Variability of formaldehyde in the Antarctic troposphere

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The annual cycle of formaldehyde (HCHO) was measured at a remote site in Antarctica in order to investigate seasonal and diurnal variations as well as chemical processes in the troposphere. The measurements were performed in 1997 (March 1997 to January 1998) and in February 1999 at the German Antarctic research station Neumayer, which is located at 70°37′S, 8°22′W. The obtained time series for formaldehyde in near-surface air clearly indicates the occurrence of diurnal and seasonal variations in Antarctica. It was found that HCHO concentrations vary from values below the detection limit (0.03 ppbv) to maximum values of 0.4 ppbv in winter and 0.7 ppbv in the austral summer. The observed concentrations show daily variations on certain days, with maxima in early afternoon and minima during the night. It was found that HCHO mixing ratios are significantly higher than those predicted so far by photochemical models.

Introduction

Oxidation by hydroxyl radicals (OH) is the dominant sink for most of the environmentally important natural and anthropogenic atmospheric trace gases such as CH_4, CO, SO_2 and dimethyl sulfide (DMS). Information about concentrations of OH and regulating compounds such as formaldehyde, ozone, nitrogen oxides and carbon monoxide helps to provide a better understanding of the chemistry of these trace gases which are relevant for the climate of the Earth. Formaldehyde (HCHO) is an important intermediate in the photochemical oxidation of atmospheric hydrocarbons. In unpolluted rural areas the dominant source of formaldehyde in the free troposphere is the reaction of methane (CH_4) with OH radicals.[1] Photolysis is on the other hand an important sink for HCHO, which, depending on the wavelength, yields H atoms and HCO radicals (1a) or hydrogen and carbon monoxide (1b).[2]

$$HCHO + h\nu \ (\lambda < 325 \ nm) \rightarrow H + HCO \quad (1a)$$

$$HCHO + h\nu \ (325 \ nm < \lambda < 360 \ nm) \rightarrow H_2 + CO \quad (1b)$$
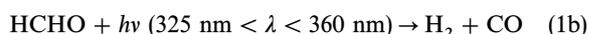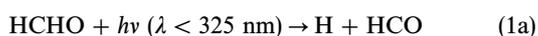
Formaldehyde is also linked with the so-called odd hydrogen family (OH, HO_2, H) by the following reactions:

$$HCO + O_2 \rightarrow HO_2 + CO \quad (2)$$

$$CO + OH + M \rightarrow H + CO_2 + M \quad (3)$$

$$H + O_2 + M \rightarrow HO_2 + M \quad (4)$$
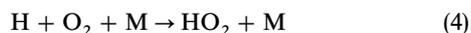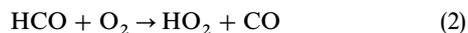
With regard to these reactions, (1)–(4), formaldehyde has to be considered as a significant radical source. Recombination of HO_2 radicals, generated by reaction (4), leads to the formation of hydrogen peroxide (5).

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \quad (5)$$
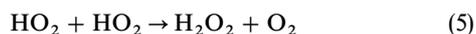
With their radical reactions, formaldehyde and hydrogen peroxide influence vastly the OH budget and the oxidative capacity of the atmosphere. Chemical decomposition of atmospheric trace gases is therefore closely linked with these two species.

Formaldehyde and hydrogen peroxide concentration records determined in ice and firn cores may potentially provide valuable information concerning the oxidative capacity of the ancient troposphere.[3] To date, there remain several open questions. There is still a lack of information about mechanisms of formaldehyde deposition, post-depositional air–snow exchange, possible chemical reactions in buried snow and firn and of the atmospheric chemistry of formaldehyde in polar regions. Hence, the aim of our investigations was to supply experimental data which are needed for the understanding of formaldehyde photochemistry in the polar and marine troposphere.[4] Thus, measurements were performed at a remote site free from anthropogenic influences to obtain results from the pristine atmosphere.

In the northern polar hemisphere, measurements were performed at Summit (Greenland) in June 1993, 1994[5] and 1996[6] and at Alert (Canada) in January, February and April 1992[7] and from February to April 1998.[8] Recently, HCHO measurements in the Arctic troposphere and snow have received considerable attention: Sumner and Shepson[8] and Hütterli et al.[6] found that formaldehyde concentrations are significantly higher than those expected and predicted by photochemical models.[9,10] The authors suggest the existence of a local HCHO source. While Sumner and Shepson[8] presume that formaldehyde is produced photochemically at the air–snow interface, Hütterli et al.[6] favour a de-gassing process for HCHO from buried winter firn layers. In any case this would be a significant source of HCHO in polar regions because large areas are covered with ice and snow.

Moreover, formaldehyde is thought to have a direct influence on hydrogen peroxide levels. Photolysis of formaldehyde yields HO_2 radicals whose recombination is the main source of hydrogen peroxide [see reaction (5)]. Model calculations suggest that observed HCHO concentrations might explain the observed hydrogen peroxide concentrations in the Arctic troposphere.[5] In Antarctica very few investigations of formaldehyde have been carried out so far. In December 1993 and January 1994, HCHO was measured during the Swedish traverse (SWEDARP) in Dronning Maud Land.[5] Values between 0.2 and 0.3 ppbv have been observed.

Our studies at Neumayer station were aimed towards the estimation of a complete annual cycle for formaldehyde in the near-surface air in Antarctica. The obtained time series will be presented and discussed in this paper.

Experimental

The measurements were carried out at the German Antarctic station Neumayer (70°37′S/08°22′W) during the overwintering season 1997/98 and during a summer campaign which was performed from January to March 1999. The station is located on the Ekstrøm Ice Shelf at a distance of 7 km from the southeast part of Atka Bay, 42 m above sea level (see Fig. 1). The instruments were installed in an Air Chemistry Observatory which is located 1500 m south of the main station. Northerly winds are hardly ever observed there. Thus, no serious contamination problem due to the main station existed. The mean annual temperature at Neumayer is −15 °C. The maximum solar incidence angle is 42.8°. The sun stays permanently above the horizon from November 19 to January 24 and permanently below the horizon from May 19 to July 27.[11]

A continuous technique was used for formaldehyde sampling and analysis. The quantitative analysis[12,13] is based on the so-called Hantzsch reaction, a liquid phase reaction of HCHO with pentane-2,4-dione and NH_3, yielding 3,5-diacetyl-1,4-dihydrolutidine (DDL). Formaldehyde was quantified fluorimetrically by exciting the end-product of the reaction (DDL) at 253 and 400 nm (Hg lamp) and detecting the fluorescence signal at 510 nm. Details of the analytical technique are described by Dong and Dasgupta[12] and Dasgupta et al.[13] In our analyser (Aerolaser HCHO analyser, Model AL4001), gaseous HCHO was stripped from a 1000 cm³ min⁻¹ air flow by acid solutions (0.05 mol l⁻¹ H_2SO_4) running at 0.3 ml min⁻¹. The stripping coil was thermostated at 16 °C, whereas the chemical reactor and fluorescence cells were kept at a constant temperature of 60 °C. The collection efficiency of formaldehyde in the stripping coil is a function of the equilibrium partitioning of HCHO between the sample air and the stripping solution and the rate at which equilibrium is reached. Under the conditions of our experiment, viz., dilute acid solutions, equilibrium is reached in the stripping coil.[14] In water, formaldehyde exists almost exclusively in the hydrated diol form[15] [$HCHO + H_2O \rightarrow H_2C(OH)_2$ with $K = 1.82 \times 10^6$ for the hydration reaction]. The temperature-dependent Henry's law expression for HCHO from 278.2 to 298.2 K is given by[16]

$$[HCHO(aq)] = 10^{[(4538/T) - 11.34]} HCHO(g)^{[(252.2/T) + 0.2088]}$$

For 16 °C (= 289.2 K) the calculated stripping efficiency for formaldehyde is higher than 96%. Breakthrough experiments
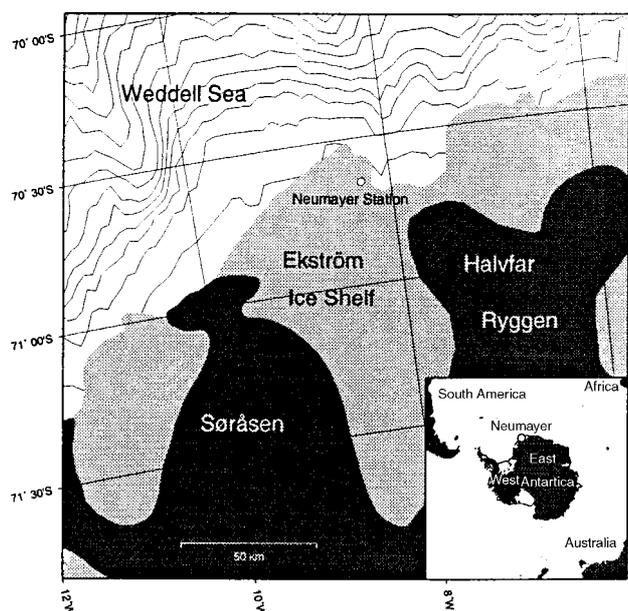
Fig. 1 Map of local area around Neumayer station on the Ekstrøm Ice Shelf. Continental areas in black, ice shelf areas in grey.

by the instrument's manufacturer yielded a stripping efficiency of 99.9%.

Formaldehyde measurements in air require a periodic determination of the fluorescence signal at zero air (clean air without HCHO) and periodic determination of the system's sensitivity by using a calibration source. An automatic gas calibration was run every 12 h. Signals of zero air and of an internal gaseous formaldehyde standard were compared and used to determine the sensitivity of the instrument. Zero air was generated internally by passing ambient air through a zero trap packed with Hopkalit®. The calibration gas was provided by an internal permeation source (paraformaldehyde, KIN-TEK™-wafer permeation). The permeation source itself was calibrated every week by standard solutions of 10⁻⁶ mol l⁻¹ HCHO, freshly prepared from a stock solution of 10⁻² mol l⁻¹ HCHO. The absolute permeation rate is calculated by comparing the permeation signal with the signal of the prepared liquid standards. The concentration of the 10⁻² mol l⁻¹ formaldehyde stock solution was determined every 3 months by iodimetric titration.

Especially during the winter season, HCHO values were sometimes close to the detection limit of the instrument. Therefore, regular zero measurements were carried out. An external zero trap filled with Hopkalit® was used to determine the daily zero value. The trap was mounted between the instrument and the inlet tube for 20–90 min each day.

The main air inlet was installed on top of the Air Chemistry Observatory 8 m above the ground. The Teflon line between the inlet and the instrument was 2.5 m long with an inner diameter of 4 mm. With an air flow of 1000 cm³ min⁻¹, this leads to a residence time of 1.9 s for the air sample in the tube. The inlet was protected against drifting snow with a specially designed tumbler. The sampling efficiency of the Teflon inlet system was determined to be in the range 0.95–0.98 by comparing measurements of indoor air (contaminated with formaldehyde) with and without the Teflon tube.

All solutions were prepared with ultrapure water (Milli-Q water) and analytical-reagent grade chemicals. Under these conditions, a detection limit of 30 pptv is achievable. This corresponds to 3σ of the standard deviation of the noise level. The accuracy of the instrument was calculated to be of the order of 15–20% at [HCHO] ≤ 200 pptv and 10–15% at [HCHO] = 200–1000 pptv. The time constant for a change from 10 to 90% signal is 90 s with a delay time of 12 min.

UV solar radiation measurements were carried out with a UV radiometer (selenium photocell pyranometer, Eppley, USA, 300–370 nm). Relative humidity was measured with two pernix hair hygrometers (Lambrecht 800L100).[17]

Results and discussion

In our all-year-round investigations of formaldehyde in the Antarctic troposphere at Neumayer station we observed diurnal and seasonal variations. Since the main source of formaldehyde in the unpolluted atmosphere is photochemical oxidation of natural hydrocarbons, it is obvious that changes in solar radiation cause variations in atmospheric HCHO concentrations. Diurnal, seasonal and latitudinal alterations of HCHO can primarily be attributed to changes in solar radiation. Fig. 2 illustrates the annual variation of formaldehyde gas-phase concentrations at Neumayer station compared with UV solar radiation for the same time period.

Polar night

In winter, we observed atmospheric HCHO concentrations around 0.15 ± 0.12 ppbv (range 0.03–0.40 ppbv). Most values (57%) are in the range from below 0.03 to 0.150 ppbv. Fig. 3(a) illustrates the frequency distribution of measured data during the winter period (April 1–September 15, 91st–258th day of
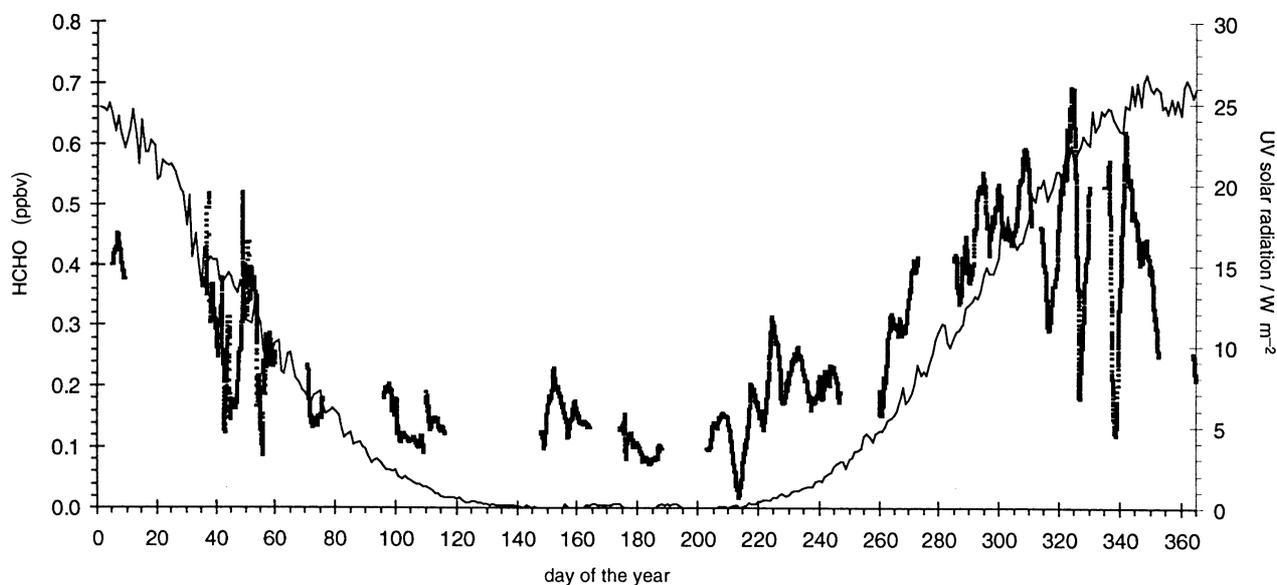
Fig. 2 Annual variation of formaldehyde: 5 d running means of HCHO gas-phase concentrations (in ppbv) are plotted against day of the year (1 = January 1 and 365 = December 31). The presented time series is a result of two different campaigns: March 1997 to January 1998 and February 1999 (thick line). The thin line shows annual variations in UV solar radiation.

the year). As expected the decline of formaldehyde concentrations coincides with the drop of solar radiation to 0.0 W m^{-2} during the polar night (139th–208th day of the year) since photochemical oxidation is the main source of HCHO.

More remarkable are some events with higher HCHO concentrations (>0.15 ppbv). Trajectory studies by Kottmeier and Fay[18] show that air parcels from lower latitudes (<60° south) can, in principle, reach Neumayer station within 5 d. Considering the fairly long lifetime of HCHO in darkness ($\tau = 160$ d[7]), photochemical formation of HCHO in sunlit areas can occur followed by transport to the measuring site.

Fig. 3 Frequency distribution of measured HCHO concentrations. Frequency (in %) is depicted against concentration intervals of 0.05 ppbv. (a) Distribution during winter period (April 1–September 15, 91st–258th day of the year) with total number of measurements $N = 2853$; (b) summer period (September 15–April 1) with $N = 3907$.

The only measurements so far reported in the literature during the polar night were performed by de Serves.[7] In 1992 he observed at Alert (Canada) noticeably higher HCHO concentrations (0.1–0.7 ppbv) compared with our results. The highest concentrations, however, were always associated with advection of continental air masses, indicated by an increase in ^{222}Rn, an inert gas that is emitted from soils and used as a tracer for continential air masses. De Serves[7] presumed that primary or secondary anthropogenic formaldehyde sources in Siberia were responsible for this increase. These anthropogenic sources are the reason for different observations made in the Arctic compared with Antarctica. The Arctic is surrounded by continents with industrialised countries, while the Antarctic continent is bounded by the Southern Ocean. There, no anthropogenic source influences the pristine atmosphere. Hence, concentrations of hydrocarbons are conspicuously higher in the Arctic than in Antarctica.[19] With regard to formaldehyde, an intermediate of hydrocarbon photooxidation, higher values in Arctic regions can be expected.

Polar day

When the sun rises during the austral summer and UV solar radiation increases to a maximum value of 26.8 W m^{-2} in the middle of the polar day (323rd day of one year to 24th day of the following year), formaldehyde concentrations between 0.1 and 0.7 ppbv (average 0.36 ± 0.20 ppbv) could be observed at Neumayer station. Fig. 3(b) illustrates the frequency distribution of the measured data. In contrast to the winter period, most values (42%) are within the interval 0.25–0.45 ppbv. Short-time variations are clearly higher than during winter. Temperatures in summer range between 0 and −15 °C. During a few years in December even temperatures above 0 °C (maximum: +2.3 °C) were reached. Comparisons with other measurements in Antarctica reported in the literature show results with similar or lower values (see Table 1).

Neftel et al.[9] used the Harvard photochemical model and calculated for summertime at Summit formaldehyde concentrations at noon of 0.09 ppbv. The discrepancies between the model and observations cannot yet be explained. Since oxidation of methane by OH radicals is assumed to be the main formaldehyde source, the model possibly underestimates the OH concentration for Antarctica. Another reason could be an as yet unknown HCHO source or long-range transport.

A good indication that primarily photochemical reactions influence the atmospheric concentrations of formaldehyde is

Table 1 Comparison of previous measurements of tropospheric formaldehyde concentrations in polar regions with our results

Measuring site	Working group	Measuring period	Atmospheric HCHO concentration (ppbv)
Alert (Canada, 82.5 °N, 62.3 °W)	de Serves[7]	Feb.–April 1992	0.03–0.6
Alert (Canada, 82.5 °N, 62.3 °W)	Sumner and Shepson[8]	Feb.–April 1998	0.052–0.69
Summit (Greenland, 72.2 °N, 37.8 °W)	Fuhrer et al.[5]	June 1993, June 1994	0.2–0.6
Summit (Greenland, 72.2 °N, 37.8 °W)	Hütterli et al.[6]	June 1996	0.1–0.45
Dronning Maud Land (Antarctica, 73–76 °S, 12–9 °W)	Fuhrer et al.[5]	Dec. 1993–Jan. 1994	0.2–0.3
Neumayer (Antarctica, 70.1 °S, 8.0 °W)	This work	April–Sept. 1997	Mean: 0.15 ± 0.12 Range: <0.03–0.40
		Sept. 1997–March 1998 and Feb. 1999	Mean: 0.36 ± 0.20 Range: 0.10–0.70

the occurrence of definite diurnal variations. In other investigations, authors do not mention any diurnal variation in formaldehyde gas-phase concentrations in northern polar regions. Only de Serves[7] investigated the daily concentration variations, but he could not find any regularity. At Neumayer station a diurnal cycle is only apparent during good weather conditions, *i.e.* wind speeds below 10 m s^{-1} and no precipitation or drifting snow. No diurnal variation in HCHO could be observed during periods of strong winds. With the thorough mixing of such weather systems, the typically present surface inversion layer vanished and also diurnal variations of the ambient temperature were absent. Even on such days with high wind velocities and precipitation the actinic radiation shows a diurnal cycle with a maximum in the early afternoon. This indicates that radiation is not the dominant factor causing the diurnal HCHO variations. Sumner and Shepson[8] favour photochemical processing in the snow layer as an additional new source of formaldehyde in the Arctic troposphere, while Hütterli et al.[6] presume de-gassing of formaldehyde from buried winter firn layers. To date, no evidence is available that comparable phenomena occur in Antarctica.

The diurnal cycle depicted in Fig. 4 was observed from October 15–24. The 24 h running mean was calculated and subtracted from each value. By this method the influence of long-term HCHO variations on a possible diurnal cycle is suppressed. The obtained differences were sorted by time of day and were again averaged (thick line). Also shown is the daily cycle of atmospheric water vapour partial pressure (thin line). During the observation period, wind speeds were below 10 m s^{-1} except on October 20 when the wind velocity increased to 19 m s^{-1}. Absolute formaldehyde concentrations reached 0.65 ppbv during daytime and 0.30 ppbv during night. A formaldehyde maximum in the early afternoon was detected. During night-time, the HCHO concentration declined to a minimum. Two different effects are presumed to
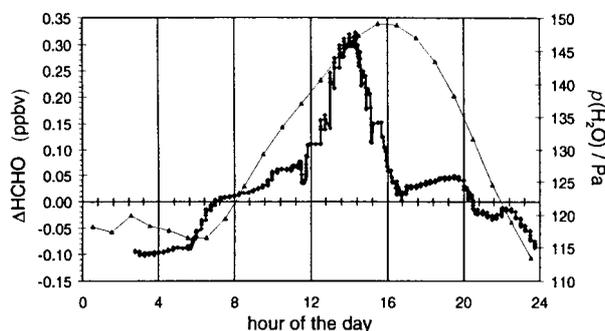
be responsible for the diurnal variation of formaldehyde. First, photochemical production of HCHO is strongly correlated with actinic radiation. The theoretical sunshine duration over the observed period was 15 h d^{-1} with a maximum solar incidence angle of 29° at noon. The maximum formaldehyde value appears to coincide with the maximum intensity of solar radiation. Another effect is caused by diurnal variation of two meterological parameters, temperature and atmospheric water vapour partial pressure. Both quantities also show a daily variation, with maximum values in the early afternoon and minima during the night. They are closely linked with the removal of formaldehyde from the atmosphere. It is possible that HCHO is adsorbed or co-deposited with hoar frost during the evening and night and is re-emitted by evaporation of hoar frost or desorption with increasing temperatures at sunrise. For hydrogen peroxide, Jacob and Klockow[20] observed a similar effect at Neumayer station. They suggested that co-condensation of gaseous H$_2$O$_2$ with atmospheric water vapour during the night leads to formation of snow and ice crystals. Under the given ambient temperature (−16.9 °C), an effective Henry's law coefficient of $H_{H_2C(OH)_2} = 6.3 \times 10^3$ M atm^{-1} was calculated.[21] In the following, we estimate how important this sink is for the observed HCHO variations. On October 14, 58.6 μg l^{-1} formaldehyde or 35.2×10^{-6} mol HCHO mol^{-1} of water were found in a fresh snow sample at Neumayer. With a diurnal variation in water vapour partial pressure of $\Delta p(H_2O)(g) = 35.6$ Pa and an average temperature of −16.9 °C (256.3 K), 1.67×10^{-2} mol water was most probably being deposited as hoar frost. Since 1 mol H$_2$O contains 35.2×10^{-6} mol HCHO this would mean that an atmospheric concentration of 5.8×10^{-10} mol m^{-3} (12.5 pptv) would be necessary to obtain the observed snow concentrations. Comparing this value with the actually observed atmospheric HCHO mixing ratios on this day (463 pptv), it is obvious that only 2.7% of the atmospheric formaldehyde could be lost by co-condensation. Thus, another as yet unknown reason for HCHO diurnal variations must exist. Most probably adsorption and desorption at firn and hoar frost layers cause the diurnal variation at Neumayer. At Summit, Sumner and Shepson[8] consider a photochemical production of HCHO by photolysis of organic material in the snowpack, but this would generate a diurnal variation even on days with a cloud-covered sky and higher wind speeds.

Concluding remarks

Our measurements at Neumayer station provide the first year-round time series of gas-phase HCHO concentrations from the Antarctic continent. We observed a seasonal variation coinciding with seasonal changes in solar radiation due to photochemical formation of formaldehyde. In addition, a diurnal variation of HCHO concentrations could be detected,

Fig. 4 Diurnal cycle of formaldehyde gas-phase concentrations (thick line), observed from October 15–24, 1997, together with the mean diurnal cycle of water vapour partial pressure measured during this period (thin line).

provided that the weather conditions permitted a stable stratification of the boundary layer. Co-condensation of HCHO with atmospheric water vapour is not assumed to be a plausible reason for the diurnal HCHO cycle. Adsorption and desorption from the firn layers are more probable. Generally, observed tropospheric HCHO concentrations are higher than those predicted by current photochemical models,[9] especially during winter. In the polar night, the lifetime of HCHO is fairly long ($\tau = 160$ d[7]) compared with the sunlit period ($\tau = 13$ h[22]) when rapid photochemical loss occurs. As a consequence, long-range transport of HCHO has only to be considered from late fall (autumn) to early spring.

In order to verify that snow is an additional formaldehyde source, the results from snow samples taken at Neumayer during the observation period and from gradient measurements, where HCHO was measured close to the snow surface and at a height of 8 m, will be evaluated with regard to HCHO de-gassing from the firn layer.

Acknowledgements

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