Seasonal variation of water-soluble ions of the aerosol at the high-alpine site Jungfraujoch (3580 m asl)

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[1] Within the Global Atmosphere Watch (GAW) Aerosol Program of the World Meteorological Organization (WMO), the aerosol chemical composition has been continuously measured since July 1999 at the Jungfraujoch (JFJ) of which the first 1.5-year data set is presented. Sampling is performed in two size classes (total suspended particles (TSP) and particles with aerodynamic diameters smaller than 1 μm). The filters are analyzed for major ions, which constitute 30% of the total dry aerosol mass collected at this site. As annual mean, a total ion mass concentration of 1.04 $\mu\text{g m}^{-3}$ was observed. Sulfate, ammonium, and nitrate were the major components of the fine aerosol fraction, while calcium and nitrate were two major water-soluble components in the coarse mode. Single particle analysis confirmed the internal mixture of calcium and nitrate in the coarse mode. The total ion mass concentration showed strong seasonal differences, with 1.25, 1.62, 0.70, and 0.25 $\mu\text{g m}^{-3}$ for spring, summer, fall, and winter, respectively. The variability was stronger for sulfate, ammonium, and nitrate than for calcium. The reason for this is believed to be local sources of calcium, which do not require vertical transport, along with Sahara dust episodes, which occur occasionally over the whole year, independent from the season. **INDEX TERMS:** 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0335 Atmospheric Composition and Structure: Ion chemistry of the atmosphere (2419, 2427); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; **KEYWORDS:** free troposphere, major ions, PM₁, TSP

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1. Introduction

[2] Aerosols play a crucial role in global climate forcing, and their chemical composition is relevant in this context for a number of reasons. The chemical composition determines the particle hygroscopicity and solubility and thus the size change with increasing relative humidity (RH). It also influences the optical properties of the aerosol via the refractive index [Adams *et al.*, 1999; Seinfeld and Pandis, 1998]. These aspects are therefore related to the direct effect of the aerosol forcing. Furthermore, the hygroscopicity has strong implications for cloud formation, which relates to the indirect effect of the aerosol forcing. These effects are strongly influenced by the size of the particles. Size discrimination into a coarse mode (particles with a diameter

$d > 1 \mu\text{m}$) and a fine mode ($d < 1 \mu\text{m}$) is therefore often applied.

[3] The chemical composition varies, depending on the origin of the aerosol particles, and is therefore important for an assessment of the contribution from various sources. Aerosols are usually split into primary and secondary aerosol, as well as anthropogenic and natural aerosol, based on their formation history. Primary aerosol refers to particles that are directly released to the atmosphere as particles. Examples of natural primary particles are sea-salt and dust particles. Due to their generation, these particles typically belong to the coarse mode of the atmospheric aerosol. Primary anthropogenic particles have various sources and may be found both in the coarse and fine mode. Secondary aerosol is formed by transformation of gaseous precursors (both from natural or anthropogenic sources) into condensable material. Most of the secondary aerosol mass is found in the fine mode. However, heterogeneous reactions occurring on coarse mode particles may also result in coarse secondary aerosol material. This was found to be important for the reaction of nitrate with sea-salt particles and dust [Raes *et al.*, 2000; Matsumoto *et al.*, 1998] and was as well observed for ammonium [Yeatman *et al.*, 2001a]. This shift changes the deposition behavior as well as the lifetime [O'Dowd *et al.*, 1999] and optical properties of the aerosol

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and is crucial to understand the life cycle and impact of atmospheric aerosol particles.

[4] It is the goal of the Global Atmosphere Watch (GAW) program to determine the spatiotemporal distribution of aerosol properties related to climate forcing and air quality up to multidecadal timescales [WMO, 2001]. Due to the short lifetime of aerosol particles, the global distribution is quite inhomogeneous, which requires a large number of stations to achieve global coverage. Presently, GAW consists of some 20 Global stations, which cover different types of aerosols, i.e., clean and polluted continental, marine, arctic, dust, biomass burning, and free troposphere (FT). The Jungfraujoch (JFJ) located at 3580 m asl in the Swiss Alps is part of this program and is designated as clean continental background station in Central Europe, together with the Sonnblick (3106 m asl, Austria) and Zugspitze (2962 m asl, Germany). The JFJ has been shown to be well suited for the study of background aerosols in climate research [Nyeki *et al.*, 1998].

[5] This paper presents the first 1.5 years of data of the water-soluble ionic aerosol fraction at the JFJ. The seasonal variation of the various components is discussed as well as their partitioning in the different size fractions and potential sources and formation processes. The data are intended to provide input for the calculation of the optical properties of the atmospheric aerosol.

2. Experimental

2.1. Experimental Site

[6] The aerosol samples were taken at the high-alpine research station JFJ (3580 m asl, 46°33'N, 7°59'E), which is situated on the northern crest of the Bernese Alps in Switzerland. Air masses reaching the JFJ from northern directions may therefore be influenced by the Swiss Mittelland. Air coming from the South passes through inner alpine regions before reaching the JFJ.

[7] The station, which is surrounded by rocks and glaciers, is located on a saddle between the two high summits Mönch (4099 m asl, northeastern direction) and Jungfrau (4158 m asl, southwestern direction). To the north, there is a steeply falling flank, and in the south, the Aletsch glacier is situated. The station is reachable by railway during the whole year. More information is given by Kromp-Kolb *et al.* [1993] and Baltensperger *et al.* [1997].

2.2. Sampling

[8] The aerosol sampling was designed to run unattended to a high degree. For this purpose a sampling unit was constructed that takes four subsequent samples in two size classes (total suspended particulate matter (TSP) and particles with an aerodynamic diameter less than 1 μm (PM_{10})) automatically. Two size classes were selected according to the recommendations of the GAW Scientific Advisory Group for Aerosols [WMO, 2001], reflecting the fact that the mass scattering efficiency is quite different for submicron and supermicron aerosols [Finlayson-Pitts and Pitts, 2000; IPCC, 2001]. Preliminary measurements with a cascade impactor had shown that indeed a size cut of 1 μm was best able to discriminate between the different chemical composition of the fine and coarse mode aerosol [Streit *et al.*, 2000]. Except for special intensive field

Figure 1. Sketch of the heated inlet, which is used for the continuous GAW aerosol measurements and also for aerosol sampling for subsequent chemical analysis. The inner diameter of the central tube is 6 cm.

campaigns, where the filters were changed more often, this setup samples air for 24 hours every sixth day. With this time resolution, the sampling unit is working stand-alone for approximately 4 weeks. After these time the filter packs have to be replaced.

[9] The aerosol filters were connected to the heated aerosol inlet, which is used for all continuous aerosol measurements at the JFJ. The inlet (see Figure 1) is located outside of the so-called Sphinx building at the JFJ on the upper platform. It is heated to a constant temperature of 20°C, to evaporate potential cloud droplets and to protect the inlet from freezing during in-cloud weather conditions. Calculations for this inlet showed that droplets smaller than 40 μm can be sampled up to a wind speed of 20 m s^{-1} [Weingartner *et al.*, 1999]. This is of importance since the station is within clouds about 40% of the time [Baltensperger *et al.*, 1998], where most of the aerosol mass is present in the cloud droplets [Henning *et al.*, 2002]. The aerosol fraction able to pass this inlet is called TSP in the following.

[10] The heating of the inlet system might lead to a reduction in particle mass due to evaporation of volatile material. The extent of this loss was estimated during a special field campaign by comparison of size distribution data performed simultaneously inside and outside the building (R. Nessler *et al.*, Simultaneous dry and ambient measurements of aerosol size distributions at the Jungfraujoch, submitted to *Tellus*, 2002). For low ambient RH (<40%) the volume loss was calculated to be about 7%. This value is an upper limit because the aerosol still contains some water at RH <40% as reported by Weingartner *et al.* [2002], and the observed volume loss is thus due to volatile material and water evaporation.

[11] Inside the building (indoor temperature $T = 20\text{--}30^\circ\text{C}$, RH < 10%), the aerosol sampling line was split into two paths (Figure 2). On one side (left), the sampling line for the TSP aerosol is situated. In the other line the upper four stages of a

Figure 2. Sketch of the automatic aerosol sampling unit consisting of two size lines TSP and PM₁. Each filter pack includes a Teflon and nylon filter.

cascade impactor [Maenhaut *et al.*, 1996] was set inline to generate a cutoff of 1 μm with a flow rate of 11 L min⁻¹ (PM₁). Flow rates were controlled by mass flow controllers (5851E Brooks Instrument, Fisher-Rosemount AG, USA) in both sampling lines. The impactor stages were treated with high-vacuum grease to prevent bouncing.

[12] To each sampling line (TSP and PM₁) four filter holders (Digital Elektronik AG, Switzerland) were connected. One filter of each line was exposed during the same time. The sampling lines were opened and closed by solenoid valves controlled by a programmable unit (Digital DPA96, Digital Elektronik AG, Switzerland), which also controlled the vacuum pump (N 0135.1 ANE, KNF Neuberger, Germany).

[13] Each filter holder included a filter pack (47 mm) consisting of a Teflon filter and a nylon filter. The Teflon filter (PTFE, Sartorius AG, Germany) with a pore size of 1.2 μm sampled the particulate matter. Downstream of the Teflon filter a nylon filter (Nylasorb, PALL/Gelman Sciences, USA) with a pore size of 1 μm was placed for collection of gas-phase nitrate, which might have evaporated from the first filter [Cheng and Tsai, 1997; Zhang and McMurtry, 1992]. Cleaning of the filters with deionized water or NaOH was found to be not necessary because of the low blank values of the filters, which were tested regularly.

[14] The loaded filter packs remained in their position until all filters had been exposed. Then the packs were replaced and transported to the laboratory at the Paul Scherrer Institut in a cooled isolated box. Afterward the

filters were stored at 4°C until processing for ion chromatography (IC) analysis.

2.3. Analysis

[15] Teflon and nylon filters were extracted with 7 mL ultra pure water (18 M Ω cm) in 12.5 mL tubes that had been precleaned with the same ultra pure water. The Teflon filters were analyzed by IC for the cations lithium (Li⁺), sodium (Na⁺), ammonium (NH₄⁺), potassium (K⁺), magnesium (Mg²⁺), and calcium (Ca²⁺) and the anions fluoride (F⁻), acetate (CH₃COO⁻), formate (HCOO⁻), methanesulfonate (CH₃SO₃⁻), chloride (Cl⁻), nitrate (NO₃⁻), sulfate (SO₄²⁻), and oxalate (C₂O₄²⁻). The nylon filters were only analyzed for NO₃⁻.

[16] For the analysis of the cations an IC setup (Sykam, Germany) was used with a guard (Dionex IonPac CG 12A, 4 mm, Dionex, USA) and an analytical column (Dionex IonPac CS 12A, 4 mm). The eluent was 20 mM methanesulfonic acid (CH₃SO₃H). The anions were analyzed with the IC system Dionex DX-500 also with guard and analytical column (Dionex IonPac AG/AS 11, 2 mm). As eluent sodium hydroxide (0.5–24 mM NaOH) was used. The detection limits of the IC analysis are shown in Table 1. More information on the used IC systems and setup is given by Döscher *et al.* [1995] and Eichler [2000].

3. Results and Discussion

3.1. Peak Identification

[17] Figure 3 gives an example of a cation chromatogram. Up to four peaks occurred that could not readily be identified (one peak between NH₄⁺ and K⁺, two peaks between K⁺ and Mg²⁺, and sometimes one after Ca²⁺). It was shown both by spiking the samples and by additional analysis of the samples by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) that the peaks were not due to elemental cations.

[18] Amines have been found by other groups in ambient air [Angelino *et al.*, 2001] and could be responsible for these

Table 1. Detection Limits of the IC Analysis for All Analyzed Ions (Calculated Based on Samples of 15.84 m⁻³ Extracted in 7 mL Water)

	Instrumental Detection Limit (IDL), $\mu\text{g L}^{-1}$	IDL, neq m ⁻³	Filter Blank, neq m ⁻³	Standard Deviation, σ neq m ⁻³
Teflon Filters				
F ⁻	0.2	0.005	0.07	0.07
CH ₃ COO ⁻	1	0.007	<IDL	
HCOO ⁻	0.8	0.008	0.05	0.01
CH ₃ SO ₃ ⁻	1	0.005	<IDL	
Cl ⁻	0.4	0.005	0.1	0.07
NO ₃ ⁻	0.7	0.005	0.04	0.03
SO ₄ ²⁻	0.6	0.006	0.01	0.01
C ₂ O ₄ ²⁻	0.7	0.007	<IDL	
Na ⁺	0.75	0.01	0.06	0.03
NH ₄ ⁺	0.5	0.04	0.08	0.03
K ⁺	1.6	0.006	0.04	0.02
Mg ²⁺	1.9	0.07	<IDL	
Ca ²⁺	1	0.02	0.22	0.12
Nylon Filters				
NO ₃ ⁻			0.03	0.01

Figure 3. Cation chromatogram of TSP filter from 24 June 2001. Two unknown peaks occurred on a regular base between ammonium and potassium and between potassium and magnesium, which might be due to amines.

peaks. Tests were performed with ethylamine, ethanolamine, diethylamine (DEA), and 2-diethylaminoethanol. All of these amines occurred as a peak with this setup, but most of them eluted at retention times different from the unidentified peaks. As an exception, DEA was possibly identified as producing the first peak between K^+ and Mg^{2+} , as shown by spike tests with DEA. Further work needs to be carried out for the identification of the other peaks, but was beyond the scope of this paper.

3.2. Data Quality Assurance

[19] Sulfur in TSP was measured by the Swiss Federal Laboratories for Materials Testing and Research (EMPA) within the Swiss national network for air pollution. Chemical analysis was performed by X-ray fluorescence analysis, which was calibrated by simultaneous IC analysis [EMPA, 2000; Filliger *et al.*, 1994]. These data (June 1999 to December 2000) were compared to our data assuming that all the sulfur detected by EMPA was sulfate. A good agreement was found, with ($R^2 = 0.71$, $n = 77$ excluding one outlier)

$$[SO_4^{2-} \text{ PSI}] = 0.96[SO_4^{2-} \text{ EMPA}] - 0.002 \text{ ng m}^{-3} \quad (1)$$

where $[SO_4^{2-} \text{ PSI}]$ is the mass concentration of sulfate determined by IC at PSI and $[SO_4^{2-} \text{ EMPA}]$ the mass concentration of sulfate calculated from the sulfur data of EMPA. This result indicates that both inlets sample both aerosol particles and cloud droplets with similar efficiency.

[20] Aerosol nitrate is more difficult to determine due to the numerous possible sampling artifacts. Gaseous nitric acid was assumed to be quantitatively lost during transport through the inlet system (4.5 m length, 11 s residence time). On average, 62% of the total nitrate in TSP and 94% of the total fine nitrate evaporated from the Teflon filters and was found on the backup nylon filter. This nitrate was assumed to originate from ammonium nitrate. An equivalent amount of ammonium was therefore added to the ammonium determined on the Teflon filter, representing 22.6% of the

total ammonium. An attempt was made to determine this evaporating ammonium by an additional backup filter (quartz fiber filter impregnated with citric acid). However, in this case, the variability of the field blanks was too high for a reliable determination of the low concentrations.

3.3. Ion Balances

[21] Ion balances of the analyzed ions (including the equivalent ammonium amount from the evaporated ammonium nitrate from the nylon filter) gave

$$[\text{Cations TSP}] = 1.2[\text{Anions TSP}] + 1.13 \text{ neq m}^{-3}, (R^2 = 0.75) \quad (2)$$

for the TSP and

$$[\text{Cations PM}_{10}] = 0.89[\text{Anions PM}_{10}] + 0.21 \text{ neq m}^{-3}, (R^2 = 0.92) \quad (3)$$

for the fine aerosol. The excess of cations and anions in the TSP and PM_{10} , respectively, is due to the components not measurable with the present IC setup. Assuming that hydrogen ions and carbonate (or actually bicarbonate) are the missing components in the fine and coarse mode, respectively, electroneutrality can be established. Based on this assumption, Figure 4 presents pie diagrams of the annual mean concentrations of all measured compounds in the coarse and the fine mode, where the coarse mode data was calculated from the difference TSP minus PM_{10} .

[22] This pie diagram does not include other compounds such as carbonaceous material, insoluble dust material or water. Organic (OC) and black carbon (BC) were determined in $PM_{2.5}$ during a summer campaign and were found to be present in appreciable amounts. The OC mass concentration was in the same range as the sulfate mass concentration, and the BC mass concentration was about a quarter of the sulfate mass concentration [Krivacsy *et al.*, 2001b].

[23] In addition, water is present even at low RH. Weingartner *et al.* [2002] showed in a case study that even at $RH = 10\%$ the particles are still supersaturated droplets. As an example, a 250 nm particle exhibits a growth factor of 1.18 at 50% RH, which yields a water mass 1.5 times the mass of sulfate.

[24] On average, the soluble ions determined within this work amounted to $1.04 \mu\text{g m}^{-3}$ corresponding to 30% of the TSP mass concentration as determined by weighing the filters under controlled temperature and humidity conditions ($RH = 50\%$, $T = 20^\circ\text{C}$) at EMPA. The share shows some seasonal variation, with 22% ($1.25 \mu\text{g m}^{-3}$), 38% ($1.62 \mu\text{g m}^{-3}$), 34% ($0.70 \mu\text{g m}^{-3}$), and 24% ($0.25 \mu\text{g m}^{-3}$) for spring (March–May), summer (June–August), fall (September–November) and winter (December–February), respectively.

[25] It is interesting to note that excess sulfate (calculated as described in section 3.5) and ammonium uncorrected for ammonium nitrate loss in the fine aerosol fraction show a high correlation, with

$$[NH_4^+] = 0.87[\text{ex } SO_4^{2-}] + 0.08 \text{ neq m}^{-3}, (R^2 = 0.89, N = 118) \quad (4)$$

Figure 4. Annual mean partitioning of ionic species in coarse (TSP minus PM_{10}) and fine (PM_{10}) aerosol mode in percent of $neq\ m^{-3}$. To obtain electroneutrality, carbonate and hydrogen ions were assumed to be the missing ions for coarse and fine mode, respectively.

This indicates that indeed any ammonium associated with nitrate evaporated during sampling, justifying the correction procedure for ammonium mentioned in section 3.2.

[26] The nitrate to sulfate ratio r in the fine aerosol mode is with $0.2\ (neq\ m^{-3}/neq\ m^{-3})$ [Krivacsy *et al.*, 2001a; this paper] quite different from sites closer to the emission sources, with $r = 0.7$ at the urban site Zurich [Hueglin, 2000], $r = 1.1$ in the Milan area [Putaud *et al.*, 2002], or 1.6 on average at coastal polluted surroundings (Weybourne) [Yeatman *et al.*, 2001b]. At other remote sites in the upper troposphere and free troposphere similar ratios as ours were found, with $r = 0.3$ in the French Alps (Vallot Observatory, 4361 m asl) [Preunkert *et al.*, 2002], $r = 0.2$ in the Himalaya region (Hidden Valley, 5050 m asl) [Shrestha *et al.*, 1997], $r = 0.2$ at Mauna Loa [Galasyn *et al.*, 1987], and $r = 0.15$ for air plane measurements during ACE 1 [Huebert *et al.*, 1998]. The seasonal variation of the ratio was low and lay between 0.2 and 0.3.

[27] Two reasons may serve as explanation for the observed low nitrate to sulfate ratio. First, NO_x shows a faster oxidation rate than SO_2 , yielding a higher nitrate to sulfate ratio close to sources [Colbeck, 1998]. Second, and probably more important, ammonium is depleted by wet and dry deposition during transport, without having a new formation source. Thus, the ratio of ammonium to the sum of sulfate and nitrate will decrease during this aging process. This in turn results in a steady decrease of the nitrate to sulfate ratio, since gaseous nitric acid is formed

under conditions of ammonium deficiency [Wexler and Seinfeld, 1990]. In the upper troposphere the nitrate to sulfate may increase again due to the enhanced solubility of nitric acid in aerosol water at colder temperatures [Adams *et al.*, 1999].

3.4. Seasonal Variation

[28] In Table 2 the annual and seasonal means of all ions in TSP and PM_{10} are given. Again, it can be seen that the ionic particulate mass concentration is dominated by sulfate, ammonium and nitrate during all seasons. Calcium represents also a high fraction, especially during winter. The annual means of sulfate, ammonium and nitrate are 9.17 , 9.48 , and $3.46\ neq\ m^{-3}$, respectively, and match well with other data from the high-alpine region [Kasper and Puxbaum, 1994]. These long-term measurements at JFJ show also good agreement with data from former campaigns more concentrated on special seasons at this site [Schwikowski *et al.*, 1995; Nyeki *et al.*, 1996].

[29] >A strong seasonal variation was observed for several components. The summer to winter ratio for sulfate, ammonium, fine nitrate and coarse nitrate was 8, 10, 10, and 8, respectively. Strong differences in the summer/winter ratios were also found for oxalate and formate, while they are much weaker for the coarse mode components calcium (summer/winter ratio 3), sodium (1), potassium (3), and magnesium (3). The observed seasonality is explained as follows: during wintertime the JFJ is

Table 2. Seasonal Variation of Ionic Species in TSP and PM₁^a

neq m ⁻³	Total (119) ^b		Spring (23) ^b		Summer (43) ^b		Fall (30) ^b		Winter (23) ^b	
	TSP Mean	PM ₁ Mean	TSP Mean	PM ₁ Mean	TSP Mean	PM ₁ Mean	TSP Mean	PM ₁ Mean	TSP Mean	PM ₁ Mean
F ⁻	0.21	0.06	0.13	0.03	0.28	0.11	0.32	0.04	0.01	0.02
CH ₃ COO ⁻	0.05	0.01	0.01	<IDL	0.04	0.02	0.14	0.01	<IDL	0.01
HCOO ⁻	0.04	0.01	0.08	0.01	0.05	0.03	0.01	<IDL	0.01	<IDL
CH ₃ SO ₃ ⁻	0.02	0.02	0.03	0.02	0.03	0.03	0.01	0.01	<IDL	<IDL
Cl ⁻	0.28	0.08	0.42	0.04	0.34	0.10	0.22	0.06	0.11	0.10
NO ₃ ⁻ (nonvolatile)	1.32	0.15	2.08	0.25	1.93	0.18	0.65	0.10	0.30	0.08
NO ₃ ⁻ (volatile)	2.14	1.92	2.40	2.00	3.35	3.10	1.59	1.45	0.40	0.25
NO ₃ ⁻ (total)	3.46	2.04	4.49	2.25	5.28	3.19	2.24	1.56	0.70	0.32
SO ₄ ²⁻	9.17	9.03	9.78	7.91	14.2	14.2	7.17	7.96	2.03	1.82
C ₂ O ₄ ²⁻	0.28	0.18	0.29	0.12	0.52	0.35	0.15	0.12	0.02	0.01
Na ⁺	0.84	0.16	1.10	0.15	1.01	0.19	0.45	0.16	0.76	0.09
NH ₄ ⁺	7.34	8.00	7.28	6.89	12.0	13.2	5.44	6.54	1.29	1.32
NH ₄ ⁺ (including volatile NH ₄ NO ₃)	9.48	9.89	9.68	8.89	15.4	16.2	7.04	7.99	1.70	1.57
K ⁺	0.31	0.19	0.34	0.14	0.50	0.29	0.15	0.14	0.18	0.12
Mg ²⁺	0.50	<IDL	0.84	<IDL	0.69	0.07	0.20	<IDL	0.20	<IDL
Ca ²⁺	7.51	0.27	14.0	0.46	10.3	0.36	2.31	0.12	2.69	0.09

^aValues below the detection limit were set to 50% of the instrumental detection limit for each ion.^bNumbers in brackets denote number of samples for each season.

mainly influenced by the clean free troposphere, resulting in low concentrations of most aerosol components. Higher mass concentrations are found during summer when convection occasionally transports polluted air masses up to the JFJ. This effect is less distinct for calcium and the other mineral dust components, because this mineral dust is also locally present and therefore independent of convection. Another important source of mineral dust are Sahara dust events, where calcium mass concentrations may be a factor of 16 higher than under regular conditions [Schwikowski *et al.*, 1995]. Sahara dust events occur independently of the season over the whole year. The results agree well with long-term aerosol surface area measurements with the Epiphaniometer [Gäggeler *et al.*, 1989] at the JFJ [Baltensperger *et al.*, 1991]. Further explanation of the influence of different weather situations on the aerosol concentration at the JFJ is given by Lugauer *et al.* [1998].

[30] Figure 5 shows the annual variation of the mass concentration in TSP and PM₁ for the most abundant ions in more detail. The symbols denote single measurements, and the lines represent the monthly means. In Figure 5a, the monthly sulfate data calculated from the EMPA sulfur measurements are also given (see also section 3.2). Both, the seasonal variation with high values in summer and the different partitioning of the ions between coarse and fine mode are evident. TSP and PM₁ values in sulfate and ammonium are very similar, indicating that these components are predominantly found in the fine particle fraction. Nitrate exhibits a significant difference between TSP and PM₁, and calcium is almost completely absent in the fine aerosol fraction. This corroborates the findings described earlier (see section 3.3) and is shown in more detail in Figure 6. The seasonal mean values of the ion concentration in the coarse mode were again calculated from the difference between TSP and PM₁ concentrations for the various species. Again sulfate and ammonium are found nearly exclusively in the fine mode, while calcium, sodium, and magnesium are almost only present in the coarse fraction, and the other ions are distributed between

Figure 5. Seasonal variation of the mass concentration of various ionic species in TSP and PM₁. Single values and monthly means are given for sulfate, ammonium, nitrate, and calcium. In the uppermost panel, the sulfate mass calculated from the TSP sulfur concentration determined within the NABEL network is also shown.

Figure 6. Partitioning of the water-soluble ionic aerosol species into coarse and fine mode for different seasons (cations right panel, anions left panel).

both fractions. This partitioning is investigated for sulfate and nitrate in the following.

3.5. Coarse and Fine Mode Sulfate

[31] Excess sulfate is the amount of sulfate that is produced by oxidation of SO_2 in the atmosphere and is predominantly found in the fine aerosol mode. As indicated in Figure 4 this fine sulfate represents the dominant part of the total sulfate. Coarse mode sulfate is known to originate from sea spray and crustal material. The portions of sea-salt sulfate and mineral dust sulfate were calculated by using sodium and calcium, respectively as tracers. The following equation was used which was established for preindustrial

conditions from an alpine ice core [Schwikowski *et al.*, 1999]:

$$[\text{ex SO}_4^{2-}] = [\text{SO}_4^{2-}] - 0.12[\text{Na}^+] - 0.175[\text{Ca}^{2+}] \quad (5)$$

It was found that 3% and 15% of the TSP sulfate originated from sea salt and dust, respectively. That means that 82% of the total sulfate was formed by oxidation of SO_2 . In the absence of biogenic and volcanic SO_2 sources (which is reasonable to assume for this site and this time period) this sulfate fraction stems from anthropogenic sources. These numbers correspond well with the findings by Eichler [2000] and Schwikowski *et al.* [1999] who found in two

Figure 7. Scatterplot of excess sulfate in TSP and total sulfate in PM₁. Six outliers (95% prediction limits) out of 112 data points were excluded from the regression.

alpine ice cores fractions of 12% and 16% for dust and 2% and 1% of sea-salt sulfate.

[32] Applying (5) to the PM₁ data it is found that 98% of the total sulfate in the PM₁ mode is secondary sulfate. A linear regression (using the logarithmical values, since the data were lognormally distributed), of the fine sulfate versus the total excess sulfate yields (Figure 7):

$$\log(\text{SO}_4^{2-} \text{PM}_1) = \log(\text{ex SO}_4^{2-} \text{TSP}) \times 0.96 + 0.08, \quad (6)$$

$$R^2 = 0.97, N = 106$$

indicating that indeed excess sulfate is exclusively found in the fine mode. For the correlation, four data points were excluded which did not lie within the 95% prediction interval. It is interesting to note that the data vary by more than 3 orders of magnitude, stressing the high variability of sulfate concentrations at such remote sites.

3.6. Coarse and Fine Mode Nitrate

[33] Nitrate is found in the fine and coarse aerosol fraction. This is caused by the different chemical compositions in which nitrate may be present. The fine mode nitrate is formed by the reaction of HNO₃ with ammonia, which leads to ammonium nitrate. Ammonium nitrate is not very stable under ambient conditions, especially at low RH, and therefore evaporated from the Teflon filter under our sampling conditions. The resulting gaseous nitrate was collected on the inline nylon filter as described in section 3.2.

[34] If calcium carbonate particles are present in the atmosphere gaseous HNO₃ may react with CaCO₃ according to [Finlayson-Pitts and Pitts, 2000]:

This reaction may initially take place on dry or wet particles. Under dry conditions this reaction rapidly ceases [Goodman *et al.*, 2000], but wet conditions result in a continuation of the reaction, due to dissolution of CaCO₃ in the aqueous solution on the surface of the particles. If dehydration takes place (e.g., during sampling), nonvolatile calcium nitrate is formed. Thus, the coarse aerosol fraction is found almost exclusively on the Teflon filter (Figure 4).

[35] To check if the coarse nitrate is present as calcium nitrate the following test was conducted: from the total measured calcium the amount which is needed to neutralize the carbonate calculated from the ion balance was subtracted. The remaining calcium amount would be available for the nitrate and should therefore show a correlation with the measured coarse nitrate. On annual average, a significant (P-value < 0.001) correlation was found with R² = 0.56 and a slope of 0.64 eliminating two values where the anion deficiency (assumed to be carbonate) was much larger than the calcium concentration. This is quite good considering the involved assumptions. Furthermore, Figure 4 shows that on average the sum of "carbonate" and nonvolatile nitrate equals 98% of the calcium. On average, 12% of the calcium is found as calcium nitrate, however, with a significant

Figure 8. Simultaneously detected positive-ion and negative-ion spectra of a mineral aerosol particles from ambient air (aerodynamic diameter 1.1 μm) measured on-line at the JFJ, 23 March 2000.

seasonal variation, with 14%, 11%, 31% and 10% for spring, summer, fall and winter; respectively. This fraction is much more than a monolayer, since for a 1 μm particle the surface atoms account for less than 0.04% of the total number of atoms in the particle [Klabunde, 1985]. On annual average, about 41% of the total particulate nitrate (TSP line, nylon plus Teflon) is present in the coarse mode. The fraction varies for the different seasons, corresponding to 50%, 40%, 31%, and 54% for spring, summer, fall, and winter, respectively. In general, an enhancement in the nonvolatile nitrate fraction with increasing calcium concentrations was observed. However, some cases with high calcium amounts and only small coarse nitrate fractions were also observed. This might be due to specific ambient conditions (e.g., low RH, which slowed the reaction efficiency, low concentrations of HNO_3 , or high Ca concentrations during Saharan dust events).

[36] The conclusion that the coarse mode nitrate is formed by the reaction of nitric acid and calcium carbonate is corroborated by single particle analysis conducted at the JFJ during a field campaign in winter 2000 with a transportable on-line time-of-flight laser mass spectrometer (LAMPAS 2) with bipolar ion detection. The LAMPAS 2 was used for a fast determination of the size and composition of individual particles [Trimborn et al., 2000]. For chemical analysis and aerodynamic size determination, the aerosol enters the instrument through a differentially pumped inlet system. Aerosol particles are analyzed in the size range between 0.2 and 10 μm using an active triggering system for highly efficient particle detection and ionization [Trimborn et al., 2002]. An example of simultaneously detected positive-ion and negative-ion spectra from a single particle at the JFJ during the field campaign in winter 2000 is shown in Figure 8. The spectra include characteristic signals of mineral components such as sodium (Na^+ at 23 m/z), magnesium (Mg^+ at 24 m/z), aluminum (Al^+ at 27 m/z), calcium (Ca^+ at 40 m/z), iron (Fe^+ at 56 m/z), and silicon ($\text{SiO}_3^-/\text{SiO}_2^-$ at 76/60 m/z) and some oxide signals. Additionally a variety of anions (e.g., nitrate fragments NO_2^- at 46 m/z and NO_3^- at 62 m/z, phosphate PO_3^- at 79 m/z, and chloride Cl^- at 35/37 m/z) can be identified. These observations support the conclusion from the bulk samples by detecting calcium and nitrate together in a typical mineral particle. More detailed information will be found in a forthcoming paper (Hinz et al., in preparation).

[37] It is interesting to note that also formate and acetate show significant fractions in the coarse mode indicating that similar neutralization reactions might take place with these compounds.

4. Conclusions

[38] The first 1.5-year aerosol chemical composition data from the high-alpine site JFJ measured within the GAW program are presented. The amount and share of the water-soluble ionic aerosol species in fine and coarse mode and their interconnections were evaluated. The cutoff between coarse and fine aerosol of 1 μm determined in former experiments proved to provide a very good distinction between the accumulation mode aerosol and the coarse mode fraction. Gaseous HNO_3 was lost in the inlet system, but ammonium nitrate was sampled without losses with the

used Teflon/nylon filter pack. This setup, however, requires a correction for the ammonium lost by the evaporation of ammonium nitrate. The ionic mass concentrations are comparable to other sites in the remote lower free troposphere. Distinct seasonal variations of the ionic species were observed, where aerosol components connected to vertical transport processes in the atmosphere showed the highest variation. Aerosol components that also had local sources showed smaller dependence on the season. A nitrate/sulfate ratio of 0.2 was found, which corroborates findings from other sites in the lower free troposphere and is much lower than at sites close to source areas. Nitrate was found both in the coarse and the fine aerosol mode. The coarse mode nitrate was explained as calcium nitrate formed by chemical reaction of calcium carbonate with nitric acid. Single particle analysis confirmed that calcium and nitrate are indeed internally mixed in coarse particles. Sulfate was almost exclusively in the fine aerosol fraction due to the facts that gas-to-particle conversion is the dominant source and that there are no mode-shifting reactions as in the case of nitrate. The used sampling setup was found to be suitable for the planned ongoing long-term measurements of the aerosol chemical properties within the GAW program at the JFJ site.

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