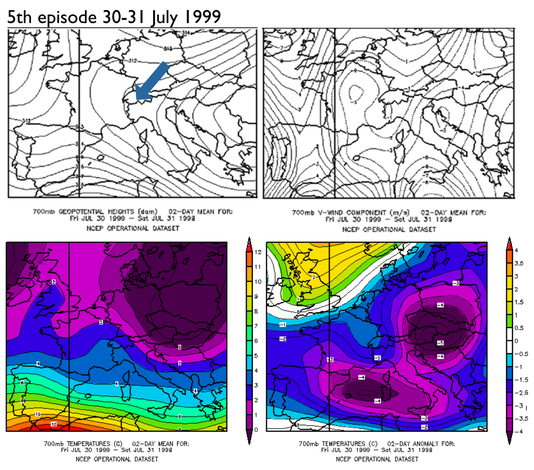
3rd episode14 July 1999



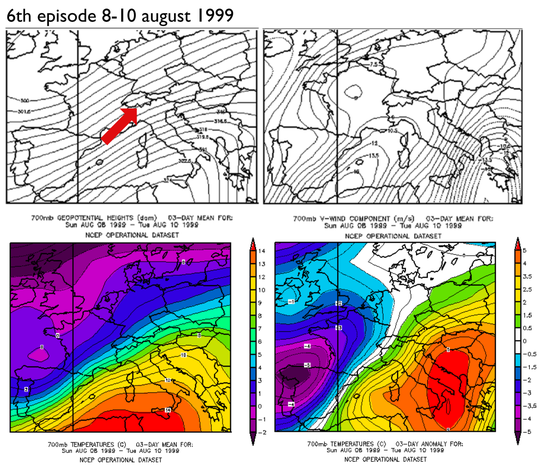
4th episode 22-23 July 1999



5th episode 30-31 July 1999



6th episode 8-10 august 1999



The three episodes, characterised by negative anomalies, are rare and well can account for decrease in the formaldehyde concentration on the 1999 summer maximum (Figure 2). Saharian dust events are usually employed as reference horizonts in ice cores dating; episodes characterised by foehn winds are even more rare. According to classification of air circulation in the mean troposphere over the Europe and Mediterranean, particularly for alpine areas, the sirocco conditions regarding the North-Western Italy have a frequency of 4% in may, 0.3% in july and they have not happened in august in the 1976-1995 period. For the precipitations due to northern airstreams in the twenty years period considered, similar episodes have happened in july for the only 0.2% of the cases (Borghi, 1992). For these reasons the 1999 summer can be considered a very anomalous summer. The events over mentioned have certainly caused a precipitation increase and thus a pollutants dilution, evidenced by formaldehyde summer decrease at 3.6 m and partially showed also by sulphate profile, not so much for ammonium and nitrate; moreover the particulate matter could have prime formaldehyde decomposition reactions both in the atmosphere and in snow layers after deposition. During the 3-4 May, 4-5 July and 8-10 August 1999 events the temperature was very high respect to mean temperatures (+2 / +4°C positive anomaly, see web site of Wyoming University in bibliography), thus the air-water equilibrium for formaldehyde in the atmosphere is shifted versus the gas phase, determining the formaldehyde depletion in the snow.

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