

# Atmosphere-to-snow-to-firn transfer studies of HCHO at Summit, Greenland

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**Abstract.** Formaldehyde (HCHO) measurements in snow, firn, atmosphere, and air in the open pore space of the firn (firn air) at Summit, Greenland, in June 1996 show that the top snow layers are a HCHO source. HCHO concentrations in fresh snow are higher than those in equilibrium with atmospheric concentrations, resulting in HCHO degassing in the days to weeks following snowfall. Maximum HCHO concentrations in firn air were 1.5-2.2 ppbv, while the mean atmospheric HCHO concentration 1 m above the surface was 0.23 ppbv. Apparent HCHO fluxes out of the snow are a plausible explanation for the discrepancy between the 0.1 ppbv atmospheric concentration predicted by photochemical modeling and the measurements. HCHO in deeper firn is near equilibrium with the lower tropospheric HCHO concentration at the annual average temperature. Thus HCHO in ice may in fact be linearly related to multi-year average atmospheric concentrations through a temperature dependent partition coefficient.

## Introduction

The main source of HCHO in the remote troposphere is oxidation of methane (CH<sub>4</sub>) by OH followed by further reactions. Past atmospheric OH levels inferred from HCHO and CH<sub>4</sub> in ice cores [Staffelbach *et al.*, 1991] could not be reproduced with photochemical modeling [Thompson, 1995], and it became evident that a better understanding of the transfer processes relating atmospheric and ice concentrations is imperative for a quantitative interpretation of ice cores.

Previous studies show that HCHO concentrations in fresh snow at Summit, Greenland are much higher than those preserved in firn, suggesting that surface snow at Summit is a HCHO source during summer [Fuhrer *et al.*, 1996]. This source has the potential to significantly affect atmospheric HCHO concentrations as well as the amount of HCHO preserved in the ice. Further, photochemical model calculations predict summertime atmospheric HCHO concentrations of about 0.1 ppbv [Staffelbach *et al.*, 1991], about half of average measured values [Fuhrer *et al.*, 1996]. The purpose of this study was to test the hypothesis that the HCHO flux out of the snow pack in summer can be attributed to a temperature dependent release of HCHO from the near-surface snow and firn as the HCHO concentrations in air and ice approach equilibrium.

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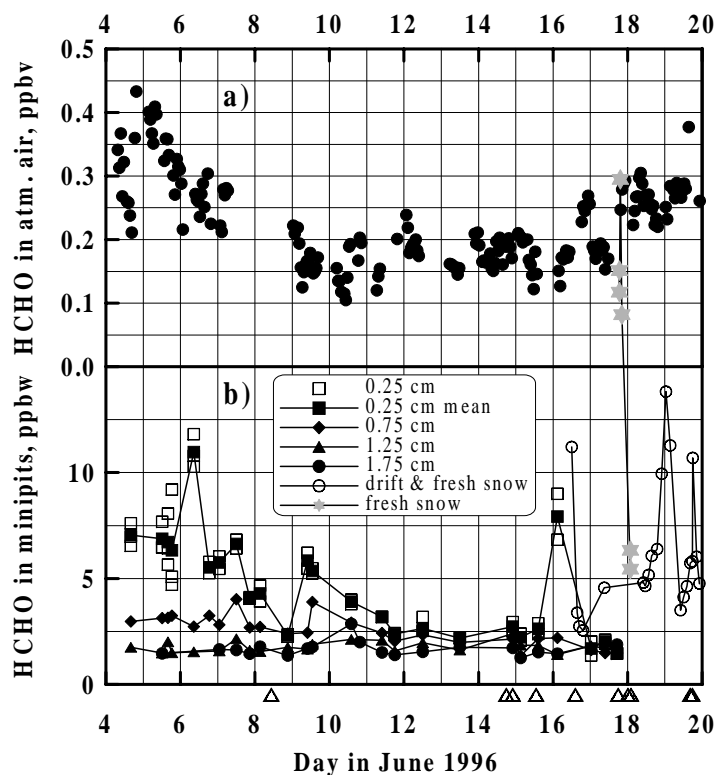
## Methods

The studies were performed at the GISP2 Camp at Summit, Greenland in June 1996. HCHO was measured in surface, fresh and drifting snow as well as in shallow firn cores. HCHO was also continuously monitored in the air 1 m above the snow and was measured several times in the firn air at various depths down to 2.5 m.

Sets of five surface snow samples were collected daily at various times in the clean air sector roughly 800 m SE of the main camp. Each set represented a 2 cm 'minipit' with a spatial resolution of 0.5 cm and with the top 0.5 cm sampled twice. Samples were collected with a stainless steel shovel and stored in air tight glass bottles. Fresh snow samples were collected with HD-PE funnels stuck in a glass bottle standing on the snow surface. During high winds, drifting snow was trapped in glass bottles by sticking them into the surface snow at a small angle. All samples were taken back to the laboratory (400 m SE of the camp), melted the same day and analyzed within two hours after melting. Firn concentration profiles were recorded by continuous flow analysis [Sigg *et al.*, 1994] of cores collected by ramming a 27-mm diameter stainless steel tube with core stoppers at the tip into the firn.

All aqueous HCHO concentrations were determined according to [Sigg *et al.*, 1994], including the eluents of the gas phase measurements, which were done using a wet effluent diffusion denuder [Simon *et al.*, 1991]. Denuder collection efficiency for HCHO was determined several times, always being higher than 96%. Calibrations were done twice a day by running liquid standards through the denuder while airflow was stopped. They were consistent with gas-phase standards, which were run several times. Baseline was determined every hour by stopping the airflow. A 5 m long 1/4" PFA intake line that was insulated and heated to prevent condensation was used to sample atmospheric air 1 m above the snow surface, 4 m upwind of the laboratory. A second, parallel tube was connected to the intake to check for contamination and losses, but neither were detected. The detection limit, defined as three times the noise of the baseline, was 60 pptv for the setup, the uncertainty in absolute concentrations was less than 20%.

For depths between 0.5 m and 2.5 m, a ram probe consisting of a stainless steel tube within an inflatable rubber tube to seal the whole was used to measure firn air. In the steel tube a double, heated and insulated PFA intake line is inserted. The tip of the probe is opened after it is vertically rammed into the snow. For firn air measurements down to 0.5 m, simple PFA tubes were placed horizontally into the



**Figure 1.** a) HCHO concentrations in the air 1 m above the snow cover in June '96. b) HCHO concentrations in the top 2 cm of the snow cover. Open triangles on the time axis represent observed snow falls.

wall of a pit. For measuring firn air in the top few centimeters, the atmospheric intake line was simply placed vertically into a small hole in the surface snow made with a PTFE tool. Air flow rates were below 9 ml/s (STP). Lab tests revealed no contamination or destruction by the materials used with the probes, including the rubber and HD-PE.

## Results

Hourly atmospheric HCHO concentrations averaged 0.23 ppbv (range 0.1–0.45 ppbv) (Fig. 1a), consistent with June '94 measurements [Fuhrer *et al.*, 1996]. Measurements of air-masses arriving from the generator and during windless periods were discarded. From June 4<sup>th</sup> to 16<sup>th</sup> wind speed was generally low (< 5 m/s), and fog built up during virtually every night, leading to different amounts of rime deposition. After June 14<sup>th</sup> there was generally less nighttime cooling and higher daily mean temperatures. The wind speed rose up to 15 m/s, resulting in drifting snow from June 16<sup>th</sup> to 21<sup>st</sup>.

HCHO snow concentration generally decreased with depth (Fig. 1b). Daily concentration in the top layer varied much more than in the lower layers. Replicate samples from the top layer also had relatively low variability. Drifting snow samples (open circles in Fig. 1b), which sometimes contained fresh snow, showed concentrations up to 15 ppbw. Through June 16<sup>th</sup> snow falls were light and not expected to contribute significantly to the surface snow samples. Fresh snow collected the night of June 17<sup>th</sup> had concentrations up to 24 ppbw (asterisks in Fig. 1b), which decreased to around five ppbw within a few hours. Surface snow and atmospheric HCHO concentrations during the whole period exhibited a similar pattern ( $r = 0.72$  for daily means).

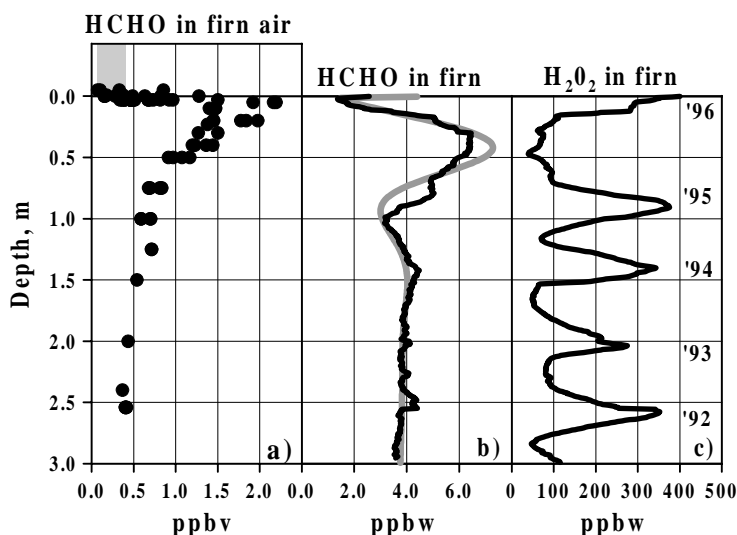
Pit measurements (Fig. 2b and 2c) showed the typical HCHO and H<sub>2</sub>O<sub>2</sub> concentration profiles. Note that the snow accumulation from summer '95 to '96 was roughly 90 cm, which is about 1.5 times average. In the HCHO profile, a steep decrease in the first centimeters to minimal values around one ppbw (see also Fig. 1b) is followed by an increase to 5–7 ppbw in last winter's snow layer. Further down, a small dip in concentration that corresponds to the previous summer's or autumn's snow is still present, but below 1.5 m no seasonal signal is left.

The HCHO in firn air peaked right below the snow surface, with levels up to ten times those in the atmosphere (Fig. 2a). This maximum is coincident with the concentration minimum in the firn. All HCHO concentrations in the firn air were above atmospheric values.

## Discussion

There are two possibilities for a HCHO source in the top snow layers: photochemical production and degassing from snow grains, or a combination of the two. Photochemical production in firn air is expected to be significantly lower than in the atmosphere due to the efficient absorption of the UV radiation by snow.

The magnitude of the HCHO source in the upper snow layers is estimated from the observed concentration gradients in the top few centimeters of firn air (4–25 ppbv/m) with a molecular diffusivity of about  $1.5 \cdot 10^{-5} \text{ m}^2/\text{s}$  [Schwander, 1989]. The fluxes for five measurements done on different days and times in June are then  $1.4\text{--}8.8 \cdot 10^{12} \text{ molecules/m}^2/\text{s}$ . True values could be 10 times or more higher because the molecular diffusivity is a lower boundary for the mixing of the firn air and neglects forced ventilation by wind with a



**Figure 2.** a) HCHO concentrations in the air in the open pore space of the firn (firn air) at different depths. The gray box above the snow cover shows the range of the atmospheric HCHO concentration. b) HCHO concentrations measured (black) and modeled (grey) in the firn as a function of depth. Note the concentration minimum right below the surface. c)  $\text{H}_2\text{O}_2$  concentrations measured in the same firn core as in b) show summer peaks and winter minima.

turbulent diffusivity  $K_{zz}$  in the range from  $10^{-3}$  to  $1 \text{ m}^2/\text{s}$  [Bales *et al.*, 1995]. Photochemical calculations for Summit in summer using a point model show that a mean HCHO flux of about  $1.5 \cdot 10^{13} \text{ molecules/m}^2/\text{s}$  doubles the HCHO concentrations in the air assuming a mixing height of 150 m, which is typical for Summit in summer [Bales *et al.*, 1995]. The photochemical model calculations predict that the same HCHO source increases the  $\text{H}_2\text{O}_2$  concentration in the air by 30%, and is thus a possible explanation for the higher than expected atmospheric  $\text{H}_2\text{O}_2$  concentrations measured at Summit [Bales *et al.*, 1995].

The observed depth profiles of HCHO in firn indicate that the upper 1.5–2 m of firn are not in equilibrium with the atmosphere. Since the equilibrium ice-air concentration ratio should decrease for warmer temperatures [Bales and Choi, 1996], the relatively warm summer snow at the surface is expected to degass to lower concentrations than the underlying colder firn layers. The previous winter's firn would also act as an HCHO source in summer because of summer warming at that depth, signifying a much larger reservoir available than the freshly fallen summer snow alone. Although there probably is an undersaturation of already depleted top snow layers during cold nights, the lower winter snow layers, which do not cool down as much at night, would still be sufficiently supersaturated to maintain the HCHO concentration in firn air above atmospheric values.

Once buried by winter snow a (depleted) buried summer layer (at 1.0 m depth in Fig. 2b) would take up HCHO. During lower winter temperatures the HCHO concentrations in the surface snow would remain higher than in summer, provided that there is a significant amount of HCHO in the polar winter atmosphere to provide high fresh snow concentrations.

We used a numerical model to test the hypothesis that reversible, temperature dependent HCHO degassing and up-take could explain the measured HCHO concentration profiles in the firn and firn air. Since observations were not

available, firn temperatures were calculated using a heat transfer equation [Schwander *et al.*, 1997]. The initial profile was calculated according to Paterson [1994] with amplitudes of  $20^\circ\text{C}$  and  $6^\circ\text{C}$  for the annual and daily temperature cycles respectively. Measured firn density was available for the top 2 m, with calculated density used deeper. Measured air temperatures (GISP AWS) were used as boundary conditions for calculating firn temperature profiles. The temperature model was run for 30 days prior to the transfer calculations in order to let the AWS temperatures diffuse into the top meters of the snow pack.

HCHO transport was described by diffusion:

$$\theta_a \frac{\partial C_a}{\partial t} = \theta_a \frac{\partial}{\partial x} \left( D_a \frac{\partial C_a}{\partial x} \right) - \theta_i \cdot k_b (C_a \cdot K_D - C_i) \quad (1)$$

where  $\theta_i$  and  $\theta_a$  are the volume fractions of ice and air respectively ( $\theta_i + \theta_a = 1$ ),  $t$  is time,  $x$  is depth,  $C_a$  is firn air concentration,  $C_i$  is firn concentration (both in  $\text{molecules/m}^3$ ) and  $D_a$  is diffusivity [Schwander, 1989]. The second term on the right describes reversible exchange between the firn and firn air, where  $k_b$  is a mass-transfer coefficient and  $K_D$  the ice-air equilibrium partition coefficient; both are temperature dependent. Measured atmospheric HCHO concentrations were used as boundary conditions for the concentration profile in the firn air. Measured HCHO surface, drift, and fresh snow concentrations served as boundary conditions for the concentration profile in the firn. Mass balance for the ice phase is:

$$\theta_i \frac{\partial C_i}{\partial t} = \theta_i \cdot k_b (C_a \cdot K_D - C_i) \quad (2)$$

The temperature dependence of  $k_b$  and  $K_D$  were expressed as:

$$k_b = k_{ba} e^{-\frac{k_{bb}}{kT}}; \quad K_D = \frac{SSA}{\theta_i} K_{Da} \sqrt{T} \cdot e^{-\frac{K_{Db}}{kT}} \quad (3)$$

with  $SSA$  the specific surface area of the firn [Narita, 1971].  $K_D$  is analogous to a linear isotherm, which is valid for

non-dissociative adsorption and low surface coverage or a Henry's law type equilibrium [Henzler and Göpel, 1994]. For a typical specific surface area of  $4000\text{m}^2/\text{m}^3$ , 10 ppbw of HCHO, each surface oxide representing an adsorption site and all molecules on the ice surface, the fractional coverage would be about 0.3%. As the actual transfer process may be a combination of adsorption and partitioning between bulk phases, equations (3) can be considered empirical relations that give the expected form of the temperature relationships [McConnell *et al.*, 1997].

In a first step  $k_{ba}$  is approximated as  $1 \cdot 10^{13}\text{s}^{-1}$ , the typical frequency of the lattice of a solid [Henzler and Göpel, 1994]. A parameter search was used to obtain the remaining three unknown sorption parameters ( $k_{bb}$ ,  $K_{Da}$ ,  $K_{Db}$ ). For each set of sorption parameters firn air concentrations were modeled for depths and times when measurements were made. Modeled and measured values were then compared and sorption parameters optimized using least squares. Modeled firn air concentrations matched those measured quite well, with an  $r^2 = 0.80$ .

The differential equations were integrated numerically with a Crank-Nicholson scheme, with a time step of 100 s and a spatial resolution of 1 cm in the top 2.5 m. Below 2.5 m, each box was increased by 2.567 % relative to the overlying box, reaching a depth of more than 20 m with 400 boxes. The temperature and HCHO gradients at the lower boundary were set to zero, since the annual temperature cycle is smoothed out in the top 15 m [Paterson, 1994] and HCHO gradients in firn air approach zero in the top 2.5 m. Snow accumulation was also considered.

In a second step the transfer model was run for 12 years with the parameters found and a constant HCHO concentration in the air of 0.23 ppbv. Atmospheric HCHO concentrations are expected to be relatively independent of season [Staffelbach *et al.*, 1991]. Accumulation rate is 60 cm/year and temperature as mentioned above. HCHO concentration in fresh snow is 10 ppbw, lying in the range of reported summer values (5-25 ppbw) and above the apparent minimal winter concentrations in the firn (6 ppbw). An extra year with 90 cm of fresh snow (8 ppbw) was added to account for the accumulation anomaly. Modeled and measured HCHO profiles in the firn are shown in Figure 2b. A mean HCHO flux of  $1 \cdot 10^{13}$  molecules/ $\text{m}^2/\text{s}$  resulted for June in excellent agreement with the other estimation. Further similar model runs revealed a linear relationship between the chosen, constant atmospheric HCHO concentration and the resulting HCHO concentration of the deeper firn layers (4 m and below).

## Conclusions

The HCHO concentration in freshly deposited snow is apparently considerably above that in equilibrium with the atmosphere, and degassing occurs until either equilibrium is reached or the snow is buried and contact with the atmosphere becomes limited by diffusive transport in the firn air. As temperatures change over both daily and annual time scales, HCHO will partition to or be released from the ice-air interfacial region, with equilibrium defined by a temperature dependent partition coefficient ( $K_D$ ). Taking the measured firn to firn air concentration ratio at 2.5 m depth gives a  $K_D$  of 450 M/atm for  $-30^\circ\text{C}$ .

Degassing of HCHO from buried layers and reversible, temperature dependent partitioning of HCHO between air and ice gives a consistent, plausible explanation for the observed firn and firn air profiles.

Estimated HCHO fluxes out of the firn are of the magnitude needed to explain the discrepancy between the atmospheric concentration predicted by photochemical modeling and measured values.

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