**Atmospheric
Chemistry
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Concentrations of higher dicarboxylic acids C$_5$–C$_{13}$ in fresh snow samples collected at the High Alpine Research Station Jungfraujoch during CLACE 5 and 6

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Abstract. Samples of freshly fallen snow were collected at the high alpine research station Jungfraujoch (Switzerland) in February and March 2006 and 2007, during the **Cl**oud and **A**erosol **C**haracterization **E**xperiments (CLACE) 5 and 6. In this study a new technique has been developed and demonstrated for the measurement of organic acids in fresh snow. The melted snow samples were subjected to solid phase extraction and resulting solutions analysed for organic acids by HPLC-MS-TOF using negative electrospray ionization. A series of linear dicarboxylic acids from C$_5$ to C$_{13}$ and phthalic acid, were identified and quantified. In several samples the biogenic acid pinonic acid was also observed. In fresh snow the median concentration of the most abundant acid, adipic acid, was 0.69 µg L^{-1} in 2006 and 0.70 µg L^{-1} in 2007. Glutaric acid was the second most abundant dicarboxylic acid found with median values of 0.46 µg L^{-1} in 2006 and 0.61 µg L^{-1} in 2007, while the aromatic acid phthalic acid showed a median concentration of 0.34 µg L^{-1} in 2006 and 0.45 µg L^{-1} in 2007. The concentrations in the samples from various snowfall events varied significantly, and were found to be dependent on the back trajectory of the air mass arriving at Jungfraujoch. Air masses of marine origin showed the lowest concentrations of acids whereas the highest concentrations were measured when the air mass was strongly influenced by boundary layer air.
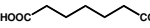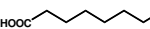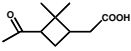
1 Introduction

Organic compounds contribute significantly (20–50% by mass) to the total fine aerosol fraction at continental mid-latitudes (Saxena and Hildemann, 1996), and as much as 90% in tropical forested areas (Andreae and Crutzen, 1997). A substantial fraction of the organic component of atmospheric particles consists of water-soluble, possibly multifunctional compounds (Saxena and Hildemann, 1996; Kavouras et al., 1998). Dicarboxylic acids are a major contributor to organic aerosol mass (Sempéré and Kawamura, 2003). Due to their low vapor pressure (Saxena and Hildemann, 1996), dicarboxylic acids are predominantly present in the aerosol phase (Baboukas et al., 2000; Limbeck et al., 2001). They are ubiquitous in the atmosphere, and measurements have been reported from urban (Kawamura and Ikushima, 1993), continental background (Limbeck and Puxbaum, 1999), remote marine (Kawamura and Sakaguchi, 1999; Mochida et al., 2003; Sempéré and Kawamura, 1996) and Arctic (Narukawa et al., 2002) environments. Oxalic acid is usually the most abundant dicarboxylic acid followed by malonic and succinic acid. The concentration and relative abundance of dicarboxylic acids is controlled both by primary sources and the secondary formation by atmospheric oxidation processes. Direct emissions originate from fossil fuel combustion (Kawamura and Kaplan, 1987), biomass burning (Lefer et al., 1994; Legrand and DeAngelis, 1996; Narukawa et al., 1999) and sources such as meat cooking (Schauer et al., 1999). Secondary sources include the photooxidation of unsaturated fatty aids (Kawamura et al., 1996; Stephanou and Stratigakis, 1993) and cyclic alkenes (Hatakeyama et al., 1987). The relative contribution of these

Table 1. Extraction efficiencies, blank values and detection limits of the analysed organic acids.

Compound name	Structure	Molecular weight [g mole^{-1}]	Extraction efficiency [%]	Blank[a] [nmol L^{-1}]	LOD[b] [nmol L^{-1}]	LOQ[c] [nmol L^{-1}]
Glutaric acid	HOOC⌒COOH	132	65	0.42	11.8	39.6
Adipic acid	HOOC⌒⌒COOH	146	102	0.57	8.2	27.3
Pimelic acid	HOOC⌒⌒COOH	160	92	0.15	6.9	22.9
Suberic acid	HOOC⌒⌒⌒COOH	174	76	0.30	4.0	15.4
Azelaic acid	HOOC⌒⌒⌒COOH	188	79	0.14	1.3	4.3
Sebacic acid	HOOC⌒⌒⌒⌒COOH	202	77	0.06	1.9	6.1
Undecanedioic acid	HOOC⌒⌒⌒⌒COOH	216	71[d]	0.02	0.6[d]	2.0[d]
Dodecanedioic acid	HOOC⌒⌒⌒⌒⌒COOH	230	61	n.d.[e]	0.9	3.0
Tridecanedioic acid	HOOC⌒⌒⌒⌒⌒COOH	244	41	n.d.	2.5	8.3
Phthalic acid	[structure]	166	83	0.95	9.6	32.0
Pinonic acid	[structure]	184	74	n.d.	29.5	98.2

[a] Blank values from extraction of pure water samples with pre-concentration factors between 100 to 200.
[b] LOD: Limit of detection of the HPLC/MS method defined as 3-fold standard deviation of background signal.
[c] LOQ: Limit of quantification of the HPLC/MS method defined as 10-fold standard deviation of background signal.
[d] Interpolated from the response factors of C_8 to C_{13} dicarboxylic acids.
[e] Not detected.

sources and their temporal and spatial variability is still unclear (Mochida et al., 2003). A recent modelling study for the North Pacific implies that C_2–C_7 dicarboxylic acids are of anthropogenic origin, whereas C_8–C_{11} species might be of natural origin, possibly emitted from the ocean (Mochida et al., 2003).

Dicarboxylic acids have been also measured in snow samples from remote and urban locations, although to date only three studies have been reported. High concentrations up to 11.5 µg L^{-1} for azelaic acid were found in Tokyo (Sempéré and Kawamura, 1994) and concentrations up to 18.5 µg L^{-1} for phthalic acid in Sapporo (Kawamura and Watanabe, 2004). Interestingly, even in the remote Arctic concentrations up to 3 µg L^{-1} for phthalic acid have been found (Narukawa et al., 2002).

The dicarboxylic acids are very water-soluble and reside mainly in the particle phase. They can also be involved in the formation of cloud condensation nuclei (Raymond and Pandis, 2002). They are effectively removed from the atmosphere by in-cloud and below cloud scavenging processes. A major point of interest is the potential role of dicarboxylic acids in the formation of ice nuclei. The soluble organic acids are expected to depress the freezing point of water. However, some of these acids can be surface active (Tervahattu et al., 2005) and hence could cause ice nucleation to occur more readily through preferential surface aggregation. In laboratory studies the ability of oxalic acid dihydrate as ice nucleator has been demonstrated (Zobrist et al., 2006), whereas higher dicarboxylic acids rather inhibit ice nucleation (Prenni

et al., 2001) to some extent. The first step in the understanding of the role of organic acids in ice nucleation is to quantify these compounds in fresh snow.

The main analytical technique applied to date for the quantification of higher organic acids in aerosol, rain and snow samples is gas-chromatography coupled with mass-spectrometry (GC/MS) after derivatization of the non-volatile organic acids to their respective volatile methylester or n-butylester (Kawamura and Ikushima, 1993) to enable gas-chromatographic separation. Liquid-chromatography coupled with mass-spectrometry (HPLC/MS) has also been applied to analyze organic acids (Warnke et al., 2006; Römpp et al., 2006). The application of liquid-chromatography has the advantage that no derivatization step is needed prior to analysis.

In this study HPLC/MS-TOF with electrospray ionization in the negative mode was applied to the measurement of dicarboxylic acids in snow samples for the first time. Pre-concentration of the analytes from the freshly precipitated snow samples was accomplished by a novel solid phase extraction method using a strong anion exchange resin. The obtained concentrations are compared with back trajectory calculations and a correlation between air mass history and amount of the acids measured is discussed. The method is demonstrated here for the analysis of fresh snow collected at a high altitude site in Central Europe.

Table 2. Snow samples collected during CLACE 5 and 6 and meteorological parameters at the time of collection.

Date	Sampling time	# of samples	Sample type[a]	Snowfall/comments	T_{air} [°C]	T_{snow} [°C]	Wind direction [°]	Wind speed [m s^{-1}]
20 Feb 2006	09:30	2	A B	snow in the morning	−15	−16	150	10.5
20 Feb 2006	17:00	1	A	after 1h snowfall	−14.5	−21	199	3.9
22 Feb 2006	15:45	2	A B	snowfall since 12:00	−12.9	−14.5	168	7.6
24 Feb 2006	12:30	2	A B	snowfall since 08:00	−17	−14	156	12.8
24 Feb 2006	19:30	2	A B	snowfall since 08:00	−13.9	−18.4	167	14.3
5 Mar 2006	09:00	2	A B	since early morning	−14.8	−26.4	340	7.2
8 Mar 2006	14:30	2	A B	snowfall since 08:00	−6	−12.4	321	20.9
11 Mar 2006	10:00	1	C	snow fall 20 cm	−18	−23.2	314	9.6
11 Mar 2006	15:15	1	C	still snowing	−17.1	−20.2	313	13.8
12 Mar 2006	10:30	1	C	still snowing	−24.9	−32	315	6.7
20 Mar 2006	18:15	1	C	snowfall since 17:00	−10.4	−12	329	2.6
24 Feb 2007	14:30	3	C	since 09:30	−12.7	–	286	1.7
25 Feb 2007	07:15	3	C	night/still snowing	−10.7	–	218	2.3
25 Feb 2007	16:35	3	C	still snowing	−13	–	74–340	2.6
26 Feb 2007	07:25	3	C	still snowing	−16	–	238	5.6
26 Feb 2007	18:30	3	C	since 16:00	−16	–	31–258	5
27 Feb 2007	07:00	3	C	during night	−17.2	–	24–175	3.2–5.9
28 Feb 2007	11:00	3	C	still snowing	−8.0	–	27-249	3.9
2 Mar 2007	09:00	3	C	during night	−12.3	−9.0	6	12
4 Mar 2007	08:00	3	C	until 22:00 night	−13.0	−7.0	56-348	3
5 Mar 2007	18:00	3	C	17:00 very little	−12.7	−6.0	290	2.2
7 Mar 2007	09:30	3	C	still snowing	−10.5	−5.0	135	8.5
8 Mar 2007	08:15	3	C	during night (5 cm)	−10.0	−7.0	35–350	1.6–4.1
10 Mar 2007	09:55	3	C	during night (50 cm)	−16.0	−9.0	99	8.8

[a] A: surface layer (2 cm), B: lower layer without surface snow, C: whole sample without separation of surface and underlying layer.

2 Methods

2.1 Sampling location

Snow sampling was performed during the CLACE 5 and 6 (CLoud and Aerosol Characterization Experiment) measurement campaigns, at the high altitude research station Jungfraujoch (JFJ, 3554 m a.s.l., 46°33′ N, 7°59′ E) in February and March 2006 and 2007, respectively. The Jungfraujoch is located in the central part of the Swiss Alps (for a topographic map see Lugauer et al., 2000). The large scale topography of the Swiss Alps along a Northwest-Southeast cross section is characterized by two mountain ranges with the Rhone valley in between. The JFJ is located on the northern crest of a saddle between the Mönch (4099 m) and Jungfrau (4158 m) mountains, and belongs to the glacier accumulation zone where monthly mean temperatures are below 0°C all year around. The wind at the JFJ is channelled into either a northwestly or southeastly direction due to the local topography. The prevailing wind is northwesterly, with a frequency of 70–80% (Lugauer et al., 2000).

Due to its high elevation, the JFJ measurement station is mostly covered in cloud during snow fall periods (Baltensperger et al., 1991). It is therefore a good remote lo-cation for studying in-cloud scavenging of organic species by snow during precipitation events, with little influence of post snowfall deposition from local sources. With the exception of occasional construction activities, local emissions from the station and tourist facilities were negligible (Baltensperger et al., 1998).

Although for most of the time the JFJ measurement station resides in the free troposphere, an influence of the boundary layer on the free troposphere has been observed previously at JFJ (Baltensperger et al., 1997). Pollution in the air at JFJ results from transport from surrounding valleys (Li et al., 2005) or from long-range transport (Reimann et al., 2004).

Meteorological data (air temperature, wind speed, wind direction, etc.) were made available from the automatic meteorological station of the Swiss weather service located at the research station JFJ. Within the Swiss air pollution network NABEL, and as part of the Global Atmospheric Watch program (GAW), chemical parameters such as CO and NO$_x$ and aerosol mass (as PM$_{10}$) were also measured at the JFJ measurement station.

Table 3a. Concentrations of dicarboxylic acids in fresh snow samples (in ng L^{-1}) during CLACE 5 (2006).

Date and time	Sample type[a]	Glutaric C$_5$	Adipic C$_6$	Pimelic C$_7$	Suberic C$_8$	Azelaic C$_9$	Sebacic C$_{10}$	Undecane-dioic C$_{11}$	Dodecane-dioic C$_{12}$	Tridecane-dioic C$_{13}$	Phthalic acid
20 Feb 2006 09:30	A	592	920	237	486	749	194	75	24	17	504
20 Feb 2006 09:30	B	415	686	210	345	452	132	63	28	17	362
20 Feb 2006 17:00	A	810	786	205	124	163	46	17	9	6	840
22 Feb 2006 15:45	A	618	1041	238	312	589	101	59	21	10	498
22 Feb 2006 15:45	B	513	4414	211	169	198	36	22	12	6	420
24 Feb 2006 12:30	A	455	681	153	249	389	198	32	20	15	322
24 Feb 2006 12:30	B	571	821	261	345	361	96	37	23	12	340
24 Feb 2006 19:30	A	560	524	182	168	219	63	24	12	8	708
24 Feb 2006 19:30	B	333	478	118	52	58	30	8	7	2	386
5 Mar 2006 09:00	A	544	3980	293	376	704	111	41	15	10	188
5 Mar 2006 09:00	B	230	346	132	120	174	29	17	10	3	93
8 Mar 2006 14:30	A	282	324	57	90	124	31	11	5	6	98
8 Mar 2006 14:30	B	280	784	144	314	496	50	52	6	2	165
11 Mar 2006 10:00	C	51	70	101	240	454	62	36	4	1	70
11 Mar 2006 15:15	C	3	73	13	35	73	10	5	0	0	3
12 Mar 2006 10:30	C	53	70	11	15	36	4	3	1	0	237
20 Mar 2006 18:15	C	1362	1315	482	679	1256	153	131	23	13	1400

[a] A: surface layer (2 cm), B: lower layer without surface snow, C: whole sample without separation of surface and underlying layer.

Table 3b. Concentrations of dicarboxylic acids in fresh snow samples (in ng L^{-1}) during CLACE 6 (2007).

Date and time	Sample type[a]	Glutaric C$_5$	Adipic C$_6$	Pimelic C$_7$	Suberic C$_8$	Azelaic C$_9$	Sebacic C$_{10}$	Undecane-dioic C$_{11}$	Dodecane-dioic C$_{12}$	Tridecane-dioic C$_{13}$	Phthalic acid	Pinonic
24 Feb 2007 14:30	C	322	43	101	166	195	366	28	32	22	519	n.d.
25 Feb 2007 07:15	C	608	931	191	184	652	113	177	n.d.	13	265	118
25 Feb 2007 16:35	C	937	720	268	375	1832	62	48	29	8	1199	69
26 Feb 2007 07:25	C	402	588	215	313	396	64	42	38	n.d.	447	22
26 Feb 2007 18:30	C	836	644	365	248	397	135	133	70	64	913	49
27 Feb 2007 07:00	C	616	701	217	148	331	92	30	21	6	21	34
28 Feb 2007 11:00	C	438	345	118	146	156	17	26	n.d.	7	362	18
2 Mar 2007 09:00	C	144	220	52	24	208	36	34	n.d.	3	151	49
4 Mar 2007 08:00	C	234	300	93	113	908	48	48	18	13	285	37
5 Mar 2007 18:00	C	1085	916	421	416	953	101	104	53	43	1329	30
7 Mar 2007 09:30	C	298	696	203	218	1164	75	121	98	27	385	90
8 Mar 2007 08:15	C	1194	1093	585	337	288	71	26	35	8	1695	159
10 Mar 2007 09:55	C	713	1240	429	966	1456	239	160	263	54	1447	46

[a] C: whole sample without separation of surface and underlying layer; Average of three samples of the same snowfall event.

2.2 Snow sampling

During the CLACE campaigns, fresh snow was collected either directly during precipitation, or in the early morning after nighttime precipitation. During CLACE 5 the snow was collected on the platform of the research station Sphinx, and during CLACE 6 on the roof of the lodge ("Berghütte").

The fresh snow samples were collected with a flat shovel (36 cm×16 cm) made of polypropylene (the flat geometry allowed the sampling of snow layers of various thicknesses) and transferred into 2 L pre-cleaned glass container (soda lime glass, Wheaton). The sampling container was then closed with a PTFE coated polypropylene cap and the snow samples stored at −18°C. Prior to use, the glass bottles were cleaned with detergent, rinsed several times with nor-

mal drinking water and finally filled with ultra-pure water (Millipore, 18 MΩ). After 24 h the water was poured out and refilled with ultra-pure water. This procedure was repeated three times. The glass bottles were then closed with polypropylene caps which provided a gas tight seal until sampling.

During CLACE 5, the usual sampling procedure involved collecting two samples: one from the top layer of the freshly precipitated snow; and a second one from below the snow surface, in order to account for possible dry deposition of organic acids after snowfall. During CLACE 6 three samples of the same snowfall event were collected without separation of surface and underlying layer in order to determine the variability of samples from the same snowfall event.

Table 4. Concentrations (in ng L^{-1}) of dicarboxylic acids in snow samples from urban and remote locations.

	Jungfraujoch, CLACE 5 Feb Mar 2006			Jungfraujoch, CLACE 6 Feb Mar 2007			Alert, Arctis[a] Feb 2000			Tokio, Japan[b] 18 Mar 1992		Sapporo, Japan[c] Feb 2003	
	min	max	median	min	max	median	min	max	median	min	max	19/20 Feb	26 Feb
Glutaric acid	3	1362	455	144	1194	608	150	670	570	630	1600	10 400	1960
Adipic acid	70	4414	686	43	1240	696	220	1860	430	940	3070	5600	1390
Pimelic acid	11	482	182	52	585	215	20	70	70	150	740		
Suberic acid	15	679	240	24	966	218	30	140	90	760	1150	2200	350
Azelaic acid	36	1256	361	156	1832	397	110	470	350	850	11 500	8800	2210
Sebacic acid	4	198	62	17	366	75	<10	30	30				
Undecanedioic acid	3	131	32	26	177	48	10	20	20				
Dodecanedioic acid	0	28	18	18	263	37							
Tridecanedioic acid	0	17	6	0	64	13							
Phthalic acid	3	1400	340	21	1695	447	460	3180	1100	2250	4070	18 500	8300

[a] Narukawa et al. (2002); [b] Sempere and Kawamura (1994); [c] Kawamura and Watanabe (2004)

2.3 Solid phase extraction

The chemical analysis of individual organic compounds at low concentration in snow requires a pre-concentration step. Two main methods have been applied for the extraction of trace organic species from aqueous solutions, namely the classical liquid-liquid extraction (LLE) and the more recent solid phase extraction (SPE). The common liquid-liquid extraction uses a non-water miscible organic solvent, in which the analytes of interest possess a higher solubility than in water. After separation of the organic phase from the aqueous phase, the resulting organic solution is concentrated by evaporation of the solvent. In contrast, with solid phase extraction, the analytes are removed from the sample solution by adsorption on solid phase resins, and subsequently eluted with a small volume of an appropriate solvent. The resins can be modified with functional end-groups for the extraction of specific classes of organic compounds. The advantage of SPE over LLE is that no large volumes of organic solvents are used and the analyte solution is not heated under vacuum, which could cause the loss of volatile analytes. Finally, SPE allows the purification of the analyte by using different solvents for elution.

In this study, organic acids have been extracted by solid phase extraction using a strong anion exchange resin (Supelco DSC-SAX). The resin consists of silica gel with functionalised carbon chains, with quaternary ammonium groups $(Si\text{-}O\text{-}(CH_2)_3\text{-}N(CH_3)_3^+)$ and Cl^- as the counter ion. After a conditioning step (in which the resin is flushed with 50 ml methanol followed by 50 ml pure water), the melted snow is flushed through the cartridge containing the permanently positively charged ammonium groups. Deprotonated organic acid anions in the aqueous solution bind to these ammonium groups, whereby the organic acids are removed from the aqueous phase. After drying of the resin the organic acids are eluted from the resin with a small volume of hydrochloric acid solution. The strong acid HCl protonates the anions

of the weaker organic acids. In the neutral form the affinity to the ammonium groups is much less and the organic acids elute with the HCl-solution.

Several methods for conditioning and elution have been tested with a standard solution of dicarboxylic acids in the $\mu mol\,L^{-l}$ to $mmol\,L^{-1}$ range. Various cartridge sizes with 1–12 mL volume and 500 mg to 2 g resin have been tested with sample volumes of 100 to 2000 mL. The breakthrough volume of the SPE cartridges was determined by conducting extraction with two cartridges in series, and it was found to be larger than 1000 mL even for the smallest sorbent amount of 100 mg (Kippenberger et al., 2008). Therefore 6 mL cartridges containing 1 g resin were used for sample volumes of 200 to 600 mL. For sample volumes below 200 mL the cartridge with 1 mL volume and 500 mg resin were selected. The extraction efficiency of the method was determined with standards of linear dicarboxylic acids (see Table 1), and was between 61±4 and 102±2 % for all C_5 to C_{12} acids, but decreases with longer chain length to 41±2% (C_{13}) probably due to increasing nonpolar interaction between the alkyl chain of the dicarboxylic acid and the solid phase. For undecanedioic acid (C_{11}) the extraction efficiency was interpolated from the standards of the available linear dicarboxylic acids, which were observed to decrease quadratically in efficiency with increasing chain length from C_8 to C_{13}. A detailed description of the method development has been published elsewhere (Kippenberger et al., 2008) and only a short description of the optimised method is given below.

The melted snow samples were drawn through the solid phase by means of a membrane pump at a flow rate between 2 and 4 mL min^{-1}. In order to remove the residual water, the cartridges have been flushed by purified air to dryness. Afterwards 2 mL HCl solution (0.1 mol L^{-1}) were placed on the resin and flushed trough the resin by means of clean pressurised air at a flow rate of 1 mL min^{-1}.

Blank values of the analytes originating either from the sample container, the SPE cartridge or the analytical
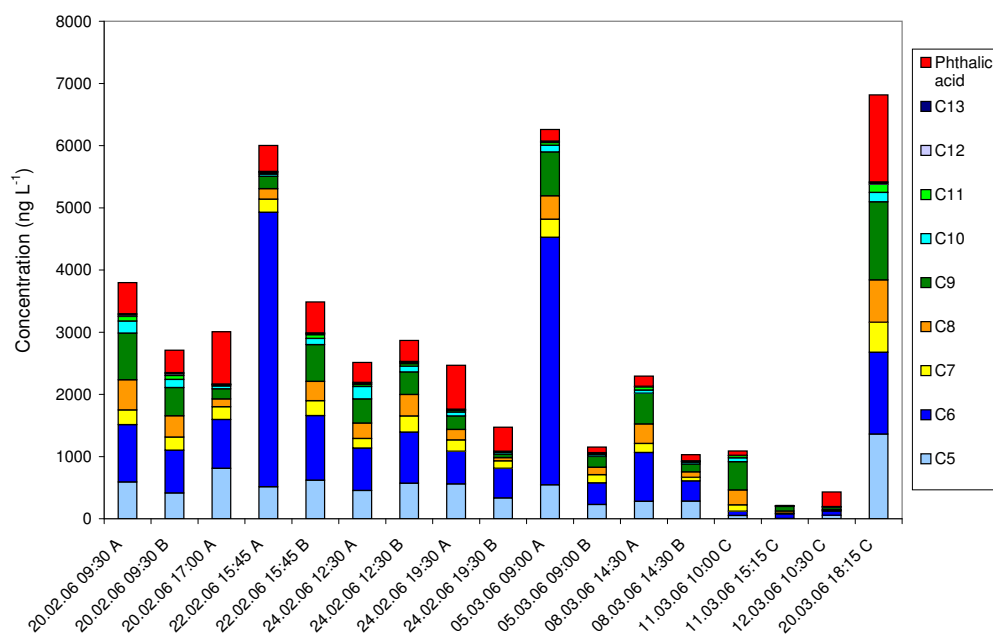
Fig. 1. Total concentrations and distribution of dicarboxylic acids in fresh snow samples collected during CLACE 5 (February and March 2006). Three types of samples were collected: A: surface layer (2 cm), B: lower layer without surface snow, C: whole sample without separation of surface and underlying layer.
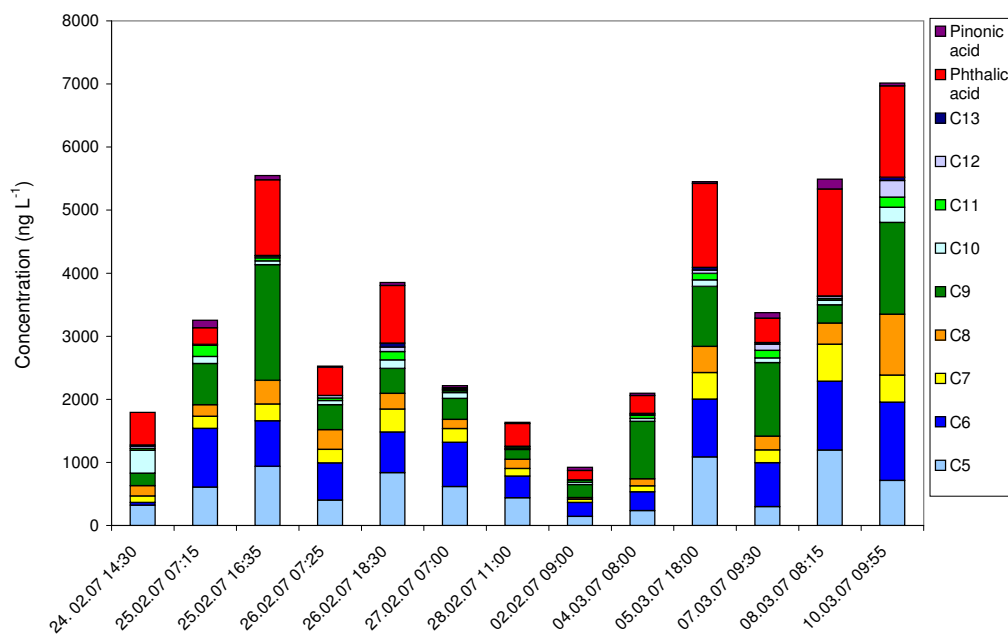

Fig. 2. Total concentrations and distribution of dicarboxylic acids in fresh snow samples collected during CLACE 6 (February and March 2007). The samples were collected without separation of surface and underlying layer; Data represents the average of three samples of the same snowfall event.

method, were obtained by storing 200–400 mL ultra-pure water ($18\,\mathrm{M\Omega}$) in the glass containers for 72 h at 23°C. The ultra-pure water was then extracted by the method described above. None of the analysed organic acids had higher blank values than $1\,\mathrm{nmol\,L^{-1}}$). The highest blank values (see Table 1) were found for phthalic acid ($0.95\,\mathrm{nmol\,L^{-1}}$), adipic acid ($0.57\,\mathrm{nmol\,L^{-1}}$), and glutaric acid ($0.42\,\mathrm{nmol\,L^{-1}}$).

Possible contamination of the snow samples with adipic acid originating from the polypropylene shovel used for sampling were tested by filling 400 mL ultra-pure water into the

tilted bucket. After four hours, the ultra-pure water was extracted as described above and compared with a blank sample of ultra-pure water treated in the same manner but without contact with the polypropylene shovel. The measured concentrations of adipic acid were the same (i.e. within the error range) for both water samples. Therefore the polypropylene shovel is not a source of contamination with adipic acid.

In order to perform sample extraction, the snow samples were melted at room temperature (23°C) and immediately extracted. The volumes of the melted snow samples ranged from 100 to 410 mL. For four snowfall events, two samples have been combined in order to obtain larger volumes for extraction up to 650 mL.

2.4 Chemical analysis (HPLC-MS)

Liquid-chromatography-mass spectrometry (LC-MS-TOF) was used for the analysis of the organic acids in the concentrated snow samples. The analytes were separated by HPLC and detected with mass spectrometry. For the formation of gas phase ions either atmospheric pressure chemical ionization (APCI) or electrospray ionization (ESI) can be applied.

The instrumental set-up utilized in this study consisted of an HPLC system, including a thermostated autosampler (Series 200, Perkin Elmer, Norwalk, Connecticut, USA), a degasser and a quaternary pump (both 1100 Series, Agilent Technologies, Waldbronn, Germany) and a hybrid mass spectrometer QSTAR (Applied Biosystems MDS SCIEX, Toronto, Canada), with an electrospray ion source as interface. This instrument combines tandem mass spectrometry (MS/MS) with the high mass resolution of a time-of-flight detector (TOF). The electrospray ion source was operated in the negative mode at 400°C and an ionization voltage of 4 kV. The selected m/z range was 120 to 300.

Aliquots of 100 μL of the extract were directly injected into the HPLC system. The analytical column was a ReproSil-Pur C18-AQ (250 mm×2 mm I.D., 5 μm particle size) in a stainless steel cartridge (Dr. Maisch GmbH, Ammerbuch, Germany). The eluents were 0.1% formic acid in water (eluent A) and acetonitrile (eluent B). The gradient of the mobile phase was as follows: 0% B from 0 to 0.5 min, gradient to 15% B from 0.5 to 4 min, gradient to 95% B from 4 to 20 min, gradient to 0% B from 20 to 23 min, and isocratic 0% B from 23 to 29 min. The flow rate was maintained at 400 μL/ min. The retention time of the longest chain acid C_{13} is 15.7 min with this gradient.

The quantitative calibration is based on available standards of linear dicarboxylic acids (C_5 to C_{14}), phthalic acid and pinonic acid. For undecanedioic acid (C_{11}) the response factor was interpolated from the authentic standards of available linear dicarboxylic acids, whose sensitivity increase was linear with increasing chain length from C_8 to C_{13}.

Small dicarboxylic acids (oxalic, malonic and succinic acid, C_2–C_4) cannot be analysed with the instrumental set-up employed here. The chromatographic separation is not
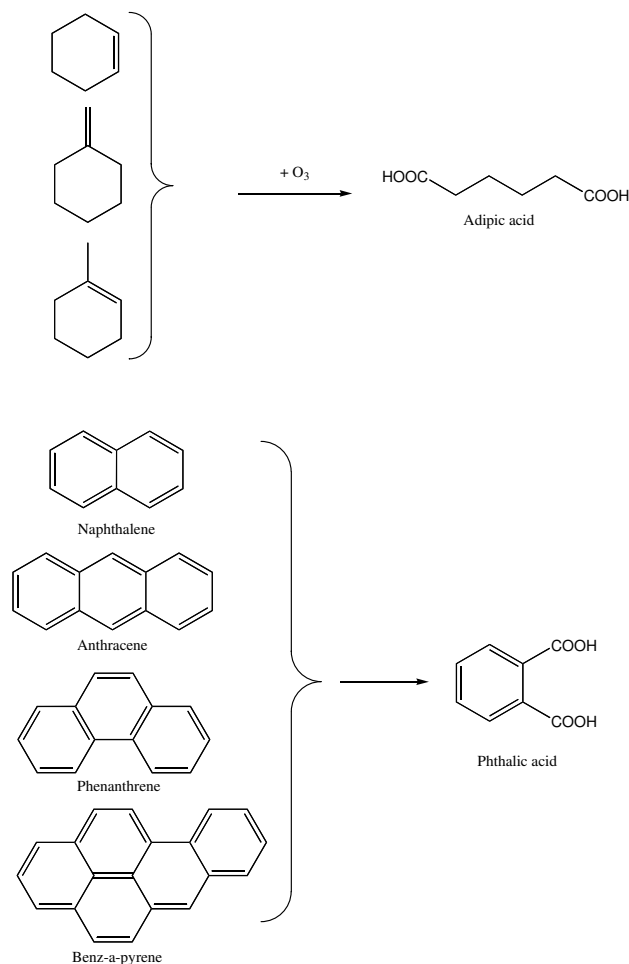

Fig. 3. Anthropogenic precursors of adipic and phthalic acid.

applicable for the very polar dicarboxylic acids, since they elute without separation from the column (with the dead volume) or form only broad peaks. Furthermore the mass spectrometric sensitivity of the small acids is much lower, due to the nature of the ionisation process, compared to the longer chain acids. Therefore no attempt was made to analyse dicarboxylic acids with less than 5 carbon atoms.

The limit of detection was calculated as three times the standard deviation of the background noise of a chromatogram from a solution of standards. The quantification limit was calculated as ten times the standard deviation of the background noise of a solution of standards. The values are summarized for each acid in Table 1. The overall reproducibility of the analytical procedure was evaluated using 4 extractions of standards. Standard deviations of the recovery rates of the authentic standards for all compounds are between 1.9 and 6.4%. The precision of the analytical method was therefore conservatively estimated as 7%.
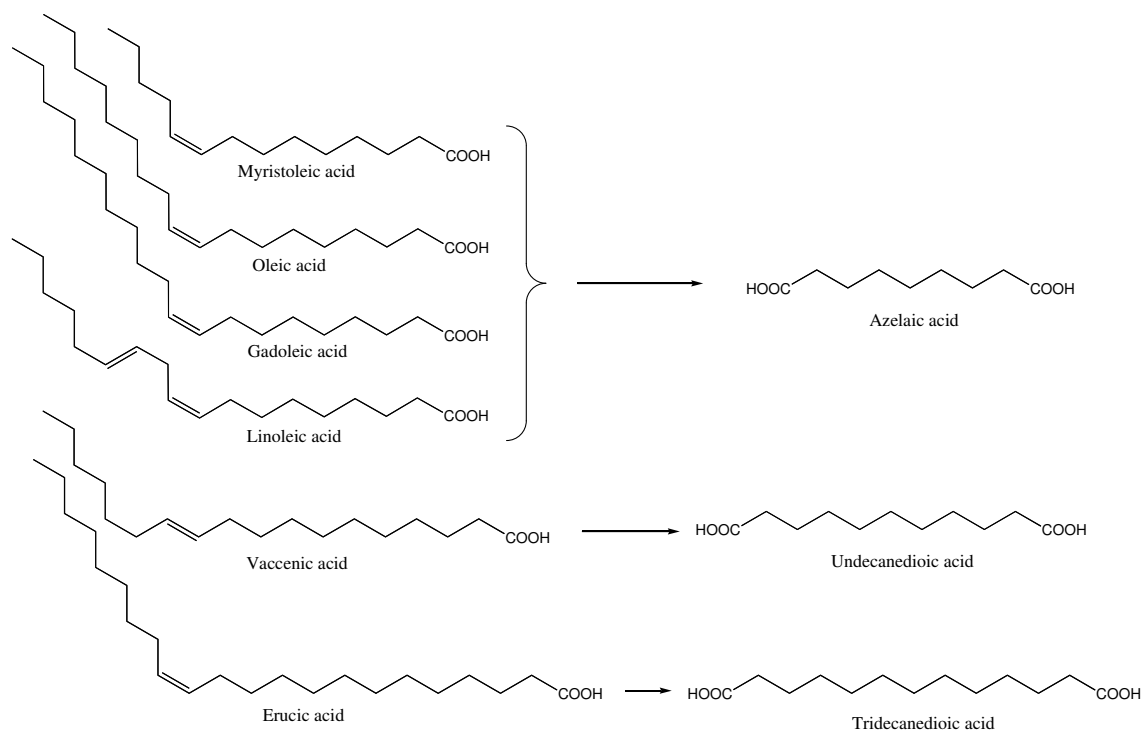
Fig. 4. Biogenic precursors of azelaic acid, undecanedioic acid and tridecanedioic acid.

2.5 Back trajectories

Back trajectories have been provided by the German Weather Service (DWD) during the CLACE campaigns using the DWD-Local model Europe (LME). For the whole campaign 5 day back trajectories have been calculated for every 6 h. For snow collection times not covered by the DWD back trajectories (i.e. not during the campaigns) the HYSPLIT model (Draxler and Rolph, 2003) was used to calculate air mass back trajectories.

2.6 Materials

The following standards of dicarboxylic acids with stated purity in parentheses were used: glutaric acid (99%), adipic acid (99%), suberic acid (98%), decanedioic acid (99%), dodecanedioic acid (99%), tridecanedioic acid (99%), pinonic acid (98%) and phthalic acid (99.5%) all from Sigma-Aldrich, Steinheim, Germany. Pimelic acid (>99%) and azelaic acid (>99%) were obtained from Fluka (Buchs, Switzerland). Solvents and eluents were as follows: "gradient grade" methanol for conditioning of the SPE cartridge and "hyper grade" methanol for the preparation of standard solutions both from Merck (Darmstadt, Germany). LC/MS grade water (with added 0.1% HCOOH) and LC/MS grade acetonitrile (Riedel de Haën, Selze, Germany) was used for HPLC. The SPE cartridges (DSC-SAX) were obtained from Supelco (Bellefonte, PA, USA). Water was purified with Purelab Ul-

tra (Vivendi, Ransbach-Baumbach, Germany) yielding water with a resistance of $18.2 \, \text{M}\Omega$.

3 Results

3.1 Organic acid concentrations in fresh snow

The single snowfall events, sampling times and meteorological conditions during both campaigns are summarized in Table 2. During CLACE 5, two samples were typically taken, one from the surface layer (type A) and one below (type B), in order to account for possible deposition of organic acids after the precipitation. During CLACE 6, this was increased to 3 samples so as to include samples without the separation of surface and underlying layer (type C), which allows the variability within different samples of the same snowfall event to be examined.

A series of linear dicarboxylic acids with 5 to 13 carbon atoms was found in all snow samples. The identified acids were glutaric (C_5), adipic (C_6), pimelic (C_7), suberic (C_8), azelaic (C_9), sebacic (C_{10}), undecanedioic (C_{11}), dodecanedioic (C_{12}) and tridecanedioic acid (C_{13}) as well the aromatic acid phthalic acid (C_8). Furthermore the biogenic acid pinonic acid (C_{10}-Oxo-monocarboxylic acid) was measured during CLACE 6. The concentrations in snow of the quantified organic acids are listed in Tables 3a and 3b for the years 2006 and 2007, respectively, and additionally plotted as bar diagrams in Figs. 1 and 2.
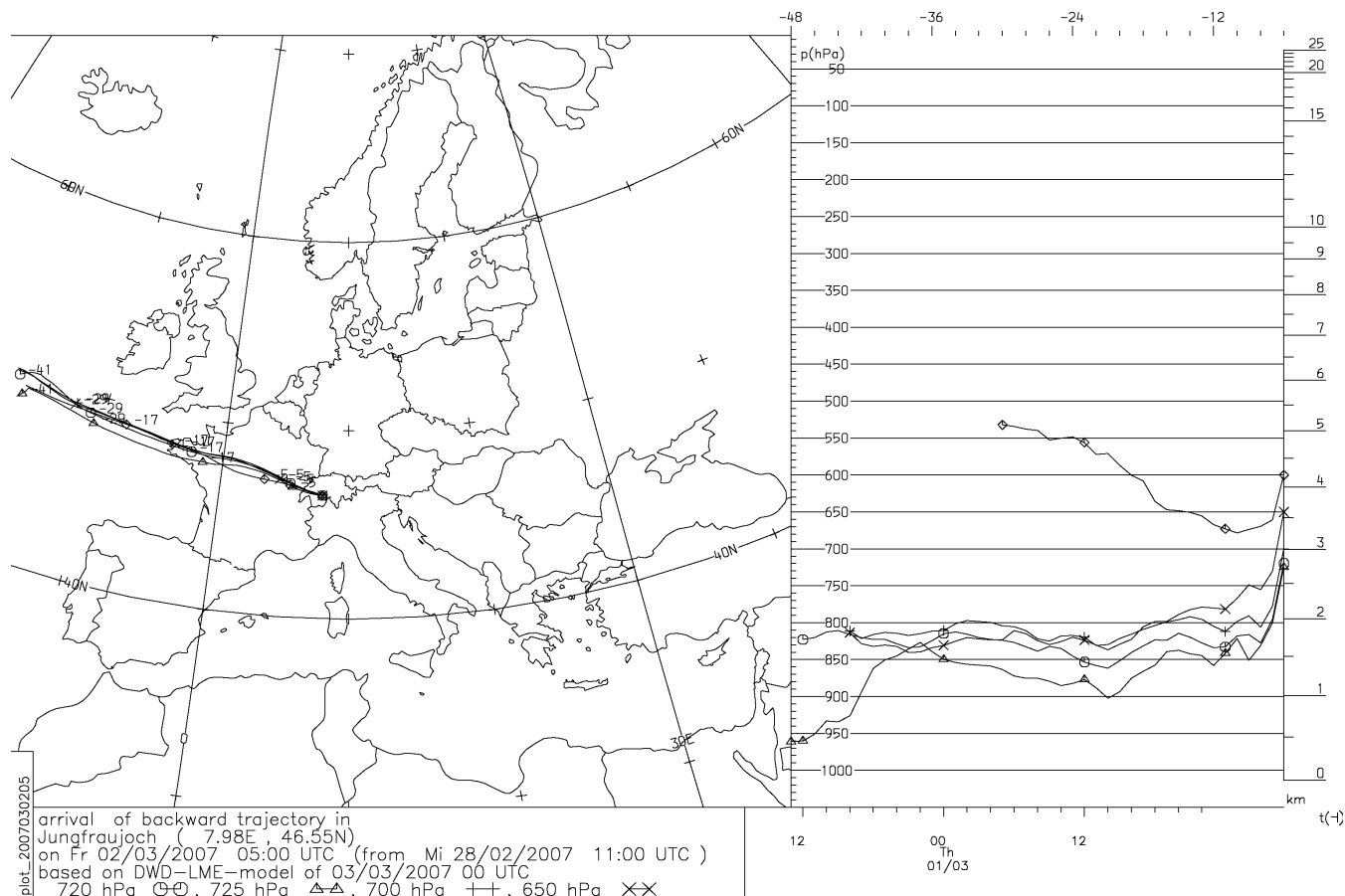
Fig. 5. Backward trajectories arriving at Jungfraujoch on 2 March 2007 at 05:00.

The most abundant acids are glutaric, adipic, azelaic and phthalic acid (3–4414 ng L^{-1}), less abundant are pimelic and suberic acid (11–966 ng L^{-1}). Generally the abundance of these organic acids decreases with longer chain length. The concentrations of the acids varied significantly between the different snow samples. The most abundant acid adipic acid ranges between 70 and 4414 ng L^{-1} during CLACE 5 and between 43 and 1240 ng L^{-1} during CLACE 6. Also the other most abundant acids were found with a wide range of concentrations. Among these compounds adipic acid, phthalic acid and azelaic acid were the most variable acids with standard deviations of 113%, 89% and 87%, respectively.

The median concentrations of acids for CLACE 5 and 6 were 445 and 608 ng L^{-1} for glutaric acid, 686 and 696 ng L^{-1} for adipic acid and 361 and 397 ng L^{-1} for azelaic acid (see Table 4). The aromatic acid phthalic acid had median concentrations of 340 and 447 ng L^{-1}. These concentrations are comparable in total amount and speciation distribution to values measured at an Arctic site (Narukawa et al., 2002), summarized in Table 4. At the remote Arctic site median concentrations of 570, 430, 350 and 110 ng L^{-1}

have been measured for glutaric, adipic, azelaic and phthalic acid, respectively. Studies from urban sites have found much higher concentrations of these acids (Sempéré and Kawamura, 1994; Kawamura and Watanabe, 2004). In two samples during CLACE 5 in 2006 significantly elevated concentrations of adipic acid (4414 and 3980 ng L^{-1}) have been observed on the 22 February 2006 and 5 March 2006.

The variability among samples of the same snowfall event can be estimated from the standard deviations of three samples of the same snowfall event collected during CLACE 6. The relative standard deviations (*n*=3) for the individual acids range from 12±9% (adipic acid) to 34±17% (phthalic acid) within a set of 13 snowfall events. These standard deviations are significantly larger than the analytical precision of 7% and the observed variability reflects the inhomogeneous distribution of these compounds in snow. Measurements of volatile organic compounds in snow and ice during CLACE 4 and 5 also showed a high variability (7 to 173%) within simultaneously collected samples (Fries et al., 2008).

The composition of organics in the snow could have changed during precipitation (due to changing air mass
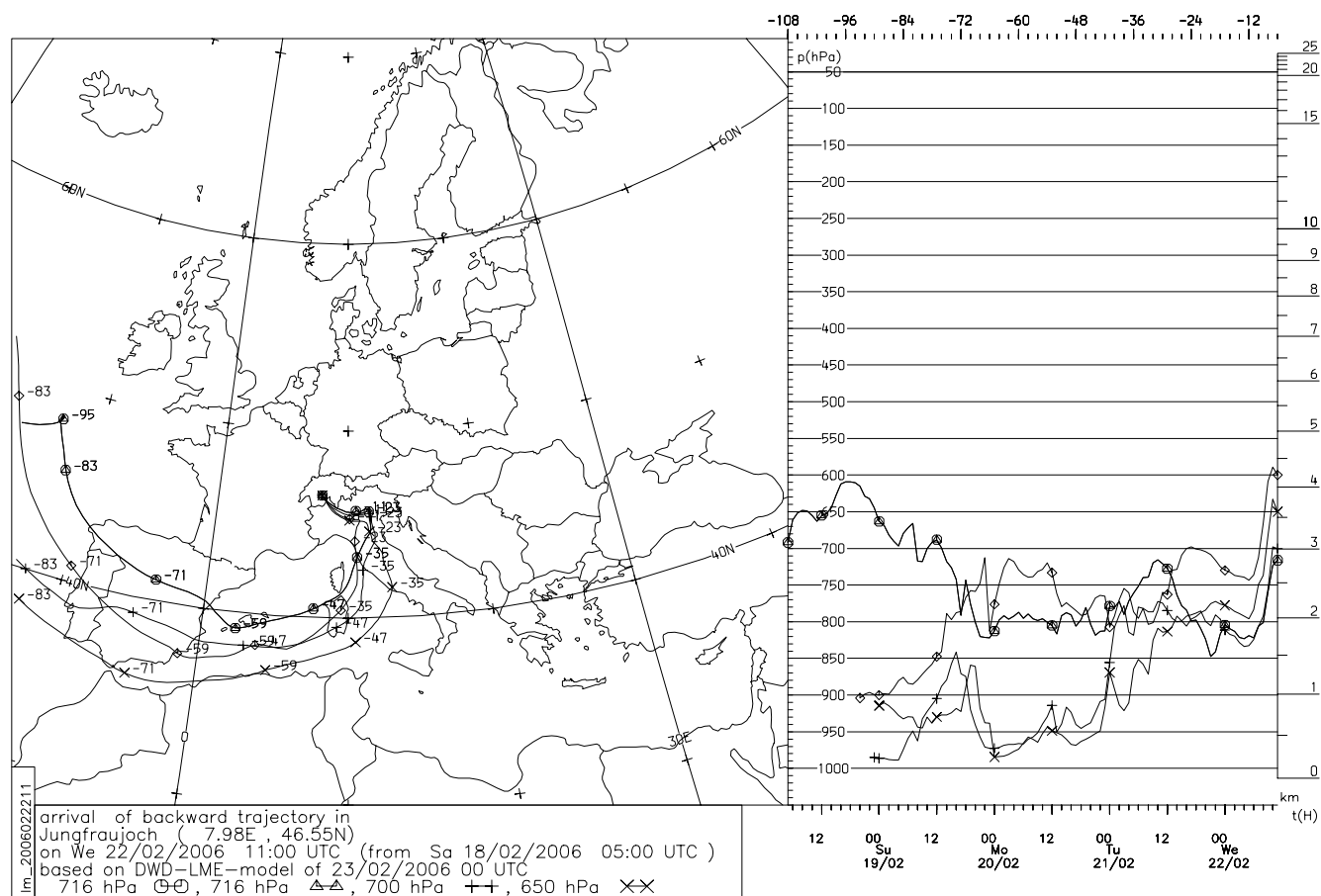
Fig. 6. Backward trajectories arriving at Jungfraujoch on 22 February 2006 at 11:00.

composition and/or variable washout efficiencies during precipitation) leading to gradients in the snow layer, which cannot be resolved by the applied method. Using a cloud particle sizer, Choularton et al. (2008) observed at the JFJ during CLACE 3 very sharp transitions (just a few meters in horizontal extent) between highly glaciated regions and regions consisting of supercooled water. It was suggested that this transition is caused by ice nucleation initiated by oxidised organic aerosol coated with sulfate in more polluted regions of the cloud. This suggestion was supported by conditional sampling of aerosol data, which showed that glaciated regions of cloud contain higher loadings of the major ions and organic material than regions dominated by supercooled water (Choularton et al., 2008). The inhomogeneous distribution of organics in the cloud could therefore be the explanation of the variability of organic acids among samples of the same snowfall event presented here.

The difference in concentrations of surface and subsurface samples collected during CLACE 5 was not completely consistent. In 5 out of 6 cases, where surface and subsurface samples were taken, higher concentrations in the surface samples were found (e.g. 20 February 2006) whereas in

one sample (24 February 2006) the opposite was observed. In two surface samples the concentration of adipic acid was significantly enhanced compared to the subsurface samples, namely on 22 February 2006 by a factor of 4 and on 5 March 2006 by a factor of 11. On these two days the concentrations of the remaining acids were either smaller in the subsurface samples compared to the surface samples (22 February 2006) or were only enhanced by a factor of 2 to 4 (5 March 2006).

The dicarboxylic acids may enter the snow through several mechanisms. Direct scavenging from the gas phase can be neglected since the dicarboxylic acids possess low vapour pressures (Bilde et al., 2003) and preferably condense on existing aerosol particles. The aerosol particles can then be effectively scavenged from the air by ice crystals and snow flakes during precipitation. Alternatively, the acid containing particles can be activated to become CCN, which accumulate water. At sufficiently low temperatures the activated CCN could freeze and grow to fall later as snow. These two mechanisms cannot be distinguished using the data presented here.
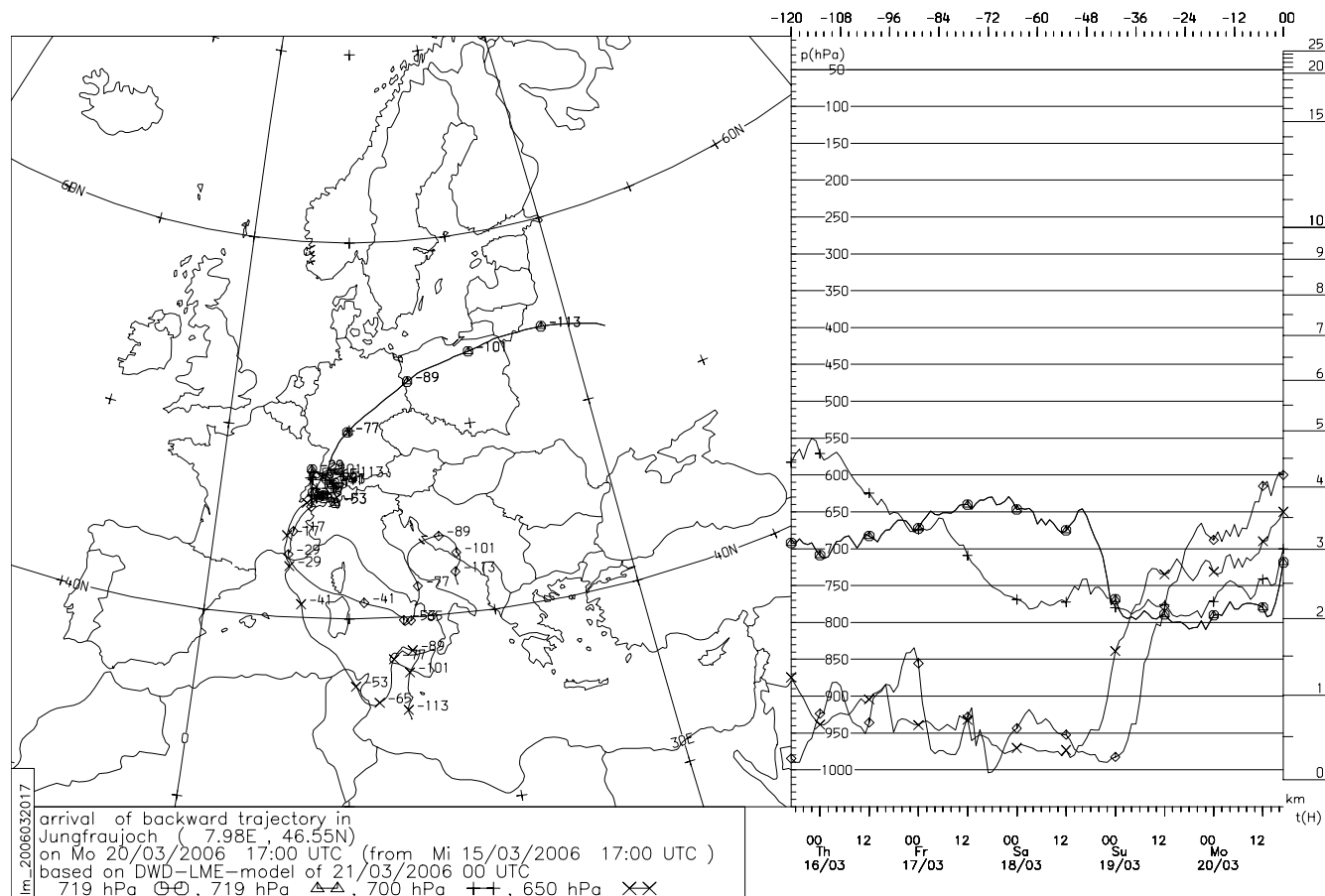
Fig. 7. Backward trajectories arriving at Jungfraujoch on 20 March 2006 at 17:00.

3.2 Sources of dicarboxylic acids

The primary atmospheric source of the various organic acids measured is the photo-oxidation of volatile to semi-volatile organic compounds. Glutaric acid has several sources, including cyclopentene and cyclohexene oxidation (from gasoline), and oxidation of glutardialdehyde.

The atmospheric oxidation of cyclohexene has been proposed as the main source of adipic acid (Fig. 3), (Grosjean et al., 1978; Hatakeyama et al., 1987). In addition, the ozonolysis of methylene-cyclohexane and 1-methyl-cyclohexene also yields adipic acid (Koch et al., 2000).

Phthalic acid is formed by the oxidation of polycyclic hydrocarbons, such as naphtalene, anthracene, and benza-pyrene (Kawamura and Ikushima, 1993) as illustrated in Fig. 3. Another source could be the hydrolysis of phthalate esters, which are widely used as plasticizers in polymers.

The high abundance of azelaic acid is due to the fact that most of the unsaturated fatty acids contain a double bond at the ninth carbon (position 9) from the acid group (Fig. 4). Oxidation (by OH or O_3) at this double bond leads to azelaic acid (Kawamura and Gagosian, 1987) as well as other

products. The main precursor of azelaic acid is thought be oleic acid, a linear C_{18} carboxylic acid with one double bond at position 9. Other fatty acids with a double bond at position 9 are for instance myristoleic acid (C_{14}), and gadoleic acid (C_{20}). Although the C_9 position is dominant in natural fatty acids there are also compounds with double bonds at positions 8, 10, 11, 12, and 13. Analogously their oxidation could be the source of the longer chain acids C_8, C_{10}, C_{11}, C_{12}, and C_{13}. For instance vaccenic acid (C_{18}, double bond at position 11) is a possible precursor of undecanedioic acid (Kawamura and Gagosian, 1987), erucic acid (C_{22}, double bond at position 13) as possible precursor of tridecanedioic acid (see Fig. 4).

Pinonic acid was detected during CLACE 6 in almost all samples, with the exception of the sample from the 24 February 2007. The origin of this biogenic keto-carboxylic acid is the oxidation of α-pinene by OH radicals and ozone (Hatakeyama et al., 1989; Hatakeyama et al., 1991).

Since adipic (C_6) and phthalic acid (Pht) are proposed as mainly originating from anthropogenic emissions and azelaic acid (C_9) as mainly from biogenic emissions, their ratios
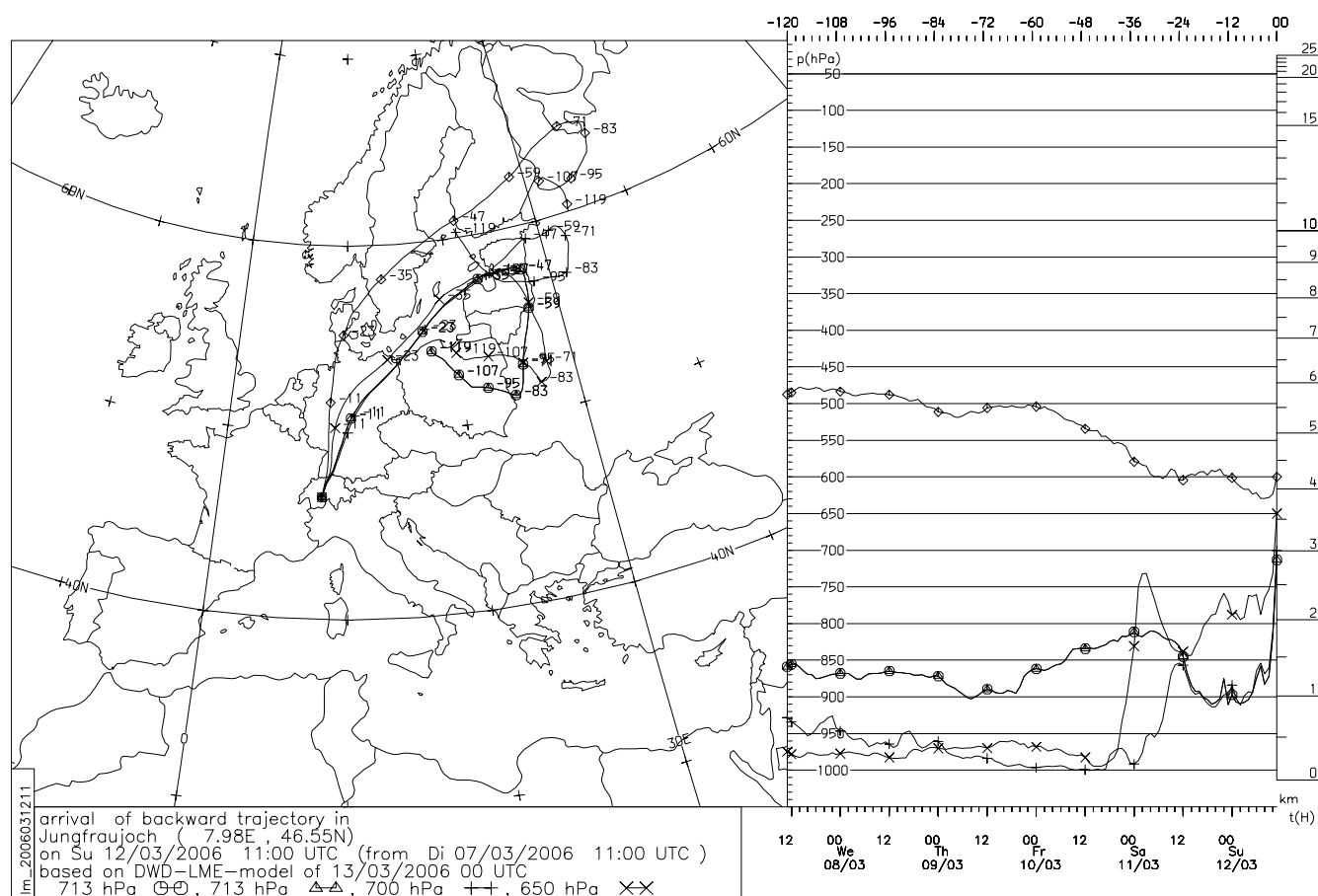
Fig. 8. Backward trajectories arriving at Jungfraujoch on 12 March 2006 at 11:00.

(C_6/C_9 and Pht/C_9) have been used previously to estimate the influence of biogenic versus anthropogenic emissions (Ho et al., 2006). The ratios C_6/C_9 and Pht/C_9 are presented in Table 5.

The C_6/C_9-ratios observed in this study range from 0.2 to 4.8, indicating the high variability of the chemical composition of the air masses arriving at JFJ, and furthermore the relative influence of anthropogenic and biogenic sources. The high C_6/C_9-ratios on 22 February 2006 and 5 March 2006 (3.5 and 4.8), coincided with elevated adipic acid values. A further large C_6/C_9-ratio (3.8) was determined on the 8 March 2007. With the exception of these three values, all other C_6/C_9-ratios were below 2.4. In six out of 24 samples, the C_6/C_9-ratio was below 1.0, indicating a biogenic influence on the air masses in these cases, but generally the air was more anthropogenic influenced. For comparison, typical average values for aerosol samples from Tokyo and Hong Kong are reported to be 0.72 and 0.91, respectively, whereas aerosol samples from Los Angeles in the early 1980s (Kawamura and Kaplan, 1987) showed a value of 7.4 for the C_6/C_9-ratio (Kawamura and Ikushima, 1993).

The Pht/C_9-ratios range from 0.04 to 6.5. In two cases (20 February 2006 and 8 March 2007) high values of Pht/C_9-ratios correlate with high values of the C_6/C_9-ratios. The largest Pht/C_9-ratio (6.5) was found on the 12 March 2006 when the C_6/C_9-ratio was 1.9. Average values reported for aerosol samples from Tokyo and Hong Kong are 0.83 and 6.12, respectively. For Los Angeles aerosol samples an average value of 8.0 has been observed for the Pht/C_9-ratio (Kawamura and Ikushima, 1993).

3.3 Back trajectories

Air masses arriving at the JFJ can be grouped in several classes according to 5-day back trajectories. These classes were: marine air from the west (Fig. 5); continental air from the south (Fig. 6); and continental air from the north (Swiss plateau) (Fig. 7); and occasionally from the northeast (Fig. 8). A short description of the air masses arriving at the JFJ prior or during precipitation is presented in Table 5 together with the total concentration of the dicarboxylic acids.

A typical example of trajectories with a clean marine origin and transport heights above 1500 m is shown in Fig. 5. This corresponds to the samples taken after the snowfall event on 2 March 2007. The trajectory arrived from the Atlantic at heights above 2 km, crossed France and arrives at

Table 5. Total concentration (in ng L^{-1}) of dicarboxylic acids, C$_6$/C$_9$, Pht/C$_9$, and air mass origin.

Date	Sampl. time	Trajectory arrival time	Total concentration	C$_6$/C$_9$	Pht/C$_9$	Air mass origin[a]
20 Feb 2006	09:30	09:00	3250	1.4	0.8	Atlantic FT, with BL air from Spain, Italy (Po valley)
20 Feb 2006	17:00	16:00	3000	4.8	5.2	Atlantic FT, with BL air from Spain, Italy (Po valley)
22 Feb 2006	15:45	11:00	4740	1.8	0.8	Atlantic FT, with BL air from Spain, Italy (Po valley)
24 Feb 2006	12:30	12:00	2690	2	0.9	Mediterranean BL lifted to FT 48 h before arrival
24 Feb 2006	19:30	19:00	1970	2.4	3.2	Mediterranean BL lifted to FT 48h before arrival
5 Mar 2006	09:00	11:00	3700	3.5	0.5	Atlantic FT (>2 km), with BL (1 km) from Spain, France
8 Mar 2006	14:30	11:00	1660	2.1	0.6	Atlantic FT (>2 km), with BL (1 km) from Ireland Wales, France
11 Mar 2006	10:00	5:00	1090	0.2	0.2	Atlantic FT (2–4 km), with BL (0.5 km) from Ireland Wales, France
11 Mar 2006	15:15	11:00	220	1.0	0.04	Atlantic FT (4 km), with BL (0.5 km) from Ireland Wales, France
12 Mar 2006	10:30	11:00	430	1.9	6.5	Arctic FT (>5 km) with BL Baltic Sea, Germany
20 Mar 2006	18:15	17:00	6820	1.8	1.9	BL Mediterranean Sea, Circulation above Switzerland for >1 day
24 Feb 2007	14:30	11:00	1790	0.2	2.7	Marine, Spain, France
25 Feb 2007	07:15	5:00	3250	1.4	0.4	Marine, France
25 Feb 2007	16:35	17:00	5550	0.4	0.7	Marine, FT over France mixing of BL air from Spain, France
26 Feb 2007	07:25	5:00	2530	1.5	1.1	Marine, BL Ireland, UK, north of Ireland, Wales, France
26 Feb 2007	18:30	17:00	3850	1.6	2.3	Marine, BL Ireland, UK, north of Ireland, Wales, France
27 Feb 2007	07:00	5:00	2220	2.1	0.1	Marine FT Iceland, Ireland, UK, France
28 Feb 2007	11:00	11:00	1630	2.2	2.3	Marine, France, with mixing of BL Portugal, Spain, France
2 Mar 2007	09:00	05:00/11:00	920	1.1	0.7	Marine FT (>1 km) France, BL (500 m)
4 Mar 2007	08:00	5:00	2100	0.3	0.3	Marine FT (>2.5 km) France
5 Mar 2007	18:00	17:00	5450	1.0	1.4	FT (>1 km) Marocco, Spain, France
7 Mar 2007	09:30	10:00	3380	0.6	0.3	mixing of FT Marine and BL from SW to South (Po valley)
8 Mar 2007	08:15	9:00	5490	3.8	5.9	mixing of FT Marine and BL from SW to South (Po valley)
10 Mar 2007	09:55	11:00	7010	0.9	1.0	mixing of FT Marine and BL from NW (France, Swiss Plateau)

[a] FT: Free troposphere, BL: Boundary layer

the JFJ within 36 h. The total concentration of dicarboxylic acids in the snow sampled was 920 ng L^{-1}. Similar trajectories have been calculated for the 24 and 28 February and the 4 March 2007; in all these cases the observed organic acid concentrations were relatively low.

On the 25 February 2007 a different meteorological situation arose. In this case the Atlantic air was mixed with boundary layer (BL) air as it traversed France and Switzerland. The increasing concentrations in snow samples from 07:15 (3250 ng L^{-1}) and 16:35 (5550 ng L^{-1}) are consistent with enhanced in-mixing of lower continental BL air during this period.

On 22 February 2006 (Fig. 6) the incident air mass came from the Atlantic (80 h prior to measurement), traversed Spain to the Mediterranean, and then moved north over Sardinia and Italy to the JFJ. BL air from Italy, especially from the highly polluted Po valley (Seibert et al., 1998), might be the cause of the very elevated concentrations of 4740 ng L^{-1}. A further high concentration (6820 ng L^{-1}) was measured on 20 March 2006 (Fig. 7). On this occasion, prior to arrival at JFJ, the air mass came from the East in the free troposphere (FT), and mixed with air masses from the Mediterranean Sea before circulating over Switzerland for approximately one day below 1 km (Fig. 7). On this occasion polluted air from the Swiss plateau might be the origin of the high concentrations observed. The highest total concentration (7010 ng L^{-1}) of the organic acid measured in fresh snow was observed on 10 March 2007. Mixing of several trajectories from the FT with BL air from northern France just prior to reaching the JFJ could be the reason for the highly polluted snow samples.

In one case of snowfall (12 March 2006) air masses arrived at the JFJ from the Northeast (Fig. 8). On this occasion the back trajectories exhibited two influences at the JFJ, one from the FT about 5 km over Finland, and another from BL air over the Baltic Sea. This BL air was lifted above 1 km, 36 h prior to arrival at the JFJ, while crossing Germany. The influence of polluted BL air in-mixing was therefore rather low in duration at heights between 1 and 2 km, and the measured total concentration of 430 ng L^{-1} is in the lower range.

In summary, low concentrations are measured when mainly FT air of marine origin arrived at the JFJ. In many cases the FT air is mixed to some extent with continental BL air, leading to higher concentrations. When the air masses originate mainly from the continental BL, in particular close to the measurement site, the observed acid concentrations were significantly higher. Although back trajectories themselves have an associated uncertainty, particular when vertical motion is experienced, they can be used in this study to reconcile the broadscale concentration patterns observed.

4 Conclusions

The concentrations of higher linear dicarboxylic acids with 5 to 13 carbon atoms, phthalic acid and pinonic acid have been measured in fresh snow samples at the high Alpine site Jungfraujoch (JFJ, Switzerland) in winter and early spring 2006 and 2007 during the CLACE campaign 5 and 6, respectively. The concentrations of the individual compounds showed a wide range between the single snowfall events. This variation can be explained by the histories of the different air masses arriving at the JFJ.

Since the subsurface samples showed no consistent difference to the surface sample, we conclude that under these circumstances postdeposition of dicarboxylic acids did not influence the results significantly.

The acids may enter the snow through two mechanisms. Firstly the gas phase dicarboxylic acids, having low vapour pressures, condense on existing aerosol. This aerosol can then be effectively scavenged from the air by falling snow. Alternatively the aerosol on which the acid has condensed can become a CCN, which accumulates water and at sufficiently low temperatures freezes to fall later as snow. These two mechanisms cannot be distinguished using the data presented here.

A strong influence of anthropogenic sources was found in many snow samples, due to in-mixing of Boundary Layer (BL) air during transport to the site. In these cases elevated total concentrations of dicarboxylic acids have been observed. The entrainment of BL air from the Italian Po valley in the South or from the Swiss Plateau in the North was found to cause the highest observed total concentrations. Using the C_6/C_9-ratio and the Pht/C_9-ratio the contribution of anthropogenic and biogenic sources to the dicarboxylic acid composition in the snow samples could be estimated, indicating that anthropogenic sources dominate over biogenic sources in air masses arriving at the JFJ during winter time.

This is therefore a successful demonstration of a new technique for the measurement of organic acids in snow. Further measurements at other locations are required to determine the spatial and seasonal distribution of these species. Based on these measurements, future laboratory studies concerning the effect of organic acids on ice nucleation should focus on the more abundant species namely in particular adipic acid, which was found twice at elevated concentrations, and also glutaric, azelaic and phthalic acid.

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