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1 Temporal changes of inorganic ion deposition in the 2 seasonal snow cover for the Austrian Alps (1983- 3 2014)

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5
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12 13 **ABSTRACT**

14 A long-term record of inorganic ion concentrations in wet and dry deposition sampled from snow
15 packs at two high altitude glaciers was used to assess impacts of air pollution on remote sites in
16 central Europe. Sampling points were located at Wurtenkees and Goldbergkees near the Sonnblick
17 Observatory (3106m above sea level), a background site for measuring the status of the atmosphere
18 in Austria's Eastern Alps. Sampling was carried out every spring at the end of the winter
19 accumulation period in the years 1983 to 2014. Concentrations of major ions (NH_4^+ , SO_4^{2-} , NO_3^- , Ca^{2+} ,
20 Mg^{2+} , K^+ , Na^+ and Cl^-) were determined using ion chromatography (IC) as well as atomic absorption
21 spectroscopy (AAS) in the earlier years. Concentration of H^+ was calculated via the measured pH of
22 the samples.

23 Trends in deposition and concentration were analysed for all major ions within the period from 1983
24 to 2014 using Kendall's tau rank correlation coefficient. From 1983-2014, total ion concentration
25 declined ~25%, i.e. solutions became ~25% more dilute, indicating reduced acidic atmospheric
26 deposition, even at high altitude in winter snow. SO_4^{2-} and NO_3^- concentrations decreased
27 significantly by 70% and 30%, respectively, accompanied by a 54% decrease of H^+ concentrations.
28 Ionic concentrations in snowpack were dominated by H^+ and SO_4^{2-} in the earliest decade measured,
29 whereas they were dominated by Ca^{2+} by the most recent decade. SO_4^{2-} and H^+ -depositions, i.e.
30 concentrations multiplied by volume, also showed a significant decrease of more than 50% at both
31 sites. This reflects the successful emission reductions of the precursor gases SO_2 and NO_x . Seasonal
32 values with significantly elevated spring concentrations of NH_4^+ , SO_4^{2-} and H^+ compared to fall snow
33 reflects the beginning of vertical mixing during spring. All other ions do not show any seasonality.
34 Source identification of the ions was performed using a principal component analysis (PCA). One

35 anthropogenic cluster (SO_4^{2-} , NO_3^- and NH_4^+) coming from road traffic or fossil fuel combustion and
36 animal husbandry, one crustal cluster (Ca^{2+} , Mg^{2+}) originating from local geological input or Saharan
37 dust events as well as one cluster of unknown origin with episodic character (Na^+ , K^+ and Cl^-) was
38 found.

39

40 **KEYWORDS (max. 6)**

41 Snow chemistry, ion deposition trends, non-sea-salt concentrations, source regions, seasonality,
42 Austrian Alps

43

44 **1. Introduction**

45 Determination of the ionic composition of high alpine snow packs plays an important role in
46 estimating the input of nutrients as well as eutrophic and acidifying components in terrestrial and
47 aquatic ecosystems. Atmospheric trace gases as well as aerosol particles are removed from the
48 atmosphere and accumulated in the snow cover via different deposition processes like the removal
49 by precipitation (wet deposition) or by direct (dry) deposition. Besides atmospheric precipitation,
50 wind-caused snowdrifts and avalanches play a relevant role for snow accumulation during winter.
51 Schöner et al. (2009) studied the annual course of snow depth for the same glacier fields investigated
52 in this paper. Based on their findings the winter accumulation period can be clearly defined as the
53 period from September to the end of April. Due to spatial and temporal variation of snowfall, the
54 chemical composition of the snow cover is heterogeneous.

55 During the winter season the deposited compounds accumulate in the snow cover and will be
56 preserved as long as melting does not occur. If melting occurs, the corresponding percolation of
57 meltwater through the snow cover causes a change in the concentration and distribution of solutes,
58 leading to a washout of ions. This is controlled by various processes such as leaching of solutes from
59 snow crystals and grains, meltwater-particulate interactions and microbial activity (Jones, 2001).
60 Additionally, physical and chemical processes further modify the chemical concentration of the snow
61 cover after deposition. Jones (2001) lists potential interactions between the dry snow cover (without
62 melting) and the atmosphere, such as dry deposition, volatilization and snow metamorphism, as
63 main processes, which could alter the concentration or could redistribute ions within the snow
64 cover. Volatilization seems to be of minor importance for non-volatile compounds, but dry deposition
65 is a dominant source for elevated concentrations in the snow cover, especially in rural and remote
66 areas as the Sonnblick region (Davies et al., 1991). Snow metamorphism seems to be unimportant for
67 absolute ion concentrations within the snow pack, but might lead to losses or gains of ions at specific
68 grain interfaces since solutes can be redistributed and concentrated on the snow grain surfaces or
69 boundaries.

70 For our study region at elevations above 3000 m a.s.l precipitation is almost exclusively solid during
71 the accumulation period. Snow stratigraphy from multi-year snow pits at altitudes higher than 3000
72 m a.s.l. show that during this period melt events are rare and restricted to the built up of surface
73 crusts only. Hence, the ionic loads are preserved in the snow cover and the chemical components
74 found in high alpine snow are stored in layers and are released or percolated during the melt period
75 in spring within only a few weeks (Williams and Melack, 1991). As high alpine snow is known to be
76 slightly acidic (Maupetit and Delmas, 1994) snow melt in spring causes an acidifying ionic pulse in
77 melt water and thus for downstream ecosystems. Melt water enriched in inorganic nutrients will also
78 serve as a nutrient supply for microbial communities. The acidification of natural ecosystems
79 observed in the 1980s spawned the idea to investigate the impact and sources of the acidifying
80 compounds incorporated in the snow as well as their neutralizing compounds. Now long-term trends
81 can be deduced.

82 The investigation of alpine snow chemistry is of major interest since the Alps are a densely populated
83 area, located between highly industrialized countries (Italy, France, Germany and Poland) and the
84 Mediterranean region, thus with intense human impact. Nickus et al. (1997) summarized the results
85 for the SNO SP (snow sampling campaign of the ALPTRAC project) study. It covered 17 high-alpine
86 sampling sites of snow chemistry, ranging from the Southwestern French Alps to the Eastern
87 Austrian Alps, investigated twice a year in March and May from 1990 to 1994. All sites showed a
88 slightly acidic snow cover and NH_4^+ , NO_3^- as well as SO_4^{2-} concentrations were two to three times
89 higher in spring snow than in winter snow. This finding can be well explained by the low vertical
90 mixing height during winter and the increasing number of events with vertical atmospheric mixing
91 up to 3000 m a.s.l. level in spring (Kuhn et al., 1998). Furthermore, concentrations of most of the ions
92 feature a west to east increase whereas no regional patterns were found for ionic loads. Snow pack
93 studies on glaciers were performed also by other studies, for example in France (Maupetit and
94 Delmas, 1994), Italy (Filippa et al., 2010) and the USA (Turk et al., 2001) trying to improve the
95 understanding of the physical and chemical processes responsible for the accumulation of major ions
96 in high alpine snow covers. All of these studies covered a maximum time span of four years at the
97 most whereas there are no long-term studies on chemical analysis of high alpine snow packs. One
98 exception is the study from Ingersoll et al. (2008), examining seasonal snow pack chemistry data for
99 the Rocky Mountain region covering the period 1993 to 2004. It shows a significant decrease of SO_4^{2-}
100 concentration and deposition, whereas NH_4^+ and NO_3^- increased significantly in the Central and
101 Southern Rockies. No trend was observed for the Northern Rockies. Regarding not only high alpine
102 sites, Avila (1996) reported a significant decrease of SO_4^{2-} concentration and deposition from 1983 to
103 1994 in precipitation samples collected in the Montsey mountains in NE Spain, as well as a pH
104 increase. A similar study for Austria combining snow and rain samples by Puxbaum et al. (1998)
105 shows also a significant decrease of SO_4^{2-} and H^+ in ion concentration and deposition. Both authors
106 explained this decrease as an indication that the reduction of SO_2 emissions has an effect on the SO_4^{2-}

107 concentration and deposition over NE Spain as well as over Austria. The first 10 years (1983-1993)
108 of the time series presented in this paper have already been published by Winiwarter et al. (1998).
109 These authors clearly identified SO_4^{2-} and NO_3^- ions as predominantly responsible for acidification,
110 but they did not provide a statistical analysis to isolate robust temporal trends.

111 Within this paper, we assess the status and temporal changes of the ionic composition in a high
112 alpine snowpack for a multi-decade period using two sampling sites in the Austrian Alps. Due to the
113 elevation of more than 3000m a.s.l. ionic loads observed in the snow cover of the Sonnblick region
114 are regarded as being driven by air of the mid or free troposphere. The unique time series from 1983
115 to 2014 is used to investigate trends and seasonal patterns for the accumulation period (autumn,
116 winter and spring) and to determine sources of the ions found in the snow cover. Then the ion
117 concentrations and depositions are compared with emission inventories for Austria and neighboring
118 countries. Finally, we conclude our work with respect to the relevance of findings for high-mountain
119 environment and changes of the status of the atmosphere in the European Alps.

120

121 **2. Experimental**

122

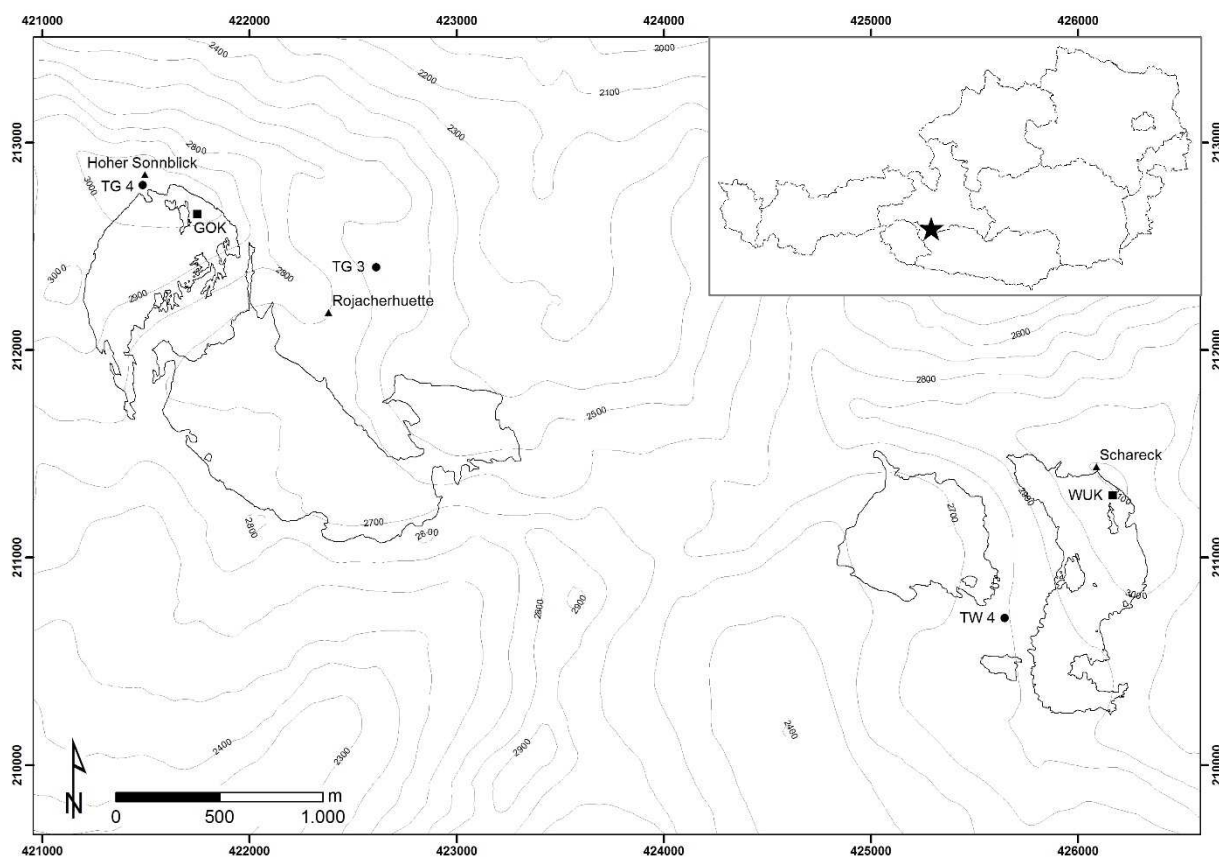
123 *2.1 Study area*

124 Samples were collected at two different sites, Goldbergkees (GOK) and Wurtenkees (WUK), both
125 located in the Austrian National Park Hohe Tauern in the Eastern Alps (see Figure 1) at an elevation
126 of more than 3000m a.s.l. These sites are distant to any anthropogenic activity and probably among
127 the most remote areas to be found in Central Europe. At GOK samples were taken annually from
128 1987-2014, whereas at WUK sampling started slightly earlier in 1983 and lasted until 2012. The GOK
129 sampling site is close to the meteorological observatory located at the summit Hoher Sonnblick
130 (SBO), which is part of the Global Atmosphere Watch Program (GAW) of the World Meteorological
131 Organization (WMO). Near the WUK sampling site a ski resort opened in 1985. As the sampling site
132 was situated clearly outside the skiing region we assume that there is no significant influence on ion
133 concentration and snow depth from the production of artificial snow. Sampling at WUK ceased in
134 2012. Presently sampling is only performed at GOK, utilizing the observatory nearby.

135 The GOK site faces towards southwest underneath a ridge just a short distance north of the alpine
136 main divide, whereas the WUK site is orientated towards west and is located south of the main
137 divide. The different orientation with respect to the Alpine main divide together with the different
138 exposure to sunlight as well as local influences cause spatial distribution of precipitation (Auer and
139 Böhm, 1998) and snow height and therefore also affects ion concentrations and, to a much higher
140 extent, ion depositions.

141

142 **Figure 1: Location of Goldberggruppe in Austria (scale 1:3.000.000), sampling sites Goldbergkees (GOK) and**
 143 **Wurtenkees (WUK) in the Eastern Alps (scale 1:50.000) and totalizers (TG 4 and TW 4) used for the calculation of**
 144 **seasonal proportions of precipitation.**



145

146

147 2.2 Snow sampling and chemical analysis

148 Sampling was performed at the end of the winter accumulation period just prior to the start of the
 149 snowmelt, usually at the end of April or beginning of May. A snow pit was dug until the horizon when
 150 winter accumulation had started was reached (firn or bare ice). Temperature as well as snow density
 151 were measured for 20cm depth-layers for verifying potential melting processes in the snow pack and
 152 to calculate the volume weighted mean concentration of the layer. Furthermore, the snow layers
 153 were stratigraphically described according to the standard snow classification scheme (Fierz et al.,
 154 2009). For the majority of years (1984-1996 and 1998-2014) sampling was performed using a
 155 stainless steel cylinder (10cm long and with 5cm diameter) to collect 10cm increments over the
 156 whole excavated profile. Note that a 10cm increment could either represent some portion of a single
 157 precipitation event or include mixed information of several events, depending on precipitation
 158 amount of the respective event and settling of the snow cover. To avoid contamination of the samples
 159 gloves and a mask were used during sampling. The samples were stored in polyethylene plastic bags
 160 and were kept frozen during transport and storage. This kind of sampling was tested and
 161 standardized during the ALPTRAC-SNOSP project and is thoroughly described by Schwikowski et al.

162 (1997). In 1983 and 1997 the size of the increments was larger (50cm and 40cm, respectively),
163 because of the extremely large snow accumulation, and samples were stored in 1 liter plastic bottles.
164 In the laboratory samples were taken from the freezer and analysed immediately after thawing.
165 Conductivity and pH were determined electrochemically, using a conductivity cell and a glass
166 electrode. Anion (Cl^- , NO_3^- , and SO_4^{2-}) and cation (Na^+ , K^+ , NH_4^+ , Ca^{2+} and Mg^{2+}) concentrations were
167 determined by ion chromatography using standard procedures and equipment from Dionex and
168 Thermo. Analytical procedures (performed at TU Wien) and equipment changed slightly during the
169 30-year period, but quality assurance was maintained by internal calibration procedures and regular
170 participation in laboratory intercomparisons like the GAW Inter-laboratory Comparison Studies
171 carried out by the World Data Center for Precipitation Chemistry.

172 Limits of detection (LOD) are defined as the threefold standard deviation (3s) of repeated analyses of
173 standard samples with concentrations close to the LOD. Anions and monovalent cations have been
174 measured via ion chromatography since the beginning of the time series. Despite small year-to-year
175 variations LODs for Cl^- , NO_3^- , Na^+ and NH_4^+ can be given as 0.01mg/l for the whole observation
176 period. LODs for SO_4^{2-} and K^+ based on 3s are 0.029 mg/l and 0.015 mg/l, respectively, until 1993
177 (Winiwarter et al. 1998) and 0.015 and 0.010 mg/l in the following years. Bivalent ions were
178 determined by atomic absorption spectroscopy until 1993, (Winiwarter et al., 1998), later also
179 bivalent cations were measured via ion chromatography, resulting in roughly doubling of the LODs
180 (0.01mg/l). This was accepted to allow the simultaneous measurement of all ions using ion
181 chromatography.

182 Concentrations lower than the LOD were replaced with values of half of the LOD. For Cl^- , NO_3^- , SO_4^{2-} ,
183 Na^+ , NH_4^+ and Ca^{2+} the number of samples below the LOD is less than 9%, but for K^+ and Mg^{2+} the
184 number increases up to 24 and 44%, respectively. Less than 1% of the collected samples were lost
185 due to missing labels, bag leakage, or other laboratory or field incidents.

187 2.3 Statistical data treatment

188
189 Single layer concentrations are given in $\mu\text{eq/l}$. Seasonal values are calculated as volume weighted
190 mean concentrations (VWM) in $\mu\text{eq/l}$ whereas annual values are given as depositions in meq/m^2 as
191 well. Statistical analyses were performed using the software package R ("The R Project for Statistical
192 Computing"). Temporal trends in ion concentration were calculated using the non-parametric Mann-
193 Kendall-Trend-Test. A significant temporal trend is defined as having a probability of 95% ($p \leq 0.05$)
194 or higher ($p \leq 0.01$ or $p \leq 0.001$). Correlations were determined with the Spearman's rank correlation
195 coefficient instead of Pearson's correlation coefficient to avoid exaggerated influence of single
196 samples above average. Major sources contributing to the ion content were evaluated using a
197 varimax rotated Principal Component Analysis (PCA). To determine whether differences between
198 two time series are significant, the non-parametric Wilcoxon-Mann-Whitney-Test was used instead

199 of the paired t-test because the former does not require normally distributed data and the
200 assumption of normality is not justified in the used data set. A difference was denoted as significant if
201 the probability lies at 95% or higher.

202

203 2.4 Quality Considerations

204 According to the rules of electroneutrality the total anion equivalents should equal the total cation
205 equivalents in precipitation samples (Granat, 1972). Hence, the calculation of the ion balance (IB) is a
206 reasonable criterion for the quality of the data, assuming that all major ions as well as the pH (to
207 calculate the H^+ concentration), are measured. Furthermore, the conductivity balance (CB) can be
208 investigated by comparing the measured conductivity and the conductivity calculated from the ion
209 concentrations and the specific conductivities.

210 We calculated the IB (\sum anions - \sum cations) and CB (measured - calculated conductivity) for every
211 single sample with all parameters analysed. The analysis of mono- and bivalent cations are missing
212 for the first years from 1983 to 1985 and in 1986 only monovalent cations were measured, thus
213 results refer to the time span from 1987 to 2014. The samples of WUK and GOK are evaluated
214 together (n=1570), since separate analyses give similar results.

215 Samples affected by the input of mineral dust, e.g. originating from the Sahara which is frequently
216 observed at an alpine site (e.g. Maupetit and Delmas, 1994; Thevenon et al., 2012), will show
217 elevated cationic input, especially Ca^{2+} but also Mg^{2+} , Na^+ and K^+ (Avila and Rodà, 1991). This leads to
218 elevated pH values and an increased influence of HCO_3^- , which is not analysed with the given
219 analytical set-up. Rogora et al. (2004) sets a limit of $pH > 5.6$ to exclude samples from the data set
220 markedly influenced by soil dust. We adopted this approach and present CB and IB for the whole
221 dataset and for the whole data set without samples with $pH > 5.6$ in Table 1.

222 We observed a negative IB for 85% of the samples. The CB resulted in higher measured than
223 calculated values for 83% of the samples. For IB as well as CB better agreement is observed when
224 samples obviously influenced by soil dust according to the criterion by Rogora et al. (2004) are
225 excluded.

226 Nickus et al. (1998), reporting a two year data set (1993 and 1994) of ion concentration and ionic
227 loads in the Eastern Alps, found 90% of their samples within a range of -1 to $+1 \mu S/cm$ of the CB and -
228 15 to $+10 \mu eq/l$ of the IB. Our 30-year long time series showed higher deviations. 80% of the samples
229 were within the range of -5 to $+5 \mu S/cm$ and -15 to $+15 \mu eq/l$. The highest deviations were found for
230 the time period 2007 to 2014, while for the earlier periods the number of samples complying with
231 the mentioned limits increases to more than 85%.

232

233 **Table 1: Slope, intercept and Spearman's rank correlation coefficient of the linear regression for the ion (IB) and**
234 **conductivity balance (CB) for the whole dataset and samples with $pH > 5.6$ (indicating Sahara dust events)**

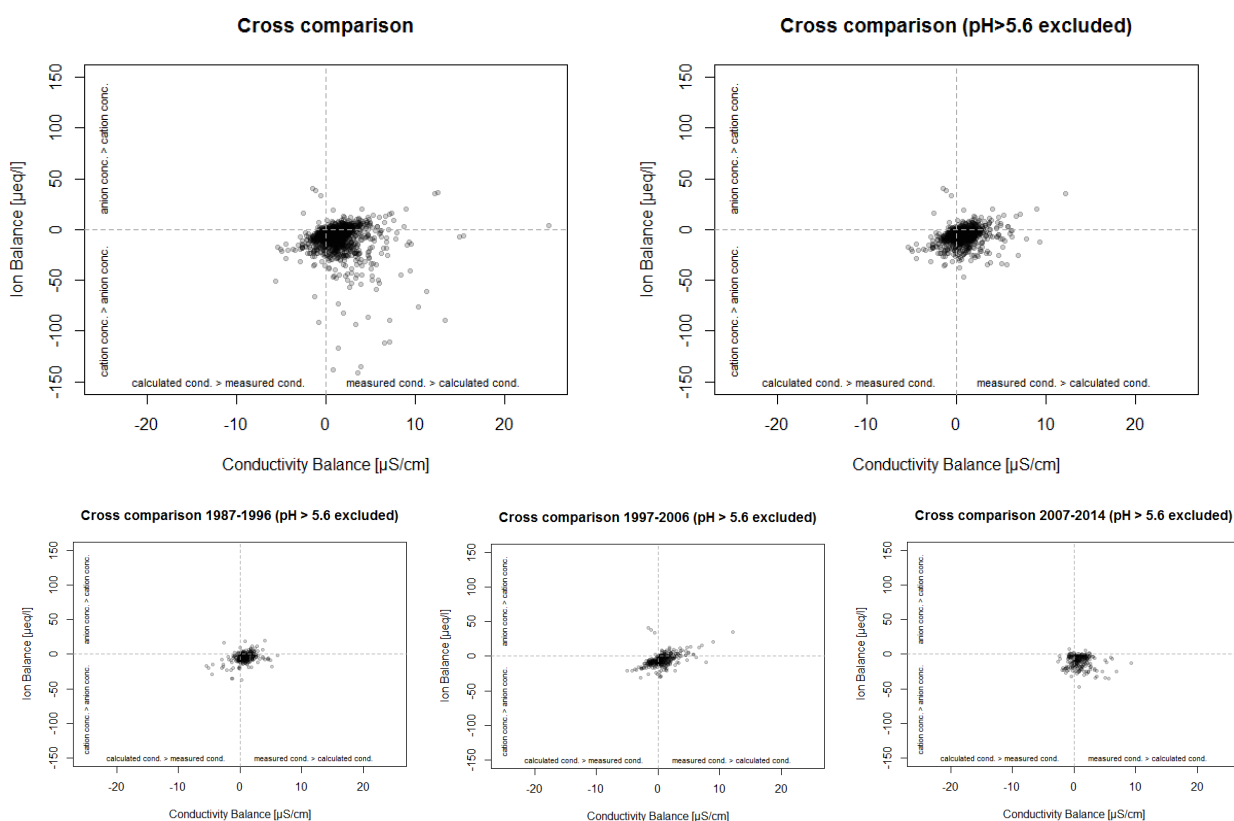
235 excluded. The x-coordinate represent the sum of the anions (IB) or the calculated conductivity (CB) and the y-
 236 coordinate the sum of the cations (IB) or the measured conductivity (CB).

	n	Slope	Intercept	Spearman
IB	1570	1.008	8.25	0.73
IB (pH > 5.6 excluded)	970	0.972	6.88	0.80
CB	1570	0.922	1.58	0.75
CB (pH > 5.6 excluded)	970	0.992	0.80	0.84

237

238 According to Miles and Yost (1982) the IB and CB were cross compared graphically and should
 239 ideally show a random scatter around the origin of the axes with no patterns. The cross comparison
 240 is displayed in Figure 2 where the pattern towards a negative IB is illustrated in more detail. In the
 241 majority of cases, the negative IB is caused by a deficit of anions (CB positive) and to a lesser extent
 242 in an excess of cations (CB negative). If data influenced by special events like soil dust are excluded,
 243 the negative IB is reduced, but the pattern of a deficit of anions (CB positive) remains. More details
 244 can be deduced from the cross comparisons done for three subsequent time periods, all of which
 245 spanning approximately a decade (1987 to 1996, 1997 to 2006 and 2007 to 2014). The deficit of
 246 anions becomes most visible during the last years (2007 to 2014). This may be due to a change of the
 247 ion composition over the time span of almost 30 years (see 3.1), pointing to an increasing
 248 importance of anions not included in the analytical setup. Over the whole time period concentrations
 249 of bicarbonates and organic acids e.g. HCOO^- and CH_3COO^- were not measured but are presumably
 250 present. The pH-dependent equilibrium concentrations of HCO_3^- were not able to explain the
 251 difference. For samples in the low pH range not affected by mineral dust, their contribution can be
 252 expected to be less than $4\mu\text{eq/l}$ (Maupetit and Delmas, 1994) – also here reducing, but not
 253 accounting for the whole difference. In the period from 1997 to 2006 a number of samples scatter
 254 along a line, indicating problems related to the determination of H^+ concentrations (Miles and Yost,
 255 1982). Points along the line in the lower left corner feature too high H^+ concentrations and are
 256 mainly from the year 2001. Points along the line in the upper right corner feature too low H^+
 257 concentrations and cannot be assigned to a respective year.

258 **Figure 2: Cross comparison of ion balance and conductivity balance for the whole dataset, samples with pH > 5.6**
 259 **(indicating Sahara dust events) excluded and different time periods for samples with pH > 5.6 excluded.**



260

261

262 3. Results and discussion

263

264 3.1 General presentation of data

265

266 The upper section of Table 2 presents the arithmetic mean, standard deviation, minimum and
 267 maximum of the annual VWM ion concentration measured on WUK and GOK over the whole time
 268 span (1983 to 2014). The results are in good agreement with previous studies of high alpine snow
 269 discussed below. For four high altitude glaciers in the French Alps mean values over three years of
 270 observation ranging from 0.4 to 6.0 µeq/l are reported (Maupetit and Delmas 1994). Nickus et al.
 271 (1997) summarize the results of three years sampling on a west to east transect stretching from
 272 France to Austria and found concentrations ranging from 1.0 to 36.5 µeq/l between the sites, showing
 273 a west to east increase for almost all ions, whereas ionic loads showed no regional patterns.
 274 Generally, NO_3^- , SO_4^{2-} and NH_4^+ were the dominant ions, but episodic high concentrations of Ca^{2+} due
 275 to mineral dust could exceed those concentrations. They report elevated concentrations of Cl^- and
 276 Na^+ at the sites in Austria and Italy with mean values of up to 5.6 and 10.2 µeq/l, respectively, with a
 277 slight increase of these concentrations from west to east. Rogora et al. (2004) investigated the
 278 atmospheric deposition chemistry of several sites in the Alps and also found sites in the Eastern Alps,

279 especially Austria, affected by high concentrations of base cations (Ca^{2+} , Mg^{2+} , K^+ and Na^+) and Cl^- in
280 wet precipitation which are mainly attributed to emission sources in Eastern Austria.

281 More recent data are available for the Italian Alps (Filippa et al., 2010) with ion concentrations
282 ranging from 0.4 to $8.7\mu\text{eq/l}$ with Na^+ and Cl^- showing above average concentrations (3.5 – 8.7
283 $\mu\text{eq/l}$), still comparable to concentrations found by Nickus et al. (1997) for the Eastern Alps.

284

285 **Table 2: Arithmetic mean, standard deviation (SD), minimum and maximum of the VWM ion concentration of both**
286 **sites GOK and WUK representing the whole accumulation period (Sept. to Apr.) from 1983 to 2014 as well as**
287 **periods from 1983 to 1996, 1997 to 2006 and 2007 to 2014.**

	GOK				WUK				
	Mean	SD	Min	Max	Mean	SD	Min	Max	
	[$\mu\text{eq/l}$]	[$\mu\text{eq/l}$]	[$\mu\text{eq/l}$]	[$\mu\text{eq/l}$]	[$\mu\text{eq/l}$]	[$\mu\text{eq/l}$]	[$\mu\text{eq/l}$]	[$\mu\text{eq/l}$]	
1983 - 2014	SO_4^{2-}	6.67	3.33	2.04	15.07	7.92	4.88	1.62	24.95
	NO_3^-	7.62	2.26	4.51	13.91	8.02	1.94	3.94	12.12
	Cl^-	3.63	2.87	1.34	15.43	4.29	3.44	1.35	14.51
	H^+	6.51	5.06	0.53	26.52	8.06	9.49	0.55	39.48
	NH_4^+	7.15	2.00	4.06	10.87	6.53	2.94	1.01	15.24
	Na^+	3.98	3.64	0.54	16.46	3.50	3.35	0.32	14.42
	* K^+	1.18	0.89	0.16	3.66	1.19	1.04	0.21	4.81
	* Mg^{2+}	1.04	0.66	0.34	2.39	0.98	0.50	0.24	2.22
	Ca^{2+}	7.11	4.35	1.51	20.45	8.89	10.58	1.06	55.45
	Total Anions	18.33	5.80	8.61	35.33	20.22	7.78	6.91	45.12
Total Cations	26.30	6.51	14.18	41.30	25.78	11.78	8.22	68.58	
1983 - 1996	SO_4^{2-}	9.39	2.14	7.24	12.91	11.39	4.74	7.38	24.95
	NO_3^-	8.60	1.96	6.06	11.82	8.66	1.66	6.21	12.12
	Cl^-	2.46	0.86	1.34	4.38	4.43	2.70	1.52	12.29
	H^+	9.98	6.49	2.22	26.52	13.09	12.00	1.42	39.48
	NH_4^+	6.78	2.28	4.19	10.87	7.08	3.20	4.32	15.24
	Na^+	2.10	1.02	0.54	3.75	2.85	1.51	1.19	5.18
	* K^+	0.79	0.59	0.16	1.97	1.00	0.66	0.21	2.32
	* Mg^{2+}	1.58	0.78	0.55	2.39	1.24	0.70	0.39	2.22
	Ca^{2+}	8.07	5.78	2.97	20.45	6.21	2.99	2.59	10.86
	Total Anions	20.45	3.85	16.05	27.28	24.50	7.22	17.64	45.12
Total Cations	27.24	3.87	20.62	30.72	25.29	1.84	22.62	27.59	
1997 - 2006	SO_4^{2-}	6.40	3.78	4.09	15.07	5.74	2.49	3.54	12.15
	NO_3^-	8.73	2.63	6.09	13.91	8.34	1.89	4.16	11.08
	Cl^-	4.50	4.23	1.65	15.43	5.13	4.89	2.04	14.51
	H^+	5.26	3.38	0.53	10.34	4.32	2.43	0.89	7.62
	NH_4^+	7.11	1.78	4.06	9.51	6.45	2.99	3.45	13.37
	Na^+	5.21	4.88	1.55	16.46	5.04	5.00	1.14	14.42
	* K^+	1.40	1.07	0.28	3.66	1.61	1.51	0.34	4.81
	* Mg^{2+}	0.89	0.43	0.42	1.94	0.93	0.36	0.35	1.29
	Ca^{2+}	5.29	2.42	1.51	10.19	6.78	2.87	1.06	10.30

	Total Anions	19.64	7.21	12.64	35.33	19.21	6.17	13.19	28.98
	Total Cations	25.16	7.82	18.04	41.30	25.13	9.37	13.16	42.14
2007 - 2014	SO ₄ ²⁻	3.73	1.20	2.04	6.00	3.44	1.19	1.62	4.70
	NO ₃ ⁻	6.46	1.28	4.51	8.53	5.97	1.37	3.94	7.62
	Cl ⁻	5.72	4.31	1.80	15.43	2.55	1.20	1.35	4.61
	H ⁺	3.78	1.15	2.12	5.18	2.54	1.55	0.55	5.10
	NH ₄ ⁺	7.35	2.13	4.73	10.03	5.65	2.60	1.01	7.67
	Na ⁺	6.10	4.98	0.86	16.46	2.10	0.99	0.32	2.92
	*K ⁺	1.64	1.13	0.30	3.66	0.85	0.26	0.56	1.23
	*Mg ²⁺	0.90	0.65	0.34	1.96	0.76	0.36	0.24	1.19
	Ca ²⁺	8.74	4.40	3.69	17.20	15.54	19.87	3.30	55.45
		Total Anions	15.46	5.50	8.61	26.83	14.21	6.75	6.91
	Total Cations	28.51	8.20	14.18	41.30	28.80	19.57	8.22	68.58

288 * For K⁺ and Mg²⁺ the number of samples lower than the LOD was 24% and 44%, respectively. Those values were replaced
 289 with half the LOD.

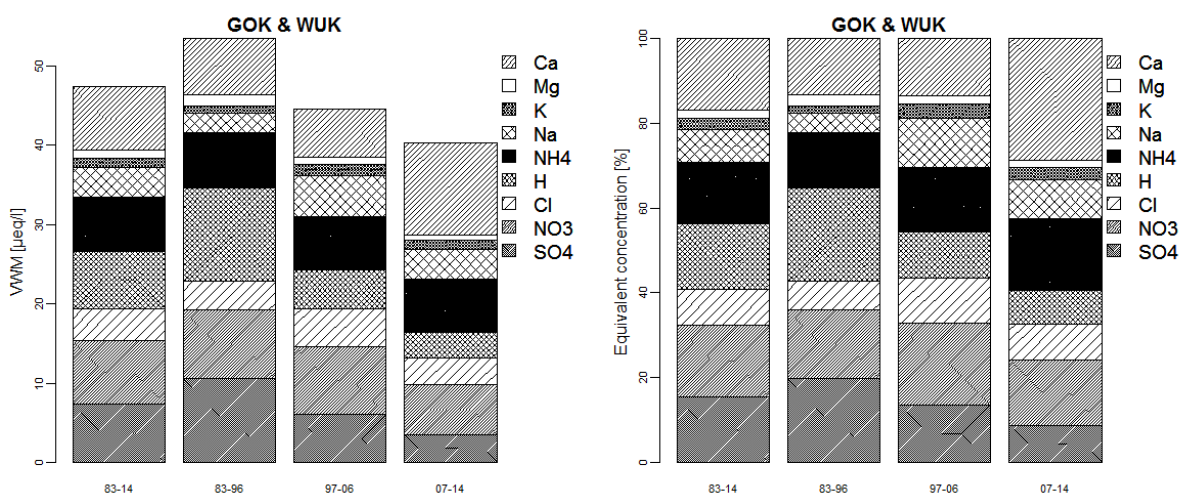
290

291 Triggered by the results of the quality control, indicating a change of the ion composition with time ,
 292 VWM ion concentrations have been also calculated separately for the periods 1983 to 1996, 1997 to
 293 2006 and 2007 to 2014 (Table 2, lower part). Additionally the ion composition for both sites is
 294 plotted in Figure 3 with absolute (left) and relative (right) contributions over the whole time span
 295 and for the three periods.

296 The total ion concentration averaged over both sites decreased from 53.5µeq/l in the first period to
 297 40.3µeq/l in the latest, mainly due to the significant decrease of SO₄²⁻, NO₃⁻ and H⁺ (see section 3.3),
 298 accompanied by a decrease of the measured conductivity, decreasing from 6.3µS/cm to 4.7µS/cm.
 299 The concentration of Na⁺, K⁺, Mg²⁺, Cl⁻ and NH₄⁺ remained almost constant over time. Ca²⁺ increased
 300 during the last period, due to an increase observed only on WUK, but without significance because of
 301 the high interannual variability.

302

303 **Figure 3: Absolute (left) and relative (right) ion composition of GOK and WUK over the whole time span (1983 to**
 304 **2014) and over approximately decades from 1983 to 1996, 1997 to 2006 and 2007 to 2014**



305

306

307 To evaluate regional variability, annual mean concentrations determined at the two sampling sites
 308 WUK and GOK were compared. Deviations are calculated for every year, according to the absolute
 309 difference of concentrations measured at the two sites divided by the average concentrations. These
 310 yearly variabilities were then averaged over the whole time period and are listed as regional
 311 variability in Table 3. While variabilities for SO_4^{2-} , NO_3^- and NH_4^+ range between 20 and 29%, much
 312 higher values were obtained for the other ions (41 – 63%). Concentrations of these ions are driven
 313 more by episodic inputs like localized storm events or weather patterns and are thus influenced
 314 stronger by spatial variations. Smaller variabilities of solutes like SO_4^{2-} or NO_3^- are probably more
 315 regionally influenced by emission reductions. The high variabilities for K^+ and Mg^{2+} might also be
 316 influenced due to concentrations close to the detection limits.

317 To evaluate the differences between GOK and WUK results of a previous study are added to Table 3.
 318 Schöner et al. (1997) investigated the variability of ion concentrations determined within one pit and
 319 between four pits located 300 to 500 m apart, but all situated on GOK. Results agree reasonably well
 320 with the variability determined within the long term study conducted at GOK and WUK. Variabilities
 321 in the long-term data set are just slightly larger.

322 A study in Wyoming's Rocky Mountains investigating the local variability among snow pits being
 323 several 100 meters apart yields similar variabilities ranging from 9-37% for SO_4^{2-} , NO_3^- and NH_4^+ and
 324 36-61% for Na^+ , K^+ , Cl^- , Ca^{2+} and Mg^{2+} (Rohrbough et al., 2003).

325 Overall, it can be concluded that differences between the two sampling sites on neighboring glaciers
 326 (WUK and GOK) resemble those observed from different sites of other glaciers.

327

328 **Table 3: Regional variability [%] according to the absolute difference of concentrations measured at the two sites**
 329 **divided by the average concentrations and coefficients of variation in [%] within one pit on GOK, between four pits**
 330 **situated on GOK and among several pits in the Rocky Mountains**

	Na^+	Cl^-	K^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	NO_3^-	NH_4^+	H^+
Regional variability	63	44	56	42	48	22	20	29	41
Variability within one pit (Schöner et al., 1997)	29	9	27	-	-	1	1	4	-
Variability for one glacier (Schöner et al., 1997)	50	41	-	56	17	12	15	21	-
Rocky Mountains (Rohrbough et al., 2003)	49	38	61	44	36	14	9	37	43

331

332 3.2 Seasonal patterns of major ion concentrations

333

334 Seasonal patterns are investigated by subdividing the snowpack into fall (September to November),
 335 winter (December to February) and spring (March and April). The split of the snow pack was based
 336 on snow depth measurements performed with totalizers nearby each sampling site (compare Figure

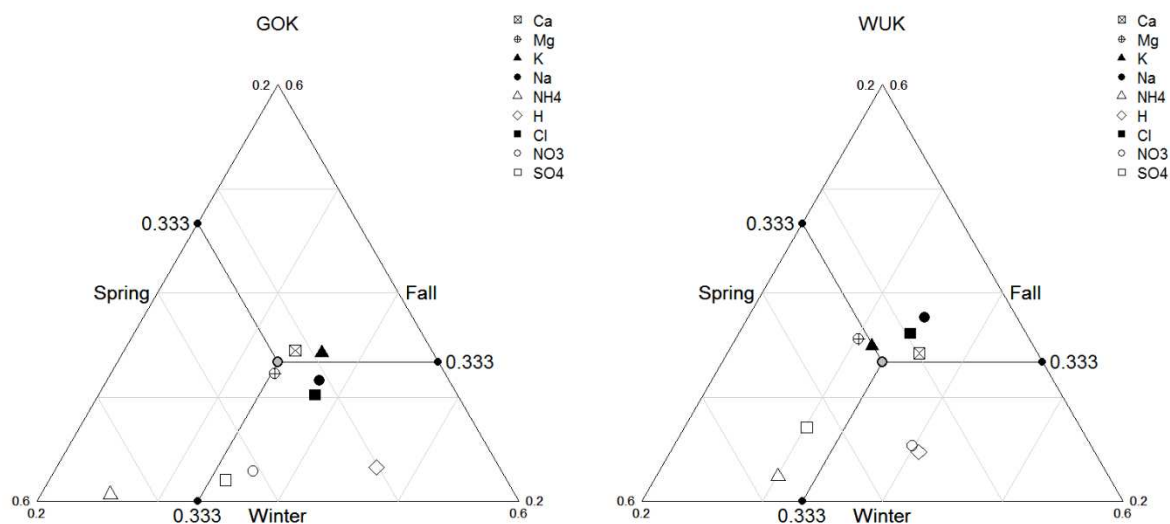
337 1), which allowed the determination of the relative amount of snow deposited within the respective
338 seasons. These relative contributions were assigned to the snow pack and thus a rough
339 categorization of the individual layers to the respective season was possible. The seasonal average
340 concentrations are again computed as liquid water volume weighted mean (VWM) concentrations in
341 $\mu\text{eq/l}$ using the water equivalents determined within the snow pack.

342 The relative ion compositions of the seasonal VWM concentrations for all ions measured are
343 displayed in form of a ternary plot in Figure 4. The analysis of mono- and bivalent cations is missing
344 for the first years from 1983 to 1985 and in 1986 only monovalent cations were measured, thus
345 results refer to the time span from 1987 to 2014. The proportions of the seasonal concentrations
346 displayed sum up to 100%, i.e. 1. In Figure 4 a zoom in of the ternary plot is shown, where the left
347 edge represents a contribution of 20% and the right edge a contribution of 60% for every side of the
348 triangle. Points in the center of the plot, as indicated by the grey dot and the corresponding lines in
349 Figure 4, represent ions showing similar concentrations within the different seasons (fall, winter,
350 spring). The Points in the bottom left corner can be interpreted as ions with high relative spring
351 concentrations. Moving to the right, relative winter concentrations increase at the expense of spring
352 values. Analogous, moving to the top, relative fall concentrations increase at the expense of spring
353 values. Possible differences between the seasons were identified with the Wilcoxon-Mann-Whitney
354 Test (significance level of 5%) based on annual averages.

355 Concentrations of NH_4^+ , SO_4^{2-} and H^+ were 2.4, 1.8 and 1.4 (respectively) times greater in spring than
356 in fall. NO_3^- spring concentrations are 1.6 times higher than fall concentrations, but the difference is
357 not significant (average values for WUK and GOK). H^+ is highest in winter, reflecting the scavenging
358 of slightly acidic aerosol. In spring the neutralizing input of NH_4^+ is most pronounced. On WUK NO_3^- ,
359 SO_4^{2-} and H^+ are shifted slightly to the center of the plot, indicating that the higher Ca^{2+} input
360 observed at this site influences these concentrations as well (Figure 4). These results for seasonality
361 slightly vary from findings by Maupetit et al. (1995) who found seasonal patterns for all ions with
362 very low winter concentrations which are increasing in spring.

363

364 **Figure 4: Relative ion composition of VWM concentrations for both sampling sites GOK (left) and WUK (right) from**
365 **1987-2014 showing increased spring concentrations especially for NH_4^+ and SO_4^{2-} .**



366

367 The increase of spring concentrations in high alpine snowpacks and precipitation samples has
 368 already been discussed (e.g. Filippa et al., 2010; Maupetit et al., 1995; Nickus et al., 1998) and seems
 369 related to an increasing influence of boundary layer air due to increasing vertical mixing (Kuhn et al.,
 370 1998). The conditions of enhanced vertical mixing during spring at SBO have already been shown by
 371 aerosol measurements (Kasper and Puxbaum, 1998). NH_4^+ displays the most pronounced seasonal
 372 variation, which is interpreted as a result of the beginning of the application of fertilizers on
 373 agricultural areas in spring. Hence, the extension of the boundary layer appears to be a controlling
 374 factor of the precipitation quality in high alpine regions. In consequence, winter precipitation is of
 375 special interest as representing the most pristine air available over central Europe.

376 Furthermore episodic events (e.g. fronts or thermal convection) can transport polluted boundary
 377 layer air up to 3km a.s.l., causing elevated levels of ionic loads. A typical episodic event is the
 378 occurrence of Saharan dust, providing a high cationic (especially Ca^{2+} and Mg^{2+} but also K^+ and Na^+)
 379 and alkaline input (Avila and Rodà, 1991). The transport of Na^+ and Cl^- to high elevation sites is
 380 supposed to be also of episodic character, originating either from sea salt or anthropogenic HCl
 381 emissions coming from neighboring countries (Möller, 1990). Consequently, ions of episodic
 382 character like Ca^{2+} , Mg^{2+} , K^+ , Na^+ and Cl^- cluster in the center of the ternary plots, having no
 383 seasonality.

384 If the seasonal patterns are investigated on basis of the deposition data, a shift toward the season
 385 with the highest snow accumulation is obtained, compensating the influence of thermal convection
 386 on the ion concentrations. On GOK highest snow depth occurred during winter, shifting the seasonal
 387 pattern toward winter whereas on WUK highest snow depth were observed during fall, shifting the
 388 pattern toward fall. Mean snow accumulation measurements from both sites for the 30 year period
 389 from 1961 to 1990 are reported by Auer and Böhm (1998). Mean values for the period from 1982 to
 390 2012 show a similar behavior of snow accumulation.

391

392 3.3 Temporal trend analysis

393

394 Temporal trends were identified based on ion concentration and deposition data, using the Mann-
 395 Kendall-Test. Trends are expressed as Kendall's tau and were regarded as significant if the two-sided
 396 p-value is below 5%. A significant negative trend for the deposition in the accumulation period (Sept.
 397 to Apr.) was found for SO_4^{2-} and H^+ (see Table 4). The SO_4^{2-} deposition, averaged over both glaciers,
 398 decreased from $17.4\mu\text{eq}/\text{m}^2$ to $6.6\mu\text{eq}/\text{m}^2$ and the H^+ deposition decreased from $16.2\mu\text{eq}/\text{m}^2$ to
 399 $4.6\mu\text{eq}/\text{m}^2$ representing a reduction of about 62% and 71%, respectively. The decline in H^+ , which
 400 corresponds to an increase in pH, is supposed to be achieved through the reduction of the acidifying
 401 ion SO_4^{2-} . The most pronounced decrease in SO_4^{2-} -deposition was before 2008. The latter years
 402 showed no significant further decrease. Significant negative trends for SO_4^{2-} and H^+ were also
 403 identified on the seasonal scale (see Table 4). When looking at concentrations (VWM for the whole
 404 period, Sept-Apr), temporal decreasing trends were identified not only for SO_4^{2-} (GOK: Kendall's
 405 tau=-0.646, 2-sided p-value<0.001; WUK: Kendall's tau=-0.628, 2-sided p-value<0.001) and H^+ (GOK:
 406 Kendall's tau=-0.411, 2-sided p-value<0.01; WUK: Kendall's tau=-0.569, 2-sided p-value<0.001), but
 407 also for NO_3^- (GOK: Kendall's tau=-0.299, 2-sided p-value<0.05; WUK: Kendall's tau=-0.278, 2-sided
 408 p-value<0.05). The high variability in the precipitation amount seems to mask the decreasing trend
 409 in NO_3^- concentration, when deposition data are considered. Likewise, the significance level for the
 410 decrease of SO_4^{2-} and H^+ is higher when VWM concentrations are used instead of deposition data.

411

412 **Table 4: Temporal trends of ion deposition in [$\mu\text{eq}/\text{m}^2$] performed with the Mann-Kendall test. Total=Sept. to Apr.,**
 413 **Fall=Sept. to Nov., Winter=Dec. to Feb., Spring=Mar. and Apr. Deposition values represent averages over all**
 414 **observed years.**

		GOK			WUK		
		Deposition meq/m ²	Kendall's tau	2-sided p-value	Deposition meq/m ²	Kendall's tau	2-sided p-value
SO_4^{2-}	Total	10.56	-0.460	<0.001	9.34	-0.594	<0.001
	Fall	2.18	-0.321	<0.05	3.54	-0.404	<0.01
	Winter	4.30	-0.400	<0.05	2.35	-0.433	<0.01
	Spring	3.86	-0.481	<0.001	3.26	-0.487	<0.001
NO_3^-	Total	12.87	n.s.	-	11.25	n.s.	-
	Fall	2.79	n.s.	-	4.02	n.s.	-
	Winter	5.62	n.s.	-	3.84	n.s.	-
	Spring	4.32	n.s.	-	3.31	n.s.	-
NH_4^+	Total	11.40	n.s.	-	9.27	n.s.	-
	Fall	2.30	n.s.	-	3.14	n.s.	-
	Winter	3.83	n.s.	-	2.21	n.s.	-

	Spring	4.88	n.s.	-	3.56	n.s.	-
H ⁺	Total	9.86	-0.328	<0.05	8.40	-0.434	<0.01
	Fall	2.15	n.s.	-	2.86	-0.317	<0.05
	Winter	5.21	-0.339	<0.01	3.16	-0.277	<0.05
	Spring	2.60	-0.407	<0.01	2.47	-0.380	< 0.01

415

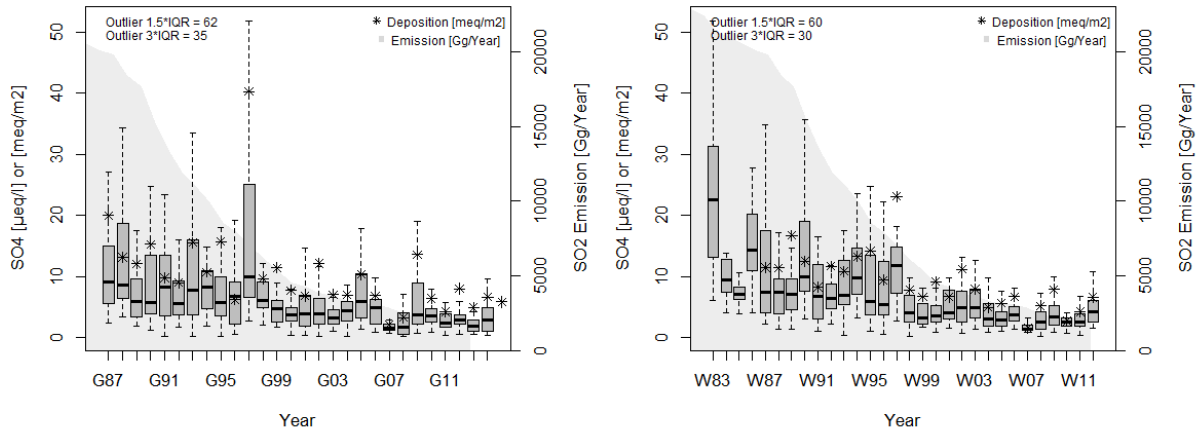
416 The reduction of SO_4^{2-} and NO_3^- reflects emission reductions of the precursor gases SO_2 and NO_x .
 417 Boxplots for SO_4^{2-} , NO_3^- and NH_4^+ concentrations in the snow (data for all 10cm increments of each
 418 years's snow cover) are displayed together with depositions during the entire accumulation period
 419 and with emissions of the precursor gases (SO_2 , NO_x and NH_3) in Figure 5. The whiskers extend to the
 420 most extreme values measured within each year data point, which is no more than 1.5 times the
 421 interquartile range (IQR) from the box. Emissions of precursors are taken from official national
 422 reports to CEIP, the EMEP Centre on Emission Inventories and Projections
 423 (http://www.ceip.at/ms/ceip_home1/ceip_home/webdab_emepdatabase/), from Austria, Germany,
 424 Czech Republic, Hungary, Italy, Slovakia, Slovenia, Switzerland, Croatia, France and Poland
 425 (according to Winiwarter et al., 1998). We assume these countries to be relevant for affecting the
 426 atmosphere in the Austrian Alps and hence provide the sum of their respective emissions here.

427 The significant decrease is much more pronounced in emission data than in the ion concentration or
 428 deposition of high alpine snow. SO_2 emissions decreased by a factor of 12 from 1987 to 2013,
 429 whereas SO_4^{2-} deposition and concentration decreased only by a factor of 3. NO_x emissions decreased
 430 by a factor of 2, NO_3^- concentrations decreased by a factor of 1.5 whereas NO_3^- deposition did not
 431 show a significant decrease at all. NH_3 emissions were reduced by a factor of 1.5 whereas no
 432 significant decrease was observed neither in the NH_4^+ deposition or concentration. Obviously only
 433 the large decrease of sulfur emissions by a factor of more than 10 can be identified in the snow pack.
 434 We attribute this to the complex chemical and physical transport and transformation processes
 435 occurring in the atmosphere. The major share of sulfur species will be deposited by dry or wet
 436 deposition (below cloud scavenging) before reaching the 3 km level. Also time series of particulate
 437 SO_4^{2-} and SO_2 measured by the Swiss National Air Pollution Monitoring Network (NABEL) on the
 438 Jungfrauoch (JFJ) and wet deposited SO_4^{2-} measured at Payerne show an attenuated decrease by a
 439 factor of only 3-4 with respect to emission data (Ballaman et al., 2004; Steinbacher and Hüglin,
 440 2007), similar to the results presented in this paper. Furthermore differences in the countries
 441 considered for emissions and source regions actually effective for transport to the Sonnblick region
 442 might exist and lead to biases when emission data and actual deposition are compared.

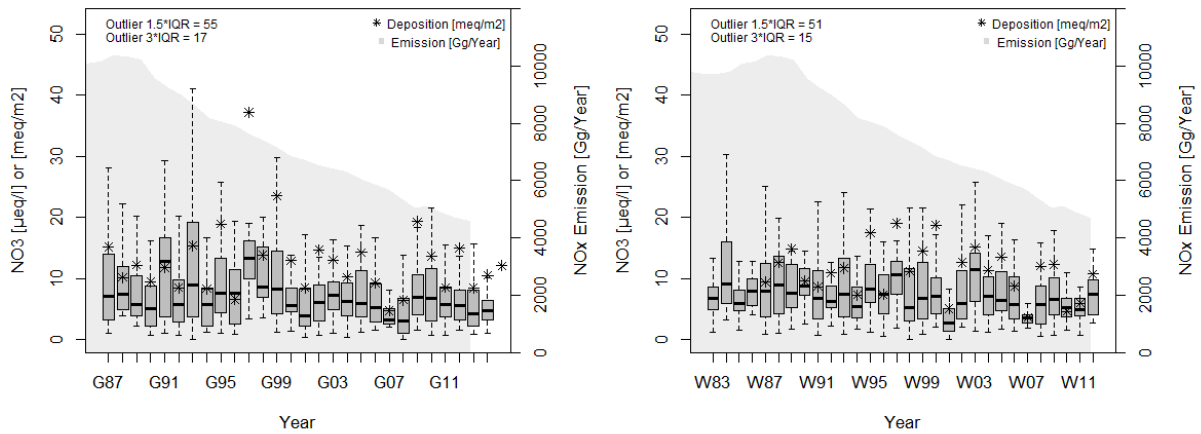
443

444 **Figure 5: Boxplots represent concentrations of all 10cm increments taken within one annual snow pack of SO_4^{2-} ,**
 445 **NO_3^- and NH_4^+ in $\mu\text{eq/l}$ on GOK (1987-2012, left) and WUK (1983-2012, right). Whiskers extend to the most**
 446 **extreme values measured within one pit, which is no more than 1.5*IQR (inter quantile range) range from the box.**

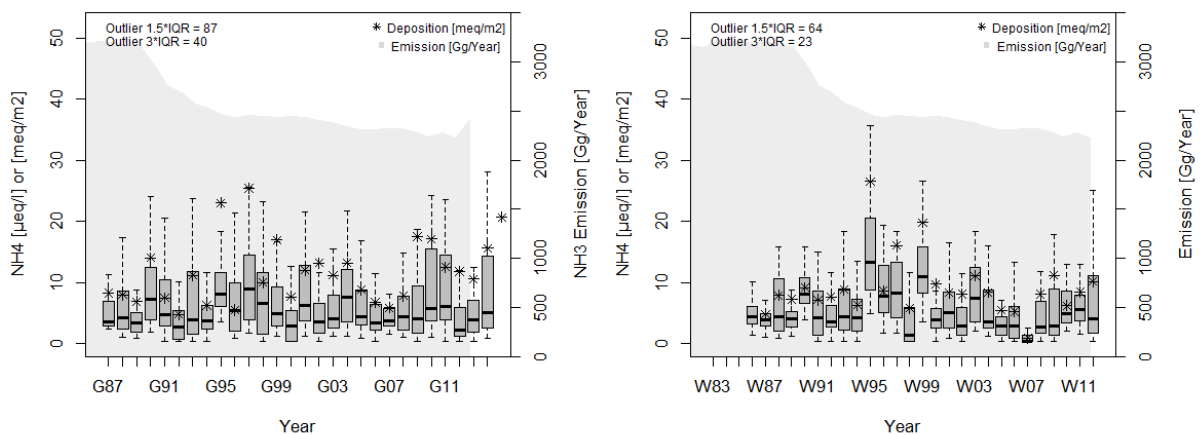
447 Number of outliers within the 1.5*IQR and within the 3*IQR are given in the top right corner of the respective
 448 graph. Deposition in meq/m² are marked with *.
 449 Emission (gray shaded area): Sum of emissions from Austria and nearby countries Germany, Czech Republic,
 450 Hungary, Italy, Slovakia, Slovenia, Switzerland, Croatia, France and Poland (compare Winiwarter et al., 1998)



451



452



453

454 3.4 Sources and their temporal changes

455

456 To identify different sources contributing to the ion composition of high alpine snow, a Principal
 457 Component Analysis (PCA) with VARIMAX rotation and calculations of non-sea-salt (nss) proportions
 458 were performed.

459

460 3.4.1 PCA

461 For interpreting high alpine snow pack chemistry data, PCA was previously used to identify possible
 462 source regions of the deposited atmospheric impurities (e.g. Maupetit and Delmas, 1994). It is
 463 assumed that every principal component (PC) accounts for a different source of origin and that these
 464 sources are uncorrelated because of the orthogonality of the PCs. However, the classification of the
 465 ions into different sources has to be interpreted with caution since atmospheric chemistry is very
 466 complex and single ions might have more than one source. The PCs represent the most dominant but
 467 not the only sources for the particular ions.

468 In this study we applied a VARIMAX rotated PCA which reduces the nine possibly interrelated ions
 469 (NH_4^+ , SO_4^{2-} , NO_3^- , Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Cl^- and H^+) to three independent PCs which explain 75% of the
 470 total variance (see Table 5). Results are based on 10cm increments where all ions were analysed and
 471 to a time span from 1987 to 2014 only (WUK n= 745 observations, GOK n= 885 observations)
 472 because the analysis of mono- and bivalent cations is missing for the first years from 1983 to 1985
 473 and in 1986 only monovalent cations were measured. Ideally, each 10cm increment represents a
 474 specific precipitation event. In practice, two categories of deviations from this ideal situation will
 475 happen. Certain events will yield more than 10 cm of snow; other events yield less precipitation and
 476 fill only part of a 10 cm snow sample. This “smearing” of individual samples may render it difficult to
 477 obtain the signal of less frequent components. But the more important components will still be
 478 accessible. As can be seen in Table 5 the results for WUK and GOK are almost identical, so the
 479 following interpretations are valid for both sites.

480

481 **Table 5: Varimax rotated PCA factor loadings and percentage of the total explained variance for the measured**
 482 **chemical species on the two sampling sites WUK (n=725 observations) and GOK (n=845 observations)**

	PC1		PC2		PC3	
	WUK	GOK	WUK	GOK	WUK	GOK
K^+	0.93	0.92	0.04	0.05	0.06	0.13
Na^+	0.96	0.96	0.03	0.03	0.08	0.09
Cl^-	0.97	0.94	0.05	0.08	0.07	0.11
SO_4^{2-}	0.16	0.13	0.86	0.83	0.04	0.24
NO_3^-	0.00	0.08	0.85	0.89	-0.02	0.05
NH_4^+	-0.06	0.07	0.76	0.76	0.21	0.25
Ca^{2+}	0.05	0.07	0.02	0.01	0.78	0.87
Mg^{2+}	0.23	0.18	0.32	0.18	0.56	0.78
H^+	0.09	-0.11	0.59	0.72	-0.57	-0.32

Variance [%]	31	30	28	29	15	18
--------------	----	----	----	----	----	----

483

484 PC1 is loaded with K^+ , Na^+ and Cl^- and covers 30 to 31% of the total variance. PC2 accounts for 28 to
485 29% of the total variance and is loaded with SO_4^{2-} , NO_3^- , NH_4^+ and H^+ . PC3 is loaded with Ca^{2+} and
486 Mg^{2+} and covers 15 to 18 % of the total variance. Obviously there is hardly any difference between
487 PC1 and PC2 regarding the coverage of the total variance, while PC3 is of less importance for the
488 variance in the data. Maupetit and Delmas (1994) who found the same ions loaded in the three
489 different factors, named the factors *sea-salt factor* (K^+ , Na^+ and Cl^-), *acid factor* (SO_4^{2-} , NO_3^- , NH_4^+ and
490 H^+) and *dust factor* (Ca^{2+} and Mg^{2+}). The dust factor is negatively loaded with H^+ , indicating the
491 neutralizing effect of carbonated dust particles (Avila and Rodà, 1991; Psenner, 1999). This pattern is
492 more noticeable on WUK which is in agreement with the stronger influence of dust deposits already
493 discussed before. The load of Mg^{2+} in PC1 and PC2 might be influenced by samples below the
494 detection limit. However, this effect and the load of NH_4^+ in PC3 are also observed by Maupetit and
495 Delmas (1994).

496

497 3.4.2 Discussion of the PCA factors

498 As Austria is located in Central Europe, surrounded by highly industrialized countries, domination of
499 anthropogenic induced ions, like the ones loaded in the acid factor, could be expected. This brings up
500 the assumption of non-maritime sources also for ions loaded in PC1, hitherto the maritime factor. It
501 is also known, that the contribution of sea-salt aerosols to particulate matter at SBO is very low (Pio
502 et al 2007).

503 Non-sea-salt (nss) proportions of ions were calculated from ion concentrations of the 10cm
504 increments where all ions were measured within the period from 1987 to 2014 on WUK and GOK
505 (n=1629 observations). These nss proportions were used to determine whether the ions loaded in
506 PC1 (Cl^- , Na^+ and K^+) are of maritime origin and to determine to which amount ions loaded in other
507 PCs, like SO_4^{2-} , Ca^{2+} and Mg^{2+} are of maritime origin. Previous studies from Schwikowski et al. (1999,
508 1995) investigated anthropogenic and natural sources of atmospheric SO_4^{2-} , based on two ice cores
509 drilled on Colle Gnifetti (Monte Rosa massif, Swiss Alps) covering the time period from 1756-1982.
510 They found that in the industrial period (1963-1982) SO_4^{2-} originates from sea-spray (2%), mineral
511 dust (13%) and from the oxidation of SO_2 (85%). The anthropogenic source of SO_4^{2-} was estimated to
512 contribute 79% of the total SO_4^{2-} , thus being most dominant. Another study of Schwikowski et al.
513 (1995) claims that Mg^{2+} originates not only from mineral dust but also from sea-spray (14%),
514 whereas Na^+ originates equally from soil erosion and sea-spray.

515 According to Möller (1990) the nss-proportions, or excess component sources, of the single ions can
516 be computed using either Na^+ or Cl^- as the seawater reference species, assuming that all Na^+ or Cl^- in
517 the snow cover originates from sea salt. The Cl^-/Na^+ ratio of the snow samples averages at 1.5 and is
518 lower than the ratio of 1.8 listed for surface sea water (Pilson, 2013). This excess of Na^+ either points

519 to a depletion of Cl⁻ due to the presence of protons or to an additional source for Na⁺, such as mineral
 520 dust (Möller, 1990). If Sahara dust events (defined over a pH>5.6 according to Rogora et al., 2004)
 521 are excluded from the data set the Cl⁻/Na⁺ ratio of the snow samples slightly increases to 1.6. If all
 522 samples with Ca²⁺ concentrations of more than 20µeq/l, 6µeq/l or 3µeq/l are excluded (compare
 523 Maupetit and Delmas, 1994) the Cl⁻/Na⁺ ratio values at 1.5, 1.6 or even 1.9, getting closer to the sea
 524 water ratio of 1.8. Thus, it seems, as mineral dust is an additional source for Na⁺. Cl⁻ can also be
 525 volatilized as HCl by strong acids (HNO₃ or H₂SO₄) (Möller, 1990) and thus may not be fully conserved.
 526 However, as Maupetit and Delmas (1994) concluded that the volatilization of Cl⁻ has only little
 527 influence on the high alpine environment and the influence of crustal Na⁺ is clearly visible the
 528 calculation of nss-concentrations were based on Cl⁻ concentrations.

529 Concentrations of the major constituents in surface sea water were derived from Pilson (2013) and
 530 ratios of the single ions to Cl⁻ (R_{sea}) are presented in Table 6 together with the nss-proportions.

531 For single cases, the nss concentration may turn negative if the respective ion concentration is lower
 532 than the product of R_{sea} with the Cl⁻ concentration. Nss concentrations presented in Table 6 refer only
 533 to differences greater than 0 (Δ>0), which is true for at least 94% of all observations (n_{Δ>0}=1326).

534

535 **Table 6: Sea water ratio (R_{sea}) and nss-proportions assuming that all Cl⁻ in the snow cover originates from sea salt.**

	R _{sea}	[µeq/l]	[%]	n
				Δ>0
nss Cl ⁻	1	-	-	-
nss Na ⁺	0.557	1.67	44	1104
nss SO ₄ ²⁻	0.140	5.75	86	1309
nss K ⁺	0.021	1.09	88	1320
nss Ca ²⁺	0.021	7.73	96	1324
nss Mg ²⁺	0.007	0.97	95	1326

536

537 As expected the vast majority of Ca²⁺ and Mg²⁺ concentrations are not of maritime origin and the PC3
 538 can be interpreted as *mineral dust factor*. Schwikowski et al. (1995) denote these ions together with
 539 K⁺ as dust tracers, coming mainly from Saharan dust or local soil abrasion. Here the majority of K⁺
 540 (88%) determined in the snow samples can be attributed to nss-origin as well. Still K⁺ is associated
 541 with PC1 and not with PC3. The same phenomenon, K⁺ loading in the assumed sea salt factor and
 542 being 86% of nss-origin, was already described by Maupetit and Delmas (1994) and interpreted as
 543 reflecting a simultaneous deposition effect rather than a common source.

544 In contrast to Schwikowski et al. (1995) we cannot conclude that K⁺, originates at least in parts from
 545 Sahara dust or soil abrasion because we cannot find these ions loaded in the dust factor (PC3). It is
 546 well known that K⁺ can be also used as a tracer for the combustion of biomass (Cachier et al., 1991;
 547 Pio et al., 2008). The impact of wood combustion to particulate matter at Sonnblick is evident during
 548 all seasons (Puxbaum et al., 2007). However, concentration ratios of both Na⁺ and Cl⁻ to K⁺ in the

549 snow pack are much higher than can be expected for aerosols originating from wood combustion
550 (Pio et al., 2008; Reid et al., 2005; Schmidl et al., 2011). Thus, PC1 cannot be labeled as 'wood
551 burning' factor, and the open question to common sources or deposition effects remains. Hence, PC1
552 will be labeled as *factor of unknown origin* or *unknown factor* from now on.

553 SO_4^{2-} was found to be to 88% of nss origin, resulting in a higher sea salt contribution than findings
554 from other studies in the Alps (Schwikowski et al., 1999; Maupetit and Delmas, 1994) which denote a
555 sea salt contribution of only 2% and 5%, respectively. Still if at least part of Cl^- is also available from
556 other sources like combustion processes this share would go further down.

557

558 **4. Summary and Conclusions**

559

560 For the investigation of temporal changes of inorganic ion concentration and deposition in a high
561 alpine seasonal snow cover, a unique time series of more than 30 years (1983 to 2014) of snow
562 chemistry measurements, sampled at two glaciers, Goldbergkees (GOK) and Wurtenkees (WUK) in
563 the Austrian Alps, was analysed. Observed ion concentrations at both sites show that the Sonnblick
564 region and average values are in the range of previous studies of high alpine snow chemistry.

565 The multi-decade measurements of high alpine inorganic snow chemistry give clear evidence that the
566 composition of the inorganic ions has significantly changed. A decrease of more than 10% in total ion
567 concentration and of more than 35% in measured conductivity was observed, mainly due to a 70%
568 and 30% decrease of the acidifying anions SO_4^{2-} and NO_3^- and a more than 54% decrease of the
569 accompanying H^+ . By cross-comparing the ion (Σ anions- Σ cations) and conductivity balance
570 (measured - calculated conductivity) a deficit of anions was found for more than 80% of the samples.
571 This pattern becomes most pronounced for the last decade (2007 to 2014) and can only partly be
572 explained with the lack of measurements of bicarbonates and organic acids.

573 Regarding the time period 1983 to 2014 significant decreasing trends were found for SO_4^{2-} and H^+
574 concentrations and depositions (2-sided p value <0.001). Also for seasonal totals (fall, winter, spring)
575 these ions showed significant decreasing trends (2-sided p value <0.05). In case of NO_3^- only
576 concentrations showed a significant decreasing trend (2-sided p-value<0.05), but not for seasonal
577 totals. Concentrations and depositions of all other ions did not show any significant long term trends.
578 The temporal decreasing trends identified for the acidifying anions SO_4^{2-} and NO_3^- reflect the
579 successful emission reductions of SO_2 and NO_x in Europe from 1980 onwards. These changes are
580 particularly relevant for high-elevation sites such as the European Alps with their fragile ecosystems
581 which are close to limit for survival. Observed trends are more pronounced in the emission data than
582 in the deposition or concentration data. Obviously, complex chemical and physical transport and
583 transformation processes occurring in the atmosphere dampen the trends observed in the snow
584 cover.

585 Winter precipitation at such remote areas like our sampling sites represents the most pristine air
586 over central Europe. Seasonality of ion concentrations was observed for NH_4^+ , SO_4^{2-} and H^+ , with
587 significantly higher spring concentrations compared to fall reflecting the beginning of vertical mixing
588 during spring. The increase in spring concentrations is most pronounced for NH_4^+ , due to agricultural
589 activities. Also for NO_3^- , an increase in spring concentrations was found, but without significance. All
590 other basic cations and Cl^- did not show any seasonality. The seasonality changes when looking at
591 depositions, shifting the pattern towards the season with the highest snow accumulation.

592 Different sources or source regions contributing to the ionic composition in the snow were
593 investigated using principal component analysis (PCA). Three uncorrelated principal components
594 (PCs) were identified. One PC is associated with SO_4^{2-} , NO_3^- , H^+ and NH_4^+ , mainly originating from
595 anthropogenic SO_2 and NO_x emissions, released during industrial fossil fuel combustion, agriculture
596 and animal husbandry. The close correlation of SO_4^{2-} and NO_3^- with NH_4^+ suggests that they were
597 mainly deposited as ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) and ammonium nitrate (NH_4NO_3) formed by gas-
598 to-particle conversion of the dissolved acids (H_2SO_4 and HNO_3) of the specific precursor gases SO_2
599 and NO_x . Another PC is associated with Ca^{2+} and Mg^{2+} , indicating a mineral soil or dust source. The
600 third PC is associated with Na^+ , Cl^- and K^+ . Sources for ions related to this PC remain undefined.
601 Calculation of non-sea-salt concentrations based on Cl^- indicates some contribution of Na^+ from
602 crustal material and mostly non-sea-salt origin for K^+ . Biomass burning as main source for the third
603 PC was rejected, as the concentration ratios of both Na^+ and Cl^- to K^+ are too high. Probably these ions
604 are grouped within one PC mainly because of similar behavior in terms of reactivity in the
605 atmosphere and deposition, rather than originating from the same source.

606 Our multi-decade time series allows a representation of the temporal development of atmospheric
607 deposition in an unprecedented way. Decreases in ionic loads of SO_4^{2-} and H^+ , but also of NO_3^-
608 concentrations reflect the success of air pollution abatement measures, but also of political changes
609 in the source regions – which cover large parts of central Europe. The fact that emission reductions
610 have been much stronger than impact reduction seems to derive from a general buffering capacity of
611 the natural environment. Further and continuous effort will thus be needed to decrease
612 anthropogenic impacts in a remote alpine environment close to natural levels.

613

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615

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629 **6. References**

- 630 Auer, I., Böhm, R., 1998. Schneepegel- und Totalisatormessungen im Sonnblickgebiet. Jahresber.
631 Sonnblick-Ver. Für Jahre 1996–1997 42–87.
- 632 Avila, A., 1996. Time trends in the precipitation chemistry at a mountain site in Northeastern Spain for the
633 period 1983–1994. *Atmos. Environ.* 30, 1363–1373. doi:10.1016/1352-2310(95)00472-6
- 634 Avila, A., Rodà, F., 1991. Red rains as major contributors of nutrients and alkalinity to terrestrial
635 ecosystems at Montseny (NE Spain). *Orsis Org. Sist.* 6, 215–229.
- 636 Ballaman, R., Buchmann, B., Gehrig, R., Weber, R., 2004. EMEP Assessment Report - Switzerland Part I:
637 Gases and Precipitation.
- 638 Cachier, H., Ducret, J., Bremond, M.P., Yoboue, V., Lacaux, J.P., Gaudichet, A., Baudet, J., 1991. Biomass
639 burning aerosols in a savanna region of the Ivory Coast. *Glob. Biomass Burn. Atmospheric,*
640 *climatic, and biospheric implications.*
- 641 Davies, T.D., (Martyn), T.M., Jones, H.G., 1991. Seasonal snowpacks: processes of compositional change ;
642 [proceedings of the NATO Advanced Research Workshop on Processes of Chemical Change in
643 Snowpacks held in Maratea, Italy, July 23 - 27, 1990]. Springer-Verlag.
- 644 Fierz, C., Armstrong, R.L., Durand, Y., Etchevers, P., Greene, E., McClung, D.M., Nishimura, K., Satyawali,
645 P.K., Sokratov, S.A., 2009. The international classification for seasonal snow on the ground.
646 UNESCO/IHP Paris.
- 647 Filippa, G., Freppaz, M., Williams, M.W., Zanini, E., 2010. Major element chemistry in inner alpine
648 snowpacks (Aosta Valley Region, NW Italy). *Cold Reg. Sci. Technol.* 64, 158–166.
649 doi:10.1016/j.coldregions.2010.07.005
- 650 Granat, L., 1972. On the relation between pH and the chemical composition in atmospheric precipitation.
651 *Tellus* 24, 550–560. doi:10.1111/j.2153-3490.1972.tb01581.x
- 652 Ingersoll, G.P., Mast, M.A., Campbell, D.H., Clow, D.W., Nanus, L., Turk, J.T., 2008. Trends in snowpack
653 chemistry and comparison to National Atmospheric Deposition Program results for the Rocky
654 Mountains, US, 1993–2004. *Atmos. Environ.* 42, 6098–6113. doi:10.1016/j.atmosenv.2008.02.030

- 655 Jones, H.G., 2001. *Snow Ecology: An Interdisciplinary Examination of Snow-Covered Ecosystems*.
656 Cambridge University Press.
- 657 Kasper, A., Puxbaum, H., 1998. Seasonal variation of SO₂, HNO₃, NH₃ and selected aerosol components at
658 Sonnblick (3106m a. sl). *Atmos. Environ.* 32, 3925–3939.
- 659 Kuhn, M., Haslhofer, J., Nickus, U., Schellander, H., 1998. Seasonal development of ion concentration in a
660 high alpine snow pack. *Atmos. Environ.* 32, 4041–4051.
- 661 Maupetit, F., Delmas, R.J., 1994. Snow chemistry of high altitude glaciers in the French Alps. *Tellus B* 46,
662 304–324. doi:10.1034/j.1600-0889.1994.t01-3-00006.x
- 663 Maupetit, F., Delmas, R.J., 1994. Carboxylic acids in high-elevation Alpine glacier snow. *J. Geophys. Res.*
664 99, 16491–16500. doi:10.1029/94JD03315
- 665 Maupetit, F., Wagenbach, D., Weddeling, P., Delmas, R.J., 1995. Seasonal fluxes of major ions to a high
666 altitude cold alpine glacier. *Atmos. Environ.* 29, 1–9. doi:10.1016/1352-2310(94)00222-7
- 667 Miles, L.J., Yost, K.J., 1982. Quality analysis of USGS precipitation chemistry data for New York.
668 *Atmospheric Environ.* 1967 16, 2889–2898. doi:10.1016/0004-6981(82)90039-7
- 669 Möller, D., 1990. The Na/Cl ration in rainwater and the seasalt chloride cycle. *Tellus* 42B, 254–262.
- 670 Nickus, U., Kuhn, M., Baltensperger, U., Delmas, R., Gaggeler, H., Kasper, A., Kromp-Kolb, H., Maupetit, F.,
671 Novo, A., Pichlmayer, F., Preunkert, S., Puxbaum, H., Rossi, G., Schoner, W., Schwikowski, M.,
672 Seibert, P., Staudinger, M., Trockner, V., Wagenbach, D., Winiwarter, W., 1997. SNOSP: Ion
673 deposition and concentration in high alpine snow packs. *Tellus B* 49, 56–71. doi:10.1034/j.1600-
674 0889.49.issue1.4.x
- 675 Nickus, U., Kuhn, M., Novo, A., Rossi, G., 1998. Major element chemistry in alpine snow along a north-
676 south transect in the Eastern Alps. *Atmos. Environ.* 32, 4053–4060. doi:10.1016/S1352-
677 2310(98)00231-3
- 678 Pilson, M.E.Q., 2013. *An introduction to the chemistry of the sea*. Cambridge University Press, Cambridge.
- 679 Pio, C.A., Legrand, M., Alves, C.A., Oliveira, T., Afonso, J., Caseiro, A., Puxbaum, H., Sanchez-Ochoa, A.,
680 Gelencsér, A., 2008. Chemical composition of atmospheric aerosols during the 2003 summer
681 intense forest fire period. *Atmos. Environ.* 42, 7530–7543. doi:10.1016/j.atmosenv.2008.05.032
- 682 Psenner, R., 1999. Living in a dusty world: airborne dust as a key factor for alpine lakes. *Water. Air. Soil*
683 *Pollut.* 112, 217–227.
- 684 Puxbaum, H., Caseiro, A., Sánchez-Ochoa, A., Kasper-Giebl, A., Claeys, M., Gelencsér, A., Legrand, M.,
685 Preunkert, S., Pio, C., 2007. Levoglucosan levels at background sites in Europe for assessing the
686 impact of biomass combustion on the European aerosol background. *J. Geophys. Res.* 112.
687 doi:10.1029/2006JD008114
- 688 Puxbaum, H., Simeonov, V., Kalina, M.F., 1998. Ten years trends (1984–1993) in the precipitation
689 chemistry in central Austria. *Atmos. Environ.* 32, 193–202. doi:10.1016/S1352-2310(97)00285-9

- 690 Reid, J.S., Koppmann, R., Eck, T.F., Eleuterio, D.P., 2005. A review of biomass burning emissions part II:
691 intensive physical properties of biomass burning particles. *Atmospheric Chem. Phys.* 5, 799–825.
- 692 Rogora, M., Mosello, R., Marchetto, A., 2004a. Long-term trends in the chemistry of atmospheric
693 deposition in Northwestern Italy: the role of increasing Saharan dust deposition. *Tellus B* 56, 426–
694 434. doi:10.1111/j.1600-0889.2004.00114.x
- 695 Rogora, M., Mosello, R., Marchetto, A., 2004b. Long-term trends in the chemistry of atmospheric
696 deposition in Northwestern Italy: the role of increasing Saharan dust deposition. *Tellus B* 56, 426–
697 434.
- 698 Rohrbough, J.A., Davis, D.R., Bales, R.C., 2003. Spatial variability of snow chemistry in an alpine snowpack,
699 southern Wyoming: SPATIAL VARIABILITY OF SNOW CHEMISTRY. *Water Resour. Res.* 39, n/a–n/a.
700 doi:10.1029/2003WR002067
- 701 Schmidl, C., Luisser, M., Padouvas, E., Lasselsberger, L., Rzaca, M., Ramirez-Santa Cruz, C., Handler, M.,
702 Peng, G., Bauer, H., Puxbaum, H., 2011. Particulate and gaseous emissions from manually and
703 automatically fired small scale combustion systems. *Atmos. Environ.* 45, 7443–7454.
704 doi:10.1016/j.atmosenv.2011.05.006
- 705 Schöner, W., Auer, I., Böhm, R., 2009. Long term trend of snow depth at Sonnblick (Austrian Alps) and its
706 relation to climate change. *Hydrol. Process.* 23, 1052–1063. doi:10.1002/hyp.7209
- 707 Schöner, W., Puxbaum, H., Staudinger, M., Maupetit, F., Wagenbach, D., 1997. Spatial variability in the
708 chemical composition of the snowcover at high alpine sites. *Theor. Appl. Climatol.* 56, 25–32.
709 doi:10.1007/BF00863780
- 710 Schwikowski, M., Döscher, A., Gäggeler, H.W., Schotterer, U., 1999. Anthropogenic versus natural sources
711 of atmospheric sulphate from an Alpine ice core. *Tellus B* 51, 938–951.
- 712 Schwikowski, M., Novo, A., Baltensperger, U., Delmas, R., Gäggeler, H.W., Kasper, A., Kuhn, M., Maupetit,
713 F., Nickus, U., Preunkert, S., Puxbaum, H., Rossi, G.C., Schöner, W., Wagenbach, D., 1997.
714 Intercomparison of snow Sampling and Analysis Within the Alpine-Wide Snowpack Investigation
715 (SNOSP). *Water. Air. Soil Pollut.* 93, 67–91. doi:10.1023/A:1022167507380
- 716 Schwikowski, M., Seibert, P., Baltensperger, U., Gaggeler, H.W., 1995. A study of an outstanding Saharan
717 dust event at the high-alpine site Jungfrauoch, Switzerland. *Atmos. Environ.* 29, 1829–1842.
718 doi:10.1016/1352-2310(95)00060-C
- 719 Steinbacher, M., Hüglin, C., 2007. Empa Materials Science and Technology - National Air Pollution
720 Monitoring Network (NABEL) (Activity Report). International Foundation HFSJG.
- 721 Thevenon, F., Chiaradia, M., Adatte, T., Hueglin, C., Poté, J., 2012. Characterization of Modern and Fossil
722 Mineral Dust Transported to High Altitude in the Western Alps: Saharan Sources and Transport
723 Patterns. *Adv. Meteorol.* 2012, 1–14. doi:10.1155/2012/674385

- 724 Turk, J.T., Taylor, H.E., Ingersoll, G.P., Tonnessen, K.A., Clow, D.W., Mast, M.A., Campbell, D.H., Melack,
725 J.M., 2001. Major-ion chemistry of the Rocky Mountain snowpack, USA. *Atmos. Environ.* 35,
726 3957–3966.
- 727 Williams, M.W., Melack, J.M., 1991. Solute chemistry of snowmelt and runoff in an Alpine Basin, Sierra
728 Nevada. *Water Resour. Res.* 27, 1575–1588. doi:10.1029/90WR02774
- 729 Winiwarter, W., Puxbaum, H., Schöner, W., Böhm, R., Werner, R., Vitovec, W., Kasper, A., 1998.
730 Concentration of ionic compounds in the wintertime deposition: results and trends from the
731 Austrian Alps over 11 years (1983–1993). *Atmos. Environ.* 32, 4031–4040. doi:10.1016/S1352-
732 2310(97)00252-5
- 733
- 734

HIGHLIGHTS (3-5 bullet points, max. 85 characters)

- SO_4^{2-} , NO_3^- and H^+ in high alpine snow decrease over 30 years of observations
- Decrease in concentrations and depositions are lower than decrease in emissions
- Seasonal patterns show maximum concentrations during spring for NH_4^+ , SO_4^{2-} and H^+
- Anthropogenic and crustal influence are the main sources for measured ions