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**n-Aldehydes (C₆–C₁₀)
in snow samples
collected at
Jungfraujoch**

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n-Aldehydes (C₆–C₁₀) in snow samples collected at the high alpine research station Jungfraujoch during CLACE 5

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Abstract

Samples of freshly fallen snow were collected at the high alpine research station Jungfraujoch, Switzerland, during the Cloud and Aerosol Characterization Experiments (CLACE) 5 in February and March 2006. Sampling was carried out on the Sphinx platform. Headspace-solid-phase-dynamic extraction (HS-SPDE) combined with gas chromatography/mass spectrometry (GC/MS) was used to quantify C₆–C₁₀ n-aldehydes in the snow samples. The most abundant n-aldehyde was n-hexanal (median concentration 1.324 μg L⁻¹) followed by n-nonanal, n-decanal, n-octanal and n-heptanal (median concentrations 1.239, 0.863, 0.460, and 0.304 μg L⁻¹, respectively). A wide range of concentrations was found among individual snow samples, even for samples taken at the same time. Higher median concentrations of all n-aldehydes were observed when air masses reached Jungfraujoch from the north-northwest in comparison to air masses arriving from the southeast-southwest. Results suggest that the n-aldehydes detected most likely are of direct and indirect biogenic origin, and that they entered the snow through the particle phase.

1 Introduction

C₆–C₁₀ n-aldehydes have previously been detected in tropospheric air (Ciccioli et al., 1993; Yokouchi et al., 1990), particularly over forests (Ieda et al., 2006; Matsunaga et al., 2003). A variety of sources of the compounds have been reported, and biogenic emissions from plants and vegetation were suggested to contribute preferentially to atmospheric concentrations of n-aldehydes (Kesselmeier and Staudt, 1999; König et al., 1995; Owen et al., 1997). Kesselmeier and Staudt (1999) distinguished between direct emissions of n-decanal from vegetation, and direct and indirect emissions of C₆–C₉ n-aldehydes from vegetation and microbial processes, respectively. Among C₆–C₁₀ n-aldehydes, n-nonanal was reported to be the most abundant n-aldehyde in the atmosphere outside urban areas, with a concentration of approximately 8 μg m⁻³

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(Kesselmeier and Staudt, 1999).

Owen et al. (1997) investigated emissions of volatile organic compounds (VOCs) from 18 Mediterranean plant species in Italy using a combination of a bag-enclosure sampling technique followed by gas chromatography. Among other VOCs (including monoterpenes), n-hexanal was detected in emissions from 1 of 18 plants, and n-nonanal and n-decanal were found in emissions from 10 of 18 plants. In emissions from 17 samples of agricultural and natural plant species from central Europe, König et al. (1995) detected n-hexanal in all 17, n-heptanal in 3, n-octanal in 1, and n-nonanal in 2 of the samples. Furthermore, aldehydes can enter the atmosphere through abrasion of leaf surfaces (Rogge et al., 1993). Moreover, atmospheric oxidation of compounds of biogenic origin, including oleic acid and linoleic acid, can lead indirectly to the formation of n-hexanal and n-nonanal (Moise and Rudich, 2002; Thornberry and Abbatt, 2004). Oleic acid as a possible source of n-nonanal has been detected in high concentrations in aerosol particles (Limbeck and Puxbaum, 1999; Yokouchi and Ambe, 1986). Apart from biogenic sources, homologous series of n-aldehydes (butanal-dodecanal) have also been detected as anthropogenic emissions in diesel engine exhaust (Schulz et al., 1999).

At low temperatures at high altitudes, wet deposition processes become increasingly important and can constitute the dominant deposition mechanism for some organic contaminants in cold environments (Lei and Wania, 2004). Most studies of organic contaminants in snow from high altitudes in Europe have focused on semi-volatile organic compounds (SVOC) recognized as persistent organic pollutants (POPs) (for a review see Daly and Wania, 2005). The interactions of gaseous hydrocarbons with snow and ice have been investigated in many field and modeling studies (for a review see Fries, 2008a). Few studies have investigated the occurrence of VOCs in snow from high altitude surface stations (Fries et al., 2008b; Gröllert and Puxbaum, 2000; Kolb and Püttmann, 2006; Kos and Ariya, 2006). Kos and Ariya (2006) detected high concentrations of alkylbenzenes and volatile halogenated compounds in snow samples from Mont Albert in Canada (1200 m.a.s.l.). Methyl tert-butyl ether (MTBE)

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was detected in snow from Schauinsland (1205 m a.s.l.) and Kandel (1241 m a.s.l.) in Germany, but not in snow collected from higher altitude locations including Zugspitze (2650 m a.s.l.) and Jungfrauojoch (3450 m a.s.l.) (Kolb and Püttmann, 2006). Fries et al. (2008b) reported the occurrence of benzene, alkylated benzenes, chlorinated hydrocarbons and monoterpenes at the high alpine research station Jungfrauojoch (Switzerland). Some studies also have addressed the occurrence of n-aldehydes in snow (Desideri et al., 1998; Gröllert and Puxbaum, 2000; Poliakova et al., 2000). Gröllert and Puxbaum (2000) detected n-aldehydes together with other organic contaminants including phthalates, alkanes, phenols, alcohols and esters in snow samples from Mount Sonnblick (Austria, 3106 m a.s.l.), and reported median concentrations of 0.5 ng L^{-1} for n-decanal (1996 and 1997) and 142 ng L^{-1} for n-nonanal (1996). Antarctic surface snow from various altitudes (up to 2960 m a.s.l.) and sampling depths has also been reported to contain aldehydes among other organic compounds (e.g. n-alkanes and phthalates), with mean concentrations of $16\text{--}227 \text{ ng L}^{-1}$ for n-nonanal and $4\text{--}96 \text{ ng L}^{-1}$ for n-decanal (Desideri et al., 1998). No correlation between concentration and altitude was observed. Higher concentrations of n-nonanal and n-decanal were detected in upper snow layers in comparison to deeper layers. n-Nonanal was the most abundant n-aldehyde in all snow samples analyzed in the study of Desideri et al. (1998). Poliakova et al. (2000) analyzed 10 snow samples from urban and rural sites in Russia and Finland, and also reported that n-nonanal was the most abundant n-aldehyde, being present in 6 of the snow samples at concentrations up to $2.8 \mu\text{g kg}^{-1}$, followed by n-decanal which was found in only 3 of the samples. Previously measured concentrations of n-aldehydes in snow are summarized in Table 1.

We present here the results of measurements of $\text{C}_6\text{--C}_{10}$ n-aldehydes in snow samples collected at Jungfrauojoch (3580 m a.s.l.) in the Swiss Alps during the Cloud and Aerosol Characterization Experiments (CLACE) 5 in February and March 2006. The snow samples were melted, and analyzed using headspace-solid-phase-dynamic-extraction (HS-SPDE) combined with gas chromatography/mass spectrometry (GC/MS). The analyte concentrations found in the snow are discussed with

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reference to the meteorological parameters provided by MeteoSwiss. Possible sources of the n-aldehydes are considered, and processes for the uptake of n-aldehydes by snow crystals are discussed.

2 Experimental

2.1 Sampling Site

Sampling was carried out at the high altitude research station Jungfraujoch (Switzerland; 3580 m a.s.l.) during CLACE 5 in February and March 2006. The station is located in the Swiss Alps on a mountain saddle between the mountains Jungfrau (4158 m a.s.l.) and Moench (4099 m a.s.l.). An online meteorological station of the Swiss Meteorological Institute is located at Jungfraujoch, and provides basic meteorological data. The geographical location (for a map see Fig. 2 in Starokozhev et al., 2008) results in air masses predominantly arriving at Jungfraujoch from the south or north. Due to the high altitude of the station, sampling in the lower free troposphere is possible. Anthropogenic emissions of fossil fuels at the station are reduced to a minimum, as heating and cooking and the Jungfraujoch train are operated using electricity. During autumn, winter and spring the station is in clouds approximately 40% of the time (Baltensperger et al., 1997), making it ideal for collection of freshly fallen snow directly in-cloud. If snow sampling is possible in clouds during precipitation, below-cloud scavenging can be excluded as an uptake process for organic compounds.

2.2 Sampling procedure

Prior to sampling the 20 ml brown glass sampling vials, septa (Silicon/PTFE, Gerstel, Mülheim an der Ruhr, Germany) and screw caps were rinsed twice with ultra pure water (Merck), treated for 15 min in an ultra sonic bath, again rinsed with ultra pure water, and finally heated at 110°C for 2 h in a drying oven. After this cleaning procedure n-aldehydes could not be detected in laboratory blank samples. A small aluminum plate

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was placed on top of each septum to avoid contamination during transport, and the vials were kept closed until snow sampling occurred.

During the sampling program 27 samples of freshly fallen snow were collected. During four snowfall events three replicate samples for analysis were taken at the same time and location; for determination of relative standard deviations (RSDs). The sampling date and time, and additional meteorological data provided by MeteoSwiss, are presented in Table 2. During sampling the vials were only opened for the short time it took to fill the vial with freshly fallen snow using a custom-made stainless steel snow scissor. Snow samples were kept frozen at -20°C in a freezer box, and were analyzed within 2 weeks. The sample amount was measured gravimetrically after analysis. The snow sampling occasions were determined by meteorological conditions throughout the sampling period, as only freshly fallen snow was collected. Analytical blank samples comprised 4 mL of ultra-pure water (Merck) placed in separate sampling vials during each snow sampling at Jungfraujoch. All blank samples were treated in the same manner as snow samples. The concentrations of n-aldehydes in the blank samples were relatively high and varied with the sampling occasion, reflecting changes in the air at Jungfraujoch. The appropriate blank values were subtracted from the concentrations found in the corresponding snow samples. Throughout the sampling program the median blank values were $0.576\ \mu\text{g L}^{-1}$ for n-hexanal, $0.151\ \mu\text{g L}^{-1}$ for n-heptanal, $0.256\ \mu\text{g L}^{-1}$ for n-octanal, $0.701\ \mu\text{g L}^{-1}$ for n-nonanal, and $0.467\ \mu\text{g L}^{-1}$ for n-decanal.

2.3 Analysis

Analysis of the snow samples in the laboratory was performed by HS-SPDE followed by GC/MS. Prior to analysis the snow samples were melted at room temperature. The aluminum plate on top of the vials was removed and the melted snow water was spiked by injection through the septum with 2 ng of fluorobenzene ($2\ \mu\text{L}$ of a $1\ \text{ng}\ \mu\text{L}^{-1}$ standard solution of fluorobenzene in methanol) as an internal standard (for details see Sieg et al., 2008).

A commercially available SPDE needle (74 mm \times 0.8 mm, Chromtech, Idstein, 8076

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Germany) was used for the analysis. The sorption material consisted of PDMS with a 10% embedded activated carbon (PDMS/AC) phase of 50 μm film thickness. The needle was preconditioned in the flushing station for 1 h at 250°C. Extraction was performed from the sample headspace. Samples were analyzed using a CTC-CombiPAL autosampler (Bender and Hobein, Zurich, Switzerland). The autosampler was equipped with a heatable CTC agitator for incubation and shaking, an extraction cooler (Chromtech, Idstein, Germany) to cool the SPDE needle to -15°C during extraction, and an additional gas station (Chromtech, Idstein, Germany) to aspire desorption gas. To prevent carryover of analytes between analyses a heated flushing station was used to recondition the SPDE needle after each analysis. Both the gas station and the heated flushing station were flushed with helium. The syringe body was held at a temperature of 35°C in the syringe adapter heater. All of the SPDE steps were fully controlled by the autosampler. Details of the development of the SPDE method have been described elsewhere (Sieg et al., 2008).

The GC-MS (Thermoquest CE Instruments Trace GC 2000 Series combined with a Voyager MS) was equipped with a 60 m DB-624 capillary column (Agilent Technologies) with a 0.32 mm internal diameter and a film thickness of 1.8 μm . Helium (purity 5.0) served as carrier gas. Desorption of the analytes from the SPDE needle was carried out in the GC injector by adjusting the injector temperature to 230°C. Measurements were carried out in the splitless mode. The column was operated in constant pressure mode at 70 kPa. The GC oven temperature program was: 32°C for 2 min; heating at 12°C/min to 190°C; 190°C for 20 min. Data acquisition, processing and instrument control were performed using Excalibur software (Thermoquest). Detection of the analytes was performed by a Thermoquest Finnigan Voyager MS in the electron ionization positive ion (EI+) and full scan modes (scan range 35–300). Quantification was achieved with the following quantification ions: m/z 57 for n-hexanal, m/z 70 for n-heptanal, m/z 84 for n-octanal, m/z 98 for n-nonanal and m/z 112 for n-decanal. A chromatogram of a snow sample with the corresponding quantification ions is shown in Fig. 1.

3 Results

3.1 Concentrations of n-aldehydes in snow during CLACE 5

The concentrations of n-aldehydes in all snow samples (n=27) analyzed during the CLACE 5 field campaign are summarized in Table 3, and the median values and 25th and 75th percentiles of n-aldehyde concentrations are summarized in Fig. 2. Error bars include 5% till 95% of the concentration values. The highest median concentration was observed for n-hexanal ($1.324 \mu\text{g L}^{-1}$), followed by n-nonanal ($1.239 \mu\text{g L}^{-1}$), n-decanal ($0.863 \mu\text{g L}^{-1}$), n-octanal ($0.460 \mu\text{g L}^{-1}$) and n-heptanal ($0.304 \mu\text{g L}^{-1}$). The concentration of n-hexanal was most variable of all the analyzed n-aldehydes, followed by n-decanal, n-nonanal, n-octanal and n-heptanal. Only n-nonanal was detected in all snow samples (see Table 3).

3.2 Heterogeneity of snow samples from individual snowfall events

During four snowfall events three replicate samples for analysis were taken at the same location; the mean values and relative standard deviations (RSDs) for these samples are shown in Table 4. The RSDs were 15–45% for n-hexanal, 6–71% for n-heptanal, 12–69% for n-octanal, 17–59% for n-nonanal, and 14–90% for n-decanal. Thus, the RSD significantly exceeded the analytical precision of the method (the RSD for $2 \mu\text{g L}^{-1}$ ranges from 6.1% for n-octanal to 16.5% for n-hexanal; see Sieg et al., 2008).

3.3 Wind direction

During the CLACE 5 campaign the prevailing wind directions at Jungfraujoch were southwest-southeast (SW-SE) and north-northwest (N-NW). Snow samples were collected when the wind direction was both SW-SE (10) and N-NW (17). Detailed information on the wind direction during each snow sampling occasion is presented in Table 2. The results show that the median concentrations of n-aldehydes were generally higher in snow samples collected at times of N-NW wind direction. Box plots for the

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concentrations of n-aldehydes with N-NW and SW-SE wind directions are presented in Fig. 3a and b, respectively. n-Nonanal provided the highest median concentration in snow samples collected during times of both wind directions (N-NW, $1.609 \mu\text{g L}^{-1}$; SW-SE, $1.031 \mu\text{g L}^{-1}$). In snow samples taken during N-NW winds, n-hexanal (median concentration $1.457 \mu\text{g L}^{-1}$) was the second most abundant n-aldehyde followed by n-decanal ($1.153 \mu\text{g L}^{-1}$), n-octanal ($0.580 \mu\text{g L}^{-1}$) and n-heptanal ($0.342 \mu\text{g L}^{-1}$). The greatest variation in concentration was found for n-hexanal, which showed the highest maximum concentration for snow samples collected during N-NW winds. In samples taken during SW-SE winds the n-aldehyde concentrations were in general lower with the second most abundant n-aldehyde being n-decanal (median concentration $0.674 \mu\text{g L}^{-1}$) followed by n-hexanal ($0.554 \mu\text{g L}^{-1}$), n-octanal ($0.281 \mu\text{g L}^{-1}$) and n-heptanal ($0.104 \mu\text{g L}^{-1}$). High variations in concentrations were preferentially observed for n-decanal and n-nonanal during SW-SE winds.

4 Discussion

The median concentrations measured in snow samples collected at Jungfraujoch during CLACE 5 ranged from $0.304 \mu\text{g L}^{-1}$ for n-heptanal to $1.324 \mu\text{g L}^{-1}$ for n-hexanal. These values are more than one order of magnitude higher than n-aldehyde concentrations determined in snow samples from Mount Sonnblick (Austria; 3106 m a.s.l.) in 1996 and 1997 (Gröllert and Puxbaum, 2000), and the Antarctic in 1993 and 1994 (Desideri et al., 1998) (see Table 1). Gröllert and Puxbaum (2000) sampled fresh surface snow of approximately 10 cm thickness using a polyethylene shovel, and stored the samples in polyethylene bags until analysis. One possible explanation for the observed differences in n-aldehyde concentrations between these studies is variation in the meteorological conditions and atmospheric concentrations of n-aldehydes at the different sampling times and sampling locations. Desideri et al. (1998) collected surface snow at different altitudes and snow from different depths at two locations in the Antarctic. During the sampling procedure the top 5 cm of snow surface was removed to

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avoid contamination of the sample, since the snow was not freshly fallen. Comparison of old and freshly fallen snow with respect to the content of VOCs and SVOCs is problematic, since snow on the ground continues to interact with the ambient atmosphere through photochemical reactions or physical processes (Domine et al., 2008; Grannas et al., 2007; Herbert et al., 2006; Kos and Ariya, 2006).

The large variations in n-aldehyde concentrations in samples collected at Jungfraujoch during the same snow event provides evidence for the heterogeneous composition of organic compounds in snow, which significantly exceeded the variability of the analytical method (Sieg et al., 2008). Large concentration variations may result from variable partitioning of n-aldehydes between the gas phase, the liquid phase and the particle phase in the atmosphere, and uptake processes by snow crystals. Various uptake processes of n-aldehydes into the snow are possible. The uptake of n-aldehydes from the gas phase into the snow seems unlikely, since for compounds more volatile than the C₆–C₁₀ n-aldehydes such as acetone and formaldehyde (Winkler et al., 2002) and benzene and alkylated benzenes (Fries et al., 2006) adsorption on ice surfaces from the gas phase was reported to be highly reversible. Therefore adsorption processes cannot explain the occurrence of VOC in snow. Another uptake mechanism for n-aldehydes into ice is through riming. For inorganic compounds the uptake processes into snow and ice through riming has been reported in various studies (Kalina and Puxbaum, 1994; Poulida et al., 1998). Similar studies reporting an uptake of organic compounds into snow and ice through riming are not available in literature. However, the uptake of n-aldehydes into snow through riming should not be excluded, although the low water solubility ranging from 5.6 g L⁻¹ (n-hexanal, at 25°C) to 0.06 g L⁻¹ (n-decanal, at 25°C) favors other uptake mechanism. A third mechanism for the incorporation of n-aldehydes into snow and ice is through particle scavenging. Model predictions (Lei and Wania, 2004) and field measurements (Halsall et al., 1997) support the idea that organic compounds with low Henry's coefficients (H) have a tendency to adsorb to aerosol particles. Particle-bound organic compounds can be scavenged by snow crystals (Miller and Wang, 1991). C₆–C₁₀ n-aldehydes have relatively low H

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values, ranging (at 25°C) from 0.021 kPa m³ mol⁻¹ for n-hexanal to 0.182 kPa m³ mol⁻¹ for n-decanal suggesting a preferential sorption onto the particles in the atmosphere. Thus, particle scavenging of the n-aldehydes by snow crystals should be an important uptake process for these compounds. Large variations in the concentrations of n-aldehydes in snow could therefore be explained by a heterogeneous distribution of particles in different snow samples. Furthermore, heterogeneous oxidation processes on acidic particle surfaces can produce n-aldehydes and result in an increase in secondary organic aerosols (SOAs; Jang et al., 2002). The occurrence of a high proportion of oxygenated organic aerosols (OOAs), in aerosol particles collected at Jungfraujoch has recently been reported (Zhang et al., 2007) and was explained to originate from secondary aerosol production. During the field campaign CLACE 5 aerosol particles in clouds were investigated by sampling air through 3 inlets. The first inlet was a heated inlet (25°C) to measure the total aerosol concentration, which consists of aerosol particles incorporated into cloud droplets and ice crystals and of interstitial (nonactivated) particles. The inlet was operated by the Paul Scherrer Institute (PSI, Switzerland) and is used for continuous measurements in the global atmosphere watch (GAW) program (Cozic et al., 2008a). Additionally the PSI operated an interstitial inlet to sample non-activated particles. A third inlet, the Ice Counterflow Virtual Impactor (Ice-CVI) was designed to sample only small ice crystals in the diameter range 5–20 μm (Mertes et al., 2007). This inlet was operated by the Leibniz-Institute for Tropospheric Research (IfT). These inlets are connected to various instruments from different groups to analyze the collected aerosol. Until today no aerosol data obtained from CLACE 5 are available in the literature. However, the chemical composition of aerosol particles for PM₁ and coarse mode are available from previous CLACE field campaigns (Cozic et al., 2008b). Cozic et al. (2008b) collected aerosol particles using the same heated total aerosol inlet (25°C) which was used during CLACE 5. The organic fraction of the aerosol was analyzed using an Aerodyne Quadrupole Aerosol Mass Spectrometer (Q-AMS, for details see Jayne et al., 2000). The authors reported that the organic fraction of the aerosol was found exclusively in the particles with an aerodynamic diameter below 1 μm (PM₁).

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In March 2004 and in February/March 2005, the over all content of organic compounds in PM₁ aerosols was 16% and 41%, respectively. The high difference between 2004 and 2005 was explained by different origins of air masses arriving at Jungfraujoch. During the measurements in 2004 there was a larger contribution from the Western Alpine region, from the upper Po valley and especially from Spain and Algeria, while in 2005 the influence of air masses arriving from the North was significantly higher. Furthermore the chemical composition of the PM₁ in February/ March 2005 was close to summer values in July/August 2005 when the Jungfraujoch is influenced by injection of boundary layer air into the lower free troposphere. High organic fractions in summer measurements were explained by higher biogenic emissions and photochemical activities in summer in comparison to the winter season (Cozic et al., 2008b). Wind directions at Jungfraujoch during the snow sampling campaign CLACE 5 were more composed of NW-N than from SW-SE. Therefore, a high organic fraction in the PM₁ fraction of the aerosol particles including the n-aldehydes during CLACE 5 seems again possible. Although these findings are consistent with the possibility of particle scavenging of n-aldehydes by snow crystals further laboratory experiments are required to study the different uptake mechanism separately.

A possible mechanism for the reaction of oleic acid and linoleic acid with ozone has been suggested previously (Katrib et al., 2004; Moise and Rudich, 2002; Thornberry and Abbatt, 2004). The chemical processes responsible for the observed atmospheric production of n-nonanal and n-hexanal by the oxidation of oleic acid and linoleic acid are summarized in Fig. 4a and b. Both n-aldehydes are produced through ozonolysis of double bonds in the respective unsaturated fatty acids. n-Aldehydes originating from biogenic precursors are termed indirect biogenic emissions. In addition to the oxidation of fatty acids, a further reaction mechanism to obtain n-aldehydes from 1-octene and 1-decene has been proposed by Alves and Pio (2005) and is shown in Fig. 4c and d. Both 1-octene and 1-decene have been suggested to originate from anthropogenic emissions (Grosjean et al., 1994). In snow from Jungfraujoch, n-hexanal and n-nonanal were the two most abundant n-aldehydes. These results are consistent

with the oxidation of unsaturated fatty acids to aldehydes, followed by scavenging of particle-bound aldehydes. A contribution of oxidation products of anthropogenic emissions of 1-octene and 1-decene seems unlikely because neither 1-octene nor 1-decene could be detected in our analyses, despite their physical and chemical characteristics indicating that they should have been detected by the methods used, if present. Heterogeneous distribution of particles loaded with n-aldehydes throughout the snow is the most likely explanation for the high RSDs found in snow samples collected at the same time and place.

Azelaic acid, a dicarboxylic acid, is a further reaction product of the oxidation of oleic acid with ozone (Fig. 4a) (Katrib et al., 2004; Moise and Rudich, 2002; Thornberry and Abbatt, 2004), and was reported to be present in snow samples collected during the CLACE 5 and CLACE 6 sampling campaigns (Winterhalter et al., 2009). Azelaic acid could not be detected in our measurements, since headspace analysis combined with GC/MS, as applied in our study, is not an appropriate method for the analysis of organic acids in water samples. Winterhalter et al. (2009) focused their analysis on the detection of dicarboxylic acids using solid phase extraction as a pre-concentration step, followed by HPLC-MS. Snow sampling by Winterhalter et al. (2009) was performed on five occasions at the same times and location as our snow samples were collected. However, no correlation was found between the azelaic acid concentrations in snow, as measured by Winterhalter et al. (2009), and the n-nonanal concentrations measured in the present study. As the data available to evaluate any correlation were inadequate, further studies using a greater number of snow samples that are analyzed for both n-nonanal and azelaic acid will be necessary to evaluate any correlations between azelaic acid and n-nonanal.

Direct emissions of C₆–C₁₀ n-aldehydes from vegetation have been reported in several studies (Ciccioli et al., 1993; Kesselmeier and Staudt, 1999; König et al., 1995; Owen et al., 1997; Wildt et al., 2003; Yokouchi et al., 1990). Yokouchi et al. (1990) analyzed n-aldehydes in the atmosphere over remote areas and reported an increase in n-aldehyde concentration from n-hexanal to n-nonanal, and a slight decrease in

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n-aldehyde concentration from n-nonanal to n-decanal (Fig. 5a). The n-aldehydes detected were considered to be of biogenic origin, and n-nonanal was reported to be the most abundant n-aldehyde. A similar pattern of C₆–C₁₀ n-aldehyde concentrations was found by Ciccioli et al. (1993) in air samples collected above urban, suburban and forest areas in Italy, and by Kesselmeier and Staudt (1999) in the atmosphere of rural areas (Fig. 5a). Our results from the analyses of snow samples from Jungfraujoch (Fig. 5b) are in agreement with these studies with respect to an increase in concentrations from n-heptanal to n-nonanal, and a slight decrease to n-decanal, but the high concentration of n-hexanal relative to n-nonanal is not consistent with previously described n-aldehyde patterns (Ciccioli et al., 1993; Kesselmeier and Staudt, 1999; Yokouchi et al., 1990). However, investigations of emissions of n-aldehydes from 18 tree and shrub species in Italy (Owen et al., 1997) and 8 plant species in Austria (König et al., 1995) revealed that the distribution of n-aldehydes depends primarily on the plant species. König et al. (1995) detected n-hexanal as the dominant n-aldehyde, and Owen et al. (1997) detected n-nonanal and n-decanal as the dominant homologues among the C₆–C₁₀ n-aldehydes. Based on these results, direct emissions from vegetation may also contribute significantly to the occurrence of n-aldehydes in snow.

Differences were noted in the n-aldehyde content of samples, depending on the dominant wind direction (N-NW or SW-SE; Fig. 3). The median concentrations of all n-aldehydes analyzed in snow samples from Jungfraujoch were higher at sampling times associated with air masses accompanying N-NW winds, relative to sampling times when air masses came from the SW-SE. These findings suggest the possibility of more intense emission sources of atmospheric n-aldehydes to the north of Jungfraujoch, which is consistent with the presence of large forest areas on the Swiss plateau in this direction. Back trajectories, provided by the German Weather Service (DWD) using the DWD-Local model Europe, do not show any further correlation with the measured concentrations of n-aldehydes in snow and are comparable to the correlation between the n-aldehydes concentration and the wind direction described above. A contribution to the concentration of n-aldehydes in snow from combustion of fuels is

unlikely, because a homogenous distribution profile without any predominance of individual aldehydes in the C₆–C₁₀ carbon chain range would be expected, if this were the case. Moreover, in case of an origin of n-aldehydes from fossil fuel combustion concentration differences between weekdays and weekends would be expected which is not supported by the dataset (Table 3).

5 Conclusions

A wide range of concentrations of n-aldehydes was found in snow samples from Jungfraujoch, even for samples collected at the same time during the same snowfall event.

According to their physico-chemical characteristics, n-aldehydes are expected to be primarily linked to aerosol particles in the atmosphere suggesting the uptake of n-aldehydes into snow via the particle phase. The high concentration variations of the n-aldehydes among the snow samples can be explained assuming that aerosol particles are heterogeneously distributed throughout the snow samples. Particle scavenging can occur during snow formation in clouds.

The sources of atmospheric n-aldehydes present at Jungfraujoch are most likely to be related to direct or indirect biogenic emissions. Evidence for direct biogenic emissions include firstly that several studies have demonstrated that all analyzed n-aldehydes could come from direct emissions from vegetation (Ciccioli et al., 1993; Wildt et al., 2003; Yokouchi et al., 1990). Secondly, the concentrations of individual n-aldehydes found at Jungfraujoch largely match (with the exception of n-hexanal) those of n-aldehydes reported previously in the studies of Ciccioli et al. (1993), Yokouchi et al. (1990) and Kesselmeier and Staudt (1999), which were attributed to biogenic origins.

Additionally, indirect biogenic emissions can contribute to the atmospheric concentrations of n-aldehydes, through oxidation of precursor compounds of biogenic origin. In this context, Moise and Rudich (2002) and Thornberry and Abbatt (2004) proposed

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the formation of n-nonanal and n-hexanal from the cleavage by ozonolysis of double bonds in unsaturated fatty acids (namely oleic acid and linoleic acids). Furthermore, Zhang et al. (2007) reported that aerosols collected at Jungfraujoch contained high proportions of oxygenated organic aerosol. The predominance of n-hexanal and n-nonanal among the C₆–C₁₀ n-aldehydes in the snow samples collected at Jungfraujoch during CLACE 5 is therefore a strong argument for the formation of the aldehydes through oxidation of unsaturated fatty acids in the atmosphere.

The occurrence of n-aldehydes in snow at Jungfraujoch from anthropogenic emissions from polluted air masses in surrounding valleys is thought to be negligible.

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Table 1. Concentrations of n-aldehydes in snow reported in previous studies.

	concentration	year	location	Reference
n-nonanal	142 ng L ⁻¹	1996	Mount Sonnblick (Austria)	Gröllert and Puxbaum (2000)
n-decanal	0.5 ng L ⁻¹	1996/1997	Mount Sonnblick (Austria)	Gröllert (2000) and Puxbaum
n-nonanal	16–227 ng L ⁻¹	1993/1994	Antarctic, surface snow at different altitudes	Desideri et al. (1998)
n-decanal	4–96 ng L ⁻¹	1993/1994	Antarctic, surface snow at different altitudes	Desideri et al. (1998)
n-nonanal	89–484 ng L ⁻¹	1993/1994	Antarctic, snow at different depths	Desideri et al. (1998)
n-decanal	<0.7–198 ng L ⁻¹	1993/1994	Antarctic, snow at different depths	Desideri et al. (1998)
n-nonanal	0.07–0.31 μg kg ⁻¹ 1.17–2.80 μg kg ⁻¹	1998	Finland Russia	Poliakova et al. (2000)
n-decanal	0.16 μg kg ⁻¹ 0.01–0.39 μg kg ⁻¹	1998	Finland Russia	Poliakova et al. (2000)

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Table 2. Details of snow sampling during CLACE 5.

sampling date	sampling time UTC+1	no. of samples	wind direction ^a [°]	temperature ^a [°C]	day of the week
20 Feb 2006	09:35	1	150	−15	Mon
20 Feb 2006	17:00	3	199	−16	Mon
22 Feb 2006	15:45	3	168	−14	Wed
24 Feb 2006	12:45	3	164	−14	Fri
25 Feb 2006	21:30	2	334	−14	Sat
26 Feb 2006	21:10	2	322	−17	Sun
01 Mar 2006	09:00	2	346	−22	Wed
01 Mar 2006	12:00	2	337	−24	Wed
01 Mar 2006	14:50	3	319	−22	Wed
02 Mar 2006	08:45	2	337	−24	Thu
05 Mar 2006	08:45	2	330	−16	Sat
05 Mar 2006	12:45	2	322	−20	Sat

^a Data provided by MeteoSwiss.

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**Table 3.** Concentrations of n-aldehydes in snow during CLACE 5.

sampling date	sampling time UTC+1	n-hexanal [$\mu\text{g L}^{-1}$]	n-heptanal [$\mu\text{g L}^{-1}$]	n-octanal [$\mu\text{g L}^{-1}$]	n-nonanal [$\mu\text{g L}^{-1}$]	n-decanal [$\mu\text{g L}^{-1}$]
20 Feb 2006	09:35	0.456	0.106	0.230	1.142	0.535
20 Feb 2006	17:00	0.585	0.088	0.217	0.609	0.602
20 Feb 2006	17:00	0.473	0.101	0.287	0.920	0.863
20 Feb 2006	17:00	0.402	0.093	0.274	0.768	0.745
22 Feb 2006	15:45	0.523	0.075	0.160	0.478	0.203
22 Feb 2006	15:45	0.686	0.176	0.357	1.176	0.542
22 Feb 2006	15:45	0.223	0.031	<QL	0.286	<DL
24 Feb 2006	12:45	1.140	0.236	0.384	1.239	0.819
24 Feb 2006	12:45	1.538	0.371	0.594	1.891	1.053
24 Feb 2006	12:45	1.759	0.505	1.101	2.872	3.189
25 Feb 2006	21:30	0.681	0.253	0.355	0.837	0.635
25 Feb 2006	21:30	<DL	0.080	<QL	0.362	0.196
26 Feb 2006	21:10	1.457	0.333	0.637	1.757	1.745
26 Feb 2006	21:10	<DL	<DL	<DL	0.378	0.303
1 Mar 2006	09:00	1.935	0.264	0.460	1.148	0.686
1 Mar 2006	09:00	1.280	0.304	0.532	1.520	1.229
1 Mar 2006	12:00	1.502	0.453	0.801	2.395	2.383
1 Mar 2006	12:00	3.777	0.535	0.657	1.921	1.520
1 Mar 2006	14:50	1.371	0.439	0.829	2.300	2.457
1 Mar 2006	14:50	3.536	0.487	0.620	1.609	1.118
1 Mar 2006	14:50	1.577	0.281	0.324	0.932	0.574
2 Mar 2006	08:45	1.324	0.366	0.693	1.992	1.722
2 Mar 2006	08:45	1.399	0.314	0.621	1.896	1.885
5 Mar 2006	08:45	1.726	0.342	0.580	1.944	1.683
5 Mar 2006	08:45	5.127	0.480	0.409	1.213	0.655
5 Mar 2006	12:45	1.324	0.403	0.578	1.493	1.094
5 Mar 2006	12:45	2.580	0.455	0.674	1.923	1.153

DL: detection limit (n-hexanal: $0.063 \mu\text{g L}^{-1}$; n-heptanal: $0.021 \mu\text{g L}^{-1}$; n-octanal: $0.043 \mu\text{g L}^{-1}$; n-nonanal: $0.023 \mu\text{g L}^{-1}$; n-decanal: $0.026 \mu\text{g L}^{-1}$)

QL: quantification limit (n-hexanal: $0.188 \mu\text{g L}^{-1}$; n-heptanal: $0.062 \mu\text{g L}^{-1}$; n-octanal: $0.130 \mu\text{g L}^{-1}$; n-nonanal: $0.069 \mu\text{g L}^{-1}$; n-decanal: $0.079 \mu\text{g L}^{-1}$)

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Table 4. Mean concentrations and relative standard deviation (RSD) of n-aldehydes in snow samples from single snow events on four separate days during CLACE 5 (2006) [$\mu\text{g L}^{-1}$].

	20 Feb 2006 17:00 (UTC+1) (<i>n</i> =3)		22 Feb 2006 15:45 (UTC+1) (<i>n</i> =3)		24 Feb 2006 12:45 (UTC+1) (<i>n</i> =3)		1 Mar 2006 14:50 (UTC+1) (<i>n</i> =3)	
	Mean	RSD	Mean	RSD	Mean	RSD	Mean	RSD
n-hexanal	0.487	15%	0.477	40%	1.479	17%	2.161	45%
n-heptanal	0.094	6%	0.091	71%	0.371	30%	0.402	22%
n-octanal	0.259	12%	0.187	69%	0.693	43%	0.591	35%
n-nonanal	0.766	17%	0.647	59%	2.001	34%	1.614	35%
n-decanal	0.737	14%	0.248	90%	1.687	63%	1.383	57%

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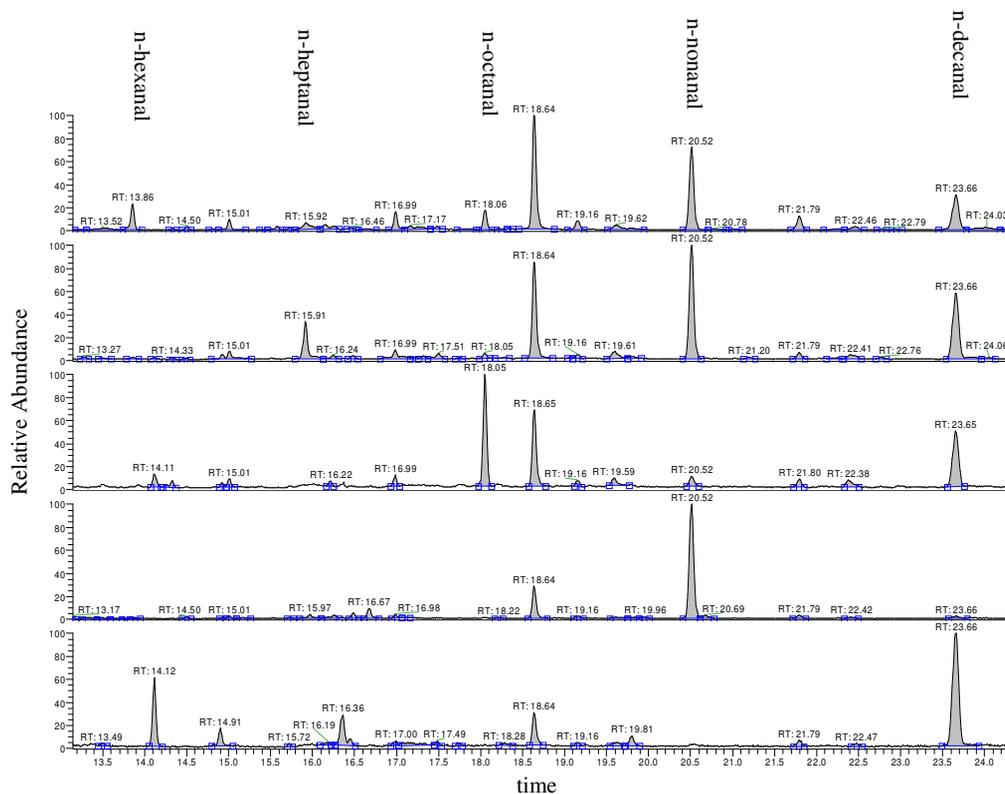
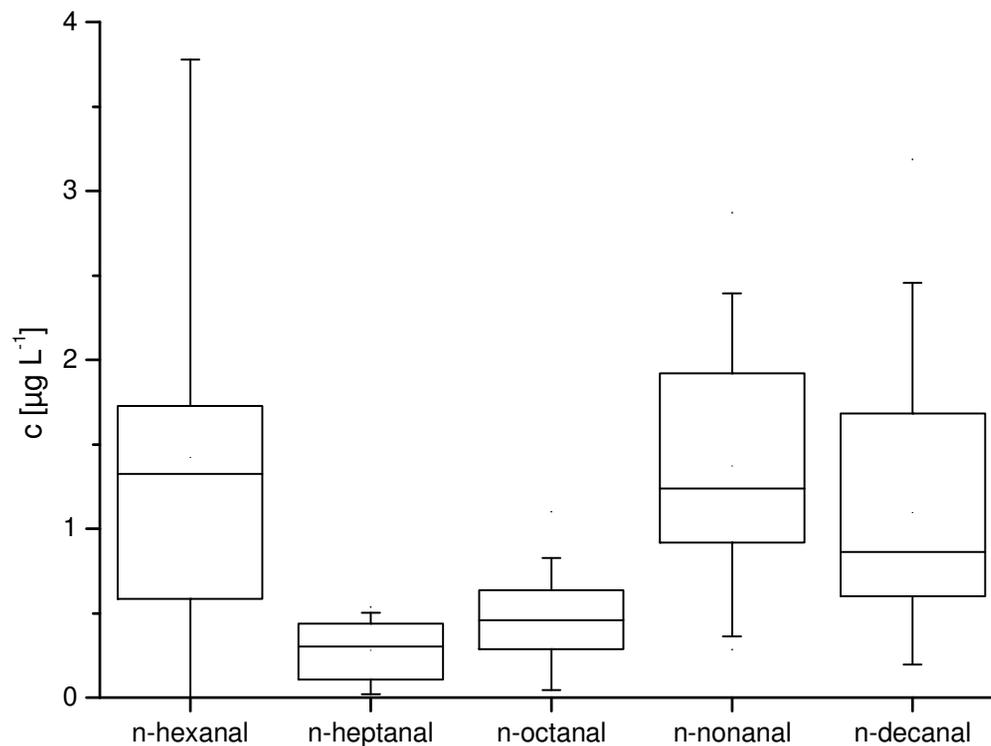


Fig. 1. n-Aldehydes (*m/z* top down, 57, 70, 84, 98, 112) in snow sample from 24 February 2006 at 12:45 (UTC+1).

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**Fig. 2.** Concentrations of n-aldehydes in snow during CLACE 5 ($n=27$).[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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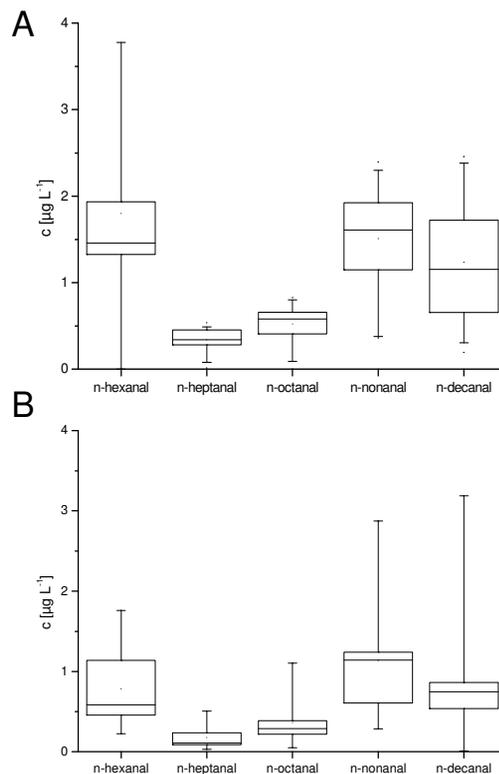


Fig. 3. Median concentrations of n-aldehydes in snow **(A)** wind direction NW-N ($n=17$) and **(B)** wind direction SW-SE ($n=10$)

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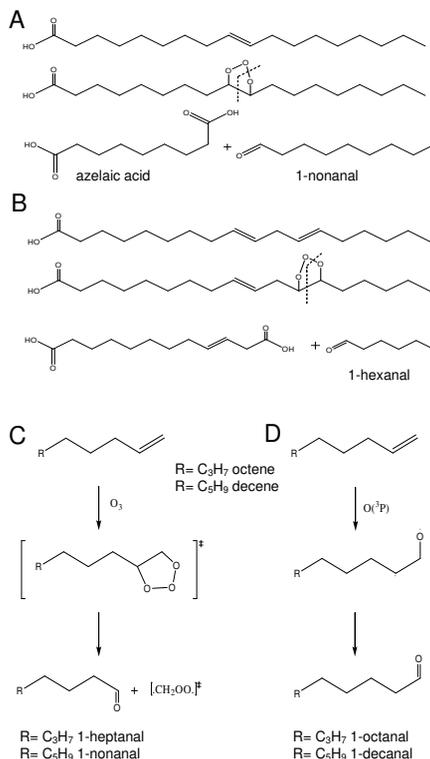


Fig. 4. Reaction scheme for formation of n-aldehydes through atmospheric oxidation with ozone and oxygen: **(A)** Formation of 1-nonanal from the ozone reaction with oleic acid. **(B)** Formation of 1-hexanal from the ozone reaction with linoleic acid. **(C)** Formation of 1-heptanal and 1-nonanal from the ozone reaction with 1-octene and 1-decene. **(D)** Formation of 1-octanal and 1-decanal from the reaction of oxygen with 1-octene and 1-decene, References for mechanism A and B: Moise and Rudich (2002), Thornberry and Abbatt (2004), References for mechanism C and D: Alves and Pio (2005).

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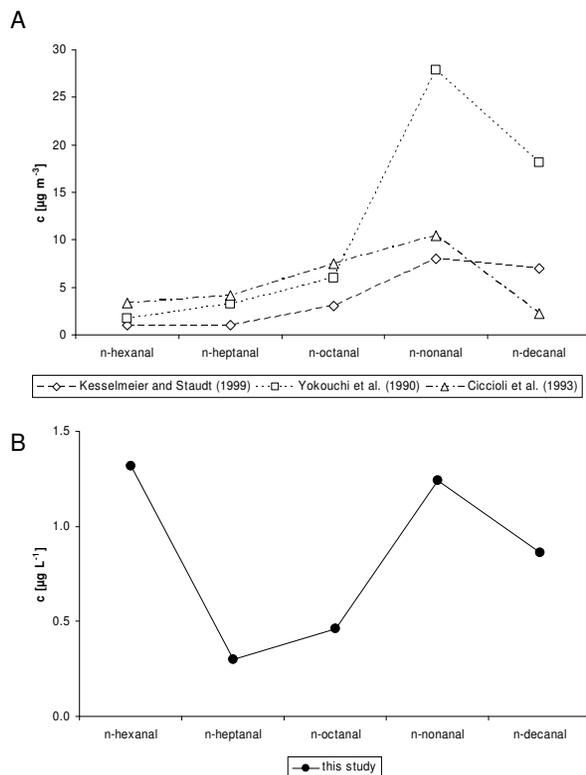


Fig. 5. (A) Distribution of individual n-aldehydes in air from different studies, for references see Kesselmeier and Staudt (1999) Table 5, Yokouchi et al. (1990) Table 1 Oki Island, and Ciccioni et al. (1993) Table 1 Monti Cimino Forest; **(B)** Distribution of individual n-aldehydes in snow collected at Jungfrauoch during CLACE 5 in 2006.

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