

SNOW CHEMISTRY OF A GLACIER IN THE CENTRAL EASTERN ALPS (HINTEREISFERNER, TYROL, AUSTRIA)¹

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With 6 figures

SUMMARY

In June and October 1984 the chemical composition of the snow cover at Hintereisferner (Öztaler Alps, Tyrol) was investigated by means of two vertical profiles at about 3100 m a. s. l. Annual deposition rates for dissolved substances were estimated from precipitation measurements, snow density profiles and chemical analyses.

One fourth of all samples showed pH values below 5.0, one third had alkalinity values equal to or less than zero. Proton activity of "acid" snow samples ($\text{pH} \leq 5.7$) was best correlated with the concentration of nitrate ($r=0.81$) and sulphate ($r=0.84$). The equivalent ratio $\text{SO}_4^- / \text{H}^+$ and $\text{NO}_3^- / \text{H}^+$ of these samples amounted to 1.14 and 0.67, respectively. From a multiple linear regression a relatively balanced share of SO_4 and NO_3 to the acidity of precipitation resulted. This might depend on the high correlation between sulphate and ammonium ($r=0.84$), the molar ratio of both ions being approximately 1:1.

The alkalinity of the whole snow cover, calculated as difference between the sum of cations (without H^+) and anions (without HCO_3^-) was zero. It was, however, strongly affected by precipitation of dust from the Sahara desert. The average mineral acidity of dust free layers was from 2 to $5 \mu\text{eq l}^{-1}$. If the ammonium in precipitation is included as a potential acid for terrestrial and aquatic ecosystems, the mineral acidity would reach values of 5 to $15 \mu\text{eq l}^{-1}$.

Between October 1983 and September 1984 the deposition of sulphate-sulphur amounted to 0.53 g m^{-2} . During this period 0.25 g m^{-2} of nitrate-nitrogen, 0.19 g m^{-2} of ammonium-nitrogen and 0.53 g m^{-2} of total dissolved nitrogen (DN) were deposited. The annual deposition of total dissolved phosphorus (DP) was 7 mg m^{-2} . The chloride deposition of 0.64 g m^{-2} was approximately twice as high as at lower situated stations, the mean concentration being 0.25 mg l^{-1} .

The average volume-weighted pH was 5.1, leading to a proton deposition of $0.024 \text{ g m}^{-2} \text{ yr}^{-1}$.

SCHNEECHEMIE EINES GLETSCHERS IN DEN ZENTRALEN OSTALPEN (HINTEREISFERNER, TIROL)

ZUSAMMENFASSUNG

Im Juni und Oktober 1984 wurde am Hintereisferner (Öztaler Alpen, Tirol) in ca. 3100 m Höhe anhand zweier Vertikalprofile der chemische Aufbau der Schneedecke untersucht. Die jährliche Deposition im Zeitraum Oktober 1983 bis September 1984 betrug für Sulfat-Schwefel $0,53 \text{ g m}^{-2}$, für Chlorid $0,64 \text{ g m}^{-2}$, für Nitrat-Stickstoff $0,25 \text{ g m}^{-2}$ und für Ammonium-Stick-

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stoff $0,19 \text{ g m}^{-2}$; an gesamtem gelöstem Stickstoff $0,53 \text{ g m}^{-2}$, an gelöstem Gesamtphosphor 7 mg m^{-2} . Der mittlere gewichtete pH-Wert lag zwischen 5,0 und 5,1, was einer jährlichen Protonendeposition von $0,024 \text{ g m}^{-2}$ entspricht. Die Alkalinität der gesamten Schneedecke betrug null. Sie sinkt auf -2 bis $-5 \mu\text{eq l}^{-1}$, wenn man die zwei von Saharastaub beeinflussten Schichten nicht berücksichtigt bzw. auf -5 bis $-15 \mu\text{eq l}^{-1}$, wenn man Ammonium als potentielle Säure betrachtet. Für Proben mit $\text{pH} \leq 5,7$ ergab sich eine hohe Korrelation zwischen Sulfat und Ammonium, H^+ und Nitrat bzw. H^+ und Sulfat ($r = 0,75 - 0,84$). Aufgrund einer multiplen linearen Regression ergab sich ein etwa gleich großer Anteil von Sulfat und Nitrat an der Azidität der Niederschläge.

1. INTRODUCTION

The concentration of dissolved substances in precipitation has been measured in Tyrol for several years. Until 1980 the major emphasis was placed on nutrients (Psenner 1984), whereas recently the acidity of rain and snow has been of greater interest (Smidt 1983, 1984, 1985; Psenner, Zaderer and Nickus 1986; Puxbaum et al. 1985). Currently, the wet and bulk precipitation in Tyrol is being studied at stations of low and middle altitude. Very little data from high mountains exist because the collection of samples by conventional methods is greatly dependent on accessibility, the availability of electric current, the presence of attending persons etc.

In 1985 a study on acidification of high mountain lakes in siliceous regions of Tyrol was initiated (Psenner, Zaderer and Nickus 1986). Reliable data on the precipitation chemistry are essential, if one wants to respond questions about the extent, the causes and the history of acidification in high mountain lakes in this area.

In order to estimate the deposition of nutrients and pollutants in a high mountain region during the winter half year and the whole year, respectively, snow samples were taken at 2 sites of Hintereisferner (Öztaler Alps, Tyrol), on 13 June 1984 — before snow melting began — and on 10 October 1984 (fig. 1). On 29 May 1985 the sampling was repeated at one site in order to find an indication of the variability of deposition in that area.

Glaciological studies have been done on Hintereisferner since 3 decades (Kuhn et al. 1985). Since 1953 a more or less continuous record of precipitation, ablation and evaporation rates exists. The sampling sites Badeeis and Teufelseck can be considered as representatives for the precipitation amount on Hintereisferner.

2. METHODS

2.1 SAMPLING

At an altitude of 3070 m (Teufelseck) and 3150 m (Badeeis), respectively, a snow pit was dug. The dirt layer of the last summer served as a marker. In a vertical profile the density and stratigraphy were determined. For chemical analysis, snow of 20 and 30 cm thick layers, respectively, was filled into air-tight polyethylene bottles. The samples were brought to the laboratory in a frozen state and thawed at room temperature.

2.2 ANALYSIS

pH, conductivity, alkalinity and ammonium were determined immediately after all samples had reached 20°C . Nitrate, total dissolved nitrogen (DN) and phosphorus

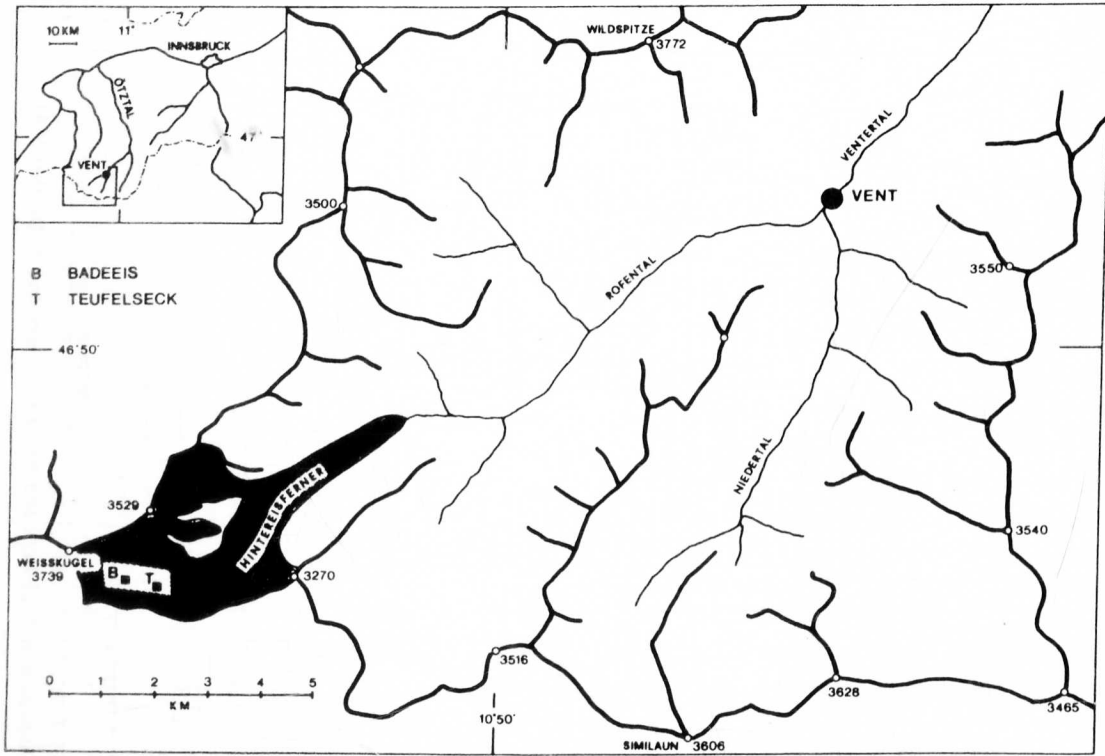


Fig. 1: Location of sampling sites. Badeeis 3150 m a. s. l., Teufelseck 3070 m a. s. l.

(DP), sulphate and chloride were analyzed within three days; the filtered samples were kept in the refrigerator at 4°C. Samples for the analysis of calcium, magnesium, sodium and potassium were stored in the deep freezer.

pH was measured with Ingold Electrodes 405-88-NS together with a WTW 530 pH meter without addition of KCl. Prior to use, the electrode was tested with a 10⁻⁴ M HCl solution according to Metcalf (1984). Conductivity was measured with a Hach conductimeter at 20°C. Equivalence alkalinity (Henriksen 1982) was determined according to Berger (unpublished). The method was slightly modified and showed good correlation with the Gran titration.

Ammonium was determined by the method of Wagner (1969), total dissolved phosphorus (DP) was analyzed according to Vogler (1965) modified by Brugger (1979). Total dissolved nitrogen (DN) was measured as NO₃⁻ - N and NO₂⁻ - N, respectively, after digestion with sodiumperoxodisulphate according to Koroleff (1969). The difference between DN and the sum of inorganic nitrogen (NO₃, NO₂, NH₄) was termed dissolved organic nitrogen (DON). Nitrate and nitrite were determined by the method of Stainton et al. (1974) on a Cenco autoanalyzer, which was also used for the analysis of chloride (Kahn 1967) and sulphate (Lazrus et al. 1966). Calcium, magnesium, sodium and potassium were measured on AAS (Perkin Elmer 360).

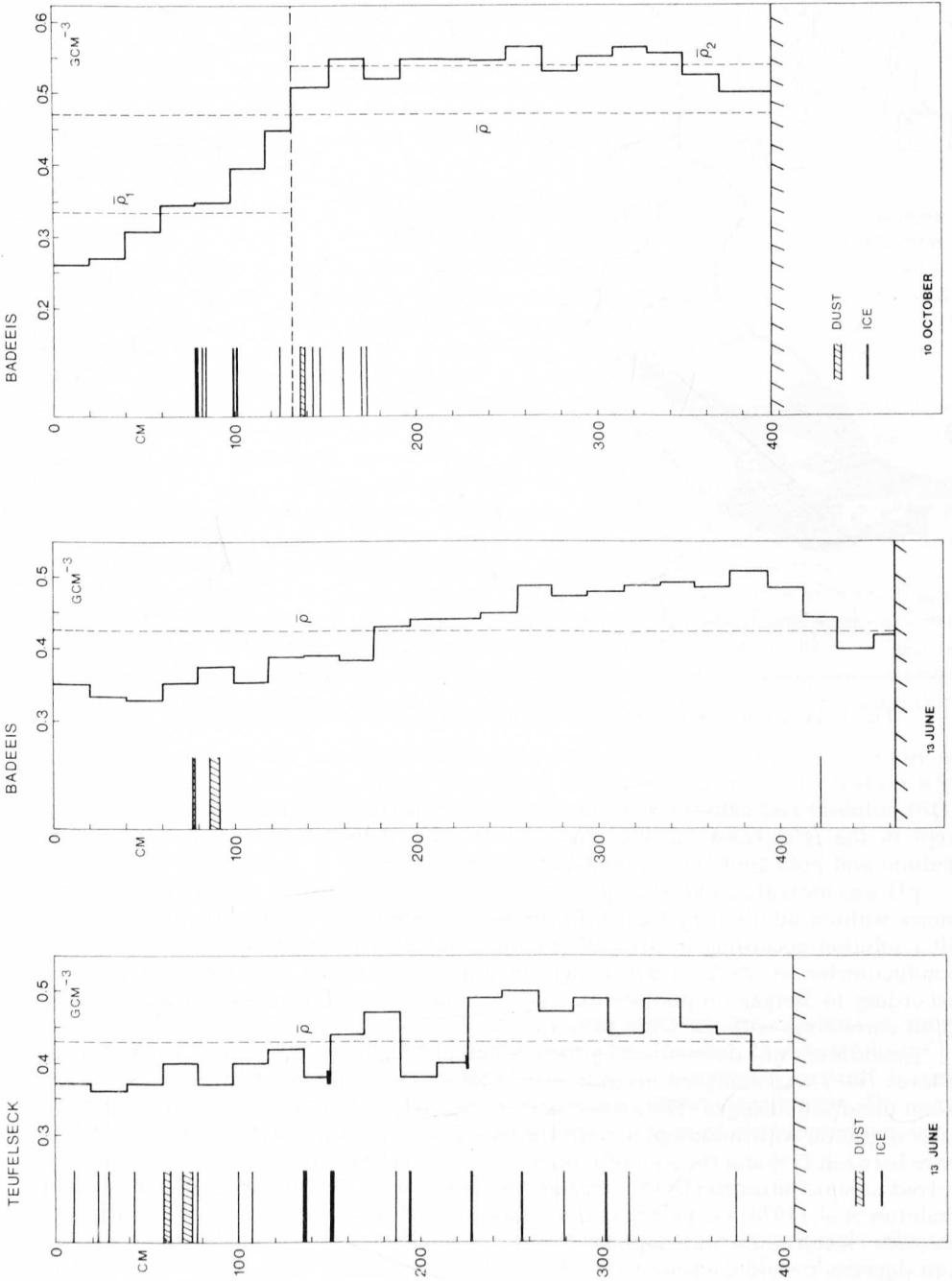


Fig. 2: Stratigraphy and density profiles of the snowpack at Teufelseck and Badeeis, 13 June and 10 October 1984

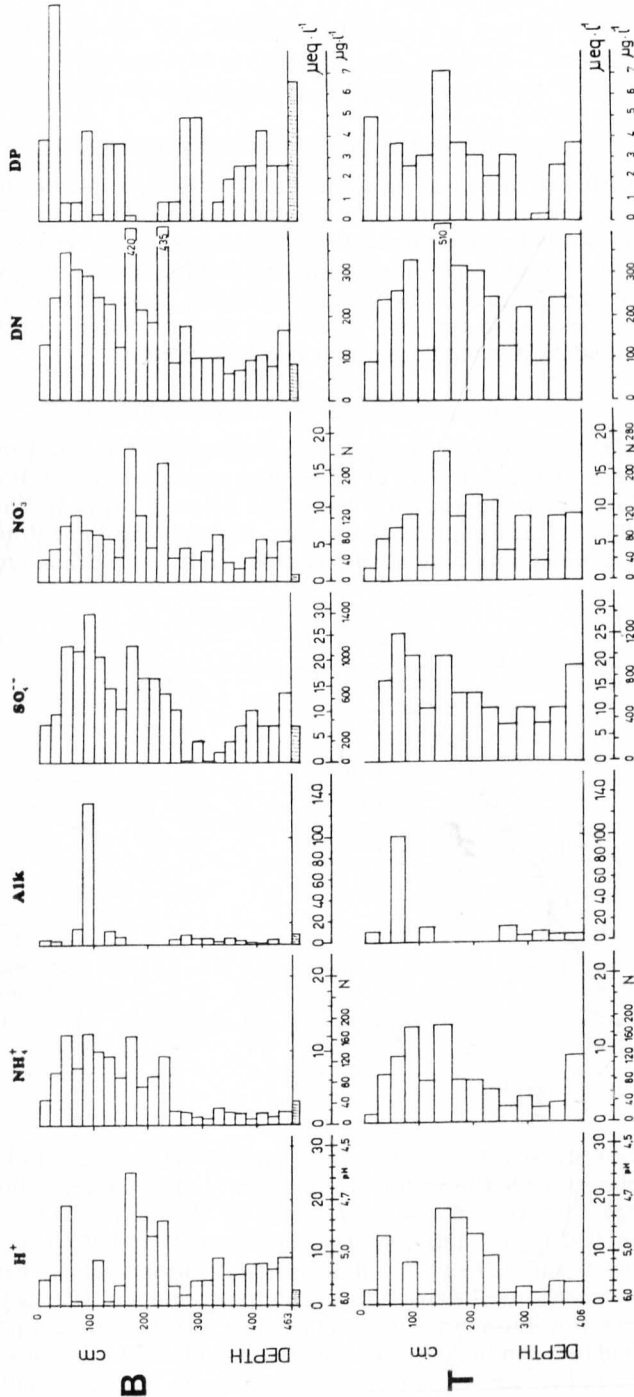


Fig. 3: Chemical composition of the snowpack at Badeeis (B) and Teufelseck (T), 13 Juni 1984. DN ... Total Dissolved Nitrogen, DP ... Total Dissolved Phosphorus

3. RESULTS

3.1 SAMPLES OF JUNE 1984

3.1.1 STRATIGRAPHY AND DENSITY PROFILES

The mean density of snow was almost identical in both pits (429 kg m^{-3} at Teufelseck and 424 kg m^{-3} at Badeeis), but they differed considerably in stratigraphy (fig. 2). Apart from a thin ice horizon at the depth of 422 cm, almost no ice layers were found at Badeeis. The pit at Teufelseck showed, on the contrary, several ice layers down to a depth of 320 cm, some of them quite thick. In both pits 2 yellowish layers of approximately 5 cm thickness could be seen, the deeper one attributable to the dustfall on 20 May 1984 caused by a strong air current from the south.

3.1.2 CHEMICAL COMPOSITION OF THE SNOW SAMPLES

Dissolved substances in both pits showed a pronounced but corresponding vertical stratification (fig. 3). The pH of 95 % of all samples was below 6.0, 80 % of the samples showed pH values below 5.6 and 20 % had a pH below 5.0 (fig. 4). The alkalinity of approximately 80 % of the samples was less than $10 \mu\text{eq l}^{-1}$ and one third had no alkalinity. The only samples with high alkalinity ($100 \mu\text{eq l}^{-1}$) were those containing dust particles.

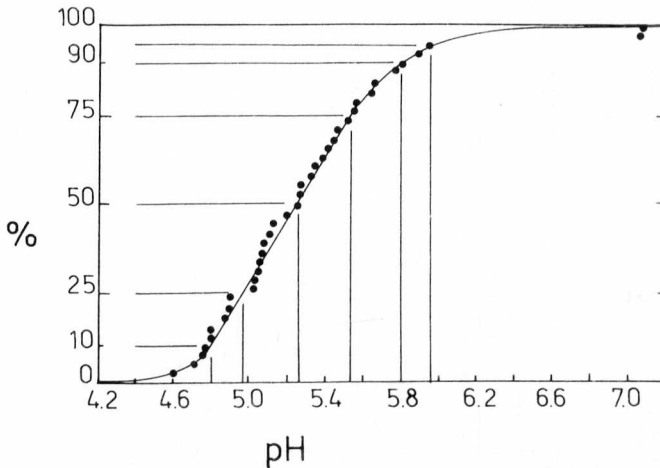


Fig. 4: Frequency distribution of pH values, 13 June 1984. All samples ($n = 37$)

Conductivity was, in general, quite low, varying between 2.8 and $17.6 \mu\text{S cm}^{-1}$. Only five samples exceeded the value of $10 \mu\text{S cm}^{-1}$. The concentration of sulphate was in the range of 0 (i. e. below $0.1 \text{ mg SO}_4^{2-} \text{ l}^{-1}$) and 1.4 mg l^{-1} , chloride was between 0.06 and 0.95 mg l^{-1} , nitrate-nitrogen between 25 and $255 \mu\text{g l}^{-1}$, ammonium-nitrogen between 9 and $187 \mu\text{g l}^{-1}$, total dissolved nitrogen (DN) between 65 and $510 \mu\text{g l}^{-1}$ and total dissolved phosphorus (DP) between 0 and $10.2 \mu\text{g l}^{-1}$.

In spite of low concentrations, the ionic balance was more or less poised (table 1 a and b). The calculated conductivity generally corresponded to the measured one.

It is remarkable that concentrations were, in general, higher at Teufelseck than at

Badeeis. This might be due to a different deposition of dust or varying evaporation rates (Kaser 1983). With respect to the deposition of pollutants, these differences were, on the other hand, partly equalized by the lower snow depth at Teufelseck.

Table 1: Chemistry of the snowpack at Badeeis (a) and Teufelseck (b), 13 June 1984
Sample 24: Dust horizon of autumn 1983 (a). DN = Total Dissolved Nitrogen, DP = Total Dissolved Phosphorus

Table 1a

No.	Depth cm	pH	Cond. $\mu\text{S}_{20} \text{cm}^{-1}$	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺	NH ₄ ⁺		SO ₄ ⁼	NO ₃ ⁻	Cl ⁻	HCO ₃ ⁻	DN	DP
				$\mu\text{eq l}^{-1}$				$\mu\text{eq l}^{-1}$							
1	0-20	5.35	3.1	8	1	1	1	3	5	7	3	2	10	130	3.9
2	20-40	5.21	4.2	8	3	2	1	7	6	9	4	3	10	245	10.2
3	40-60	4.72	10.0	—	—	—	—	12	19	23	8	3	0	350	0.9
4	60-80	5.95	6.3	40	3	3	1	8	1	22	9	27	16	310	0.9
5	80-100	7.09	17.6	158	21	10	3	12	0	29	7	14	133	295	4.3
6	100-120	5.03	7.0	16	3	1	0	10	9	21	6	5	9	245	0.3
7	120-140	5.90	5.1	25	3	2	1	9	1	15	6	7	14	230	3.7
8	140-160	5.45	4.1	15	2	2	1	7	4	10	3	5	12	125	3.7
9	160-180	4.60	12.2	7	1	1	0	12	25	23	18	2	0	420	0.3
10	180-200	4.76	8.7	8	1	2	1	5	17	17	9	8	0	215	0.0
11	200-220	4.90	7.1	16	1	1	1	7	13	17	5	6	2	185	0.0
12	220-240	4.80	8.7	11	1	1	0	9	16	14	16	11	0	435	0.9
13	240-260	5.42	3.0	8	1	1	1	2	4	10	3	3	7	90	0.9
14	260-280	5.66	3.1	—	—	—	—	2	2	0	5	3	9	175	4.9
15	280-300	5.34	2.8	8	2	4	1	1	5	4	3	11	7	100	4.9
16	300-320	5.28	3.8	8	3	3	1	1	5	0	4	9	7	100	0.0
17	320-340	5.06	4.5	3	1	2	0	2	9	2	6	4	3	100	0.9
18	340-360	5.26	3.2	3	1	2	0	2	6	4	3	7	6	65	2.0
19	360-380	5.27	3.0	5	0	0	0	2	6	7	2	3	5	70	2.6
20	380-400	5.08	4.6	3	1	1	0	1	8	10	3	3	2	95	2.6
21	400-420	5.07	4.4	—	—	—	—	1	8	7	6	4	1	106	4.3
22	420-440	5.13	4.2	3	2	2	1	8	7	7	3	8	4	85	2.6
23	440-463	5.05	5.7	4	2	3	1	2	9	14	5	4	0	165	2.6
24	463-470	5.57	2.9	—	—	—	—	3	3	7	1	10	13	85	6.6

Table 1b

No.	Depth cm	pH	Cond. $\mu\text{S}_{20} \text{cm}^{-1}$	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺	NH ₄ ⁺		SO ₄ ⁼	NO ₃ ⁻	Cl ⁻	HCO ₃ ⁻	DN	DP
				$\mu\text{eq l}^{-1}$				$\mu\text{eq l}^{-1}$							
1	0-25	5.25	2.8	14	1	3	1	1	3	0	2	3	14	90	4.9
2	25-50	4.90	7.8	6	1	3	1	8	13	16	6	6	2	240	0.0
3	50-75	7.08	13.6	122	14	10	2	9	0	25	7	18	100	260	3.7
4	75-100	5.11	7.7	23	3	5	1	13	8	21	9	13	8	330	2.6
5	100-130	5.81	3.8	15	2	4	2	6	2	10	3	13	15	115	3.1
6	130-160	4.75	10.8	14	3	4	1	13	18	21	18	12	0	510	7.1
7	160-190	4.80	8.9	8	2	3	2	6	16	14	9	8	1	315	3.7
8	190-220	4.88	7.6	13	2	6	2	6	13	14	11	6	3	305	3.1
9	220-250	5.04	6.3	12	2	5	2	4	9	10	11	9	9	245	2.1
10	250-280	5.78	3.3	14	3	7	2	2	2	7	4	17	16	125	3.1
11	280-310	5.56	5.0	12	3	7	2	4	3	10	9	7	10	220	0.0
12	310-340	5.65	2.8	13	2	4	1	2	2	7	3	5	11	90	0.3
13	340-370	5.46	4.6	20	3	5	2	3	4	10	9	12	11	240	2.6
14	370-406	5.39	6.6	13	3	5	2	9	4	19	9	3	11	385	3.7

Volume-weighted means of the analyzed parameters (table 2) are all more or less strongly affected by the dust layer. Therefore, it is quite problematic to calculate average values, for example, of pH and alkalinity or acidity. If alkalinity of the whole snow cover is determined as the sum of cations (without protons) minus the sum of anions (without bicarbonate) a value of $1.2 \mu\text{eq l}^{-1}$ results at Badeeis and of $5.7 \mu\text{eq l}^{-1}$ at Teufelseck. Without dust layers, these values would be $-5.5 \mu\text{eq l}^{-1}$ and $-2.4 \mu\text{eq l}^{-1}$, respectively.

Table 2: Ionic balance, alkalinity, pH and concentrations of total dissolved nitrogen (DN) dissolved organic nitrogen (DON), and phosphorus (DP) of the weighted mean, 13 June 1984

	Badeeis		Teufelseck	
	$\mu\text{eq l}^{-1}$	%	$\mu\text{eq l}^{-1}$	%
Ca ⁺⁺	16.1	22	20.0	23
Mg ⁺⁺	2.3	3	3.0	3
Na ⁺	2.4	3	5.2	6
K ⁺	0.8	1	1.6	2
NH ₄ ⁺	5.1	7	5.7	7
H ⁺	8.6	12	6.7	8
Cations	35.4	48	42.2	49
SO ₄ ⁼	12.2	17	12.7	15
NO ₃ ⁻	6.2	8	7.8	9
Cl	7.1	10	9.3	11
HCO ₃ ⁻	12.6	17	14.2	16
Anions	38.1	52	44.0	51
Ion sum	73.5	100	86.2	100
ALK* a) total	1.2		5.7	
b) without dust	-5.5		-2.4	
pH	5.06		5.18	
DN	192		239	$\mu\text{g l}^{-1}$
DON	34		50	$\mu\text{g l}^{-1}$
DP	2.6		2.7	$\mu\text{g l}^{-1}$

* $\text{ALK} = 2(\text{Ca}^{++}) + 2(\text{Mg}^{++}) + (\text{Na}^{+}) + (\text{K}^{+}) + (\text{NH}_4^{+}) - 2(\text{SO}_4^{=}) - (\text{NO}_3^{-}) - (\text{Cl}^{-})$.

3.1.3 DEPOSITIONS

Between October 1983 and June 1984, 17 meq m^{-2} of protons were deposited at Badeeis and 12 meq m^{-2} at Teufelseck (table 3). The deposition of sulphate-sulphur amounted to 0.38 g m^{-2} (0.35 g m^{-2}). 37 % of total dissolved nitrogen ($0.38-0.42 \text{ g m}^{-2}$) was present as $\text{NH}_4^{+} - \text{N}$, 45 % as $\text{NO}_3^{-} - \text{N}$ and 18 % as dissolved organic nitrogen (DON). The deposition of phosphorus showed values below 5 mg m^{-2} .

Table 3: Snow depth, water equivalent and mean density of the snow cover; deposition for the period October 1983—June 1984 at Badeeis and Teufelseck. Alkalinity calculated assuming a total oxidation of ammonium to nitrate

	Badeeis		Teufelseck	
	meq m ⁻²	g m ⁻²	meq m ⁻²	g m ⁻²
Snow cover (m)	4.63		4.06	
Water equivalent (m)	1.96		1.74	
Density (kg m ⁻³)	420		430	
Ca ⁺⁺	31.5	0.63	34.8	0.70
Mg ⁺⁺	4.5	0.05	5.2	0.06
Na ⁺	4.7	0.10	9.1	0.21
K ⁺	1.7	0.06	2.8	0.11
NH ₄ ⁺ - N	10.0	0.14	9.9	0.14
H ⁺	17.0	0.02	11.7	0.01
SO ₄ ⁻ - S	23.9	0.38	22.1	0.35
NO ₃ ⁻ - N	12.3	0.17	13.6	0.19
Cl ⁻	13.9	0.49	16.2	0.57
HCO ₃ ⁻	23.9		24.6	
DN		0.38		0.42
DON		0.07		0.09
DP		0.005		0.005
ALK* a) total	2.4		9.9	
b) without dust	-10.7		-4.2	
ALK** a) total	-17.6		-9.9	
b) without dust	-30.9		-24.0	

* $ALK = 2(Ca^{++}) + 2(Mg^{++}) + (Na^+) + (K^+) + (NH_4^+) - 2(SO_4^-) - (NO_3^-) - (Cl^-)$.

** $NH_4^+ \rightarrow NO_3^-$

3.2 SAMPLES OF OCTOBER 1984

3.2.1 STRATIGRAPHY, DENSITY PROFILES AND CHEMISTRY

Net accumulation from October 1983 till the first days of September 1984 amounted to 260 cm of snow with a mean density of 538 kg m⁻³ (fig. 2), corresponding to a water equivalent of 141 cm. Above it lay about 130 cm of new snow which had fallen between 6 September and 10 October 1984 with a mean density of 336 kg m⁻³ and a water equivalent of 45 cm. The dust layer, distinctly visible in June, could hardly be seen in October. Obviously, the bulk of dust had been washed into deeper layers by melting water. In all samples taken at depths greater than 130 cm dust particles were found.

pH values of the freshly fallen snow ranged between 4.6 and 5.3 (fig. 5), comparing quite well with dust-free samples from June. The same is valid for alkalinity, conductance and other dissolved substances. Below the hardly distinguishable dust horizon at a depth of 130—150 cm, the chemical composition of the snow was altered in comparison to June. A slight decrease of phosphorus concentrations (2.2 µg l⁻¹) and a pronounced decrease of the ammonium concentrations (54 µg l⁻¹) was observed. Generally spoken, a levelling of dissolved substances can be ascertained in older snow layers affected by melting processes. They cannot be used for estimating yearly deposition rates. Similar changes in concentrations were observed by Johannessen and Henriksen (1978) in Norway and by Jeffries and Snyder (1981) in Canada.

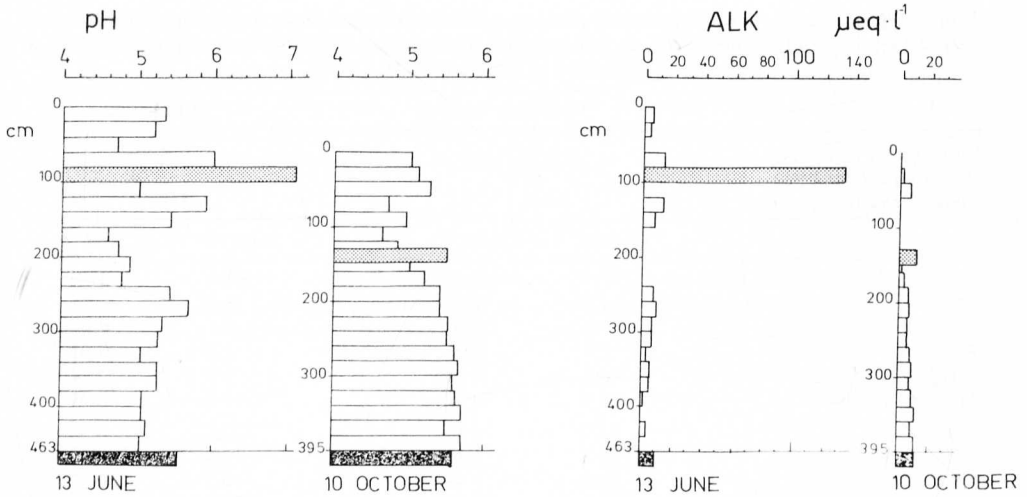


Fig. 5: pH and alkalinity profiles at Badeeis on 13 June and 10 October 1984

From the analysis of the upper 120 cm, however, we could suppose that the chemistry of precipitation in September did not differ widely from that in winter and spring. Precipitation between June and September 1984 amounted to approximately 500 mm at 3100 m a. s. l., estimated from measurements with rain gauges in the surroundings and precipitation-height-profiles from other years. If we assume that the chemical composition of the missing 500 mm of precipitation is identical to the snow layers of

Table 4: Calculated annual deposition on Hintereisferner (3150 m a. s. l.) for the period October 1983—September 1984. 83 % measured, 17 % inferred

	Deposition		Concentration	
	meq m ⁻¹	g m ⁻²	meq l ⁻²	mg l ⁻¹
Ca ⁺⁺	39.6	0.80	14.3	0.29
Mg ⁺⁺	5.8	0.07	2.1	0.03
Na ⁺	6.4	0.14	2.3	0.05
K ⁺	2.2	0.08	0.8	0.03
NH ₄ ⁺ - N	14.1	0.19	5.1	0.07
H ⁺	24.4	0.02	8.8	pH 5.05
SO ₄ ⁻ - S	33.2	0.53	12.0	0.19
NO ₃ ⁻ - N	17.5	0.25	6.3	0.09
Cl ⁻	18.6	0.64	6.7	0.23
HCO ₃ ⁻	28.1		10.1	
DN		0.53		0.19
DON		0.08		0.03
DP		0.007		0.003
ALK*	- 2.4		- 0.4	
ALK**	-29.4		-10.6	

* ALK = 2(Ca⁺⁺) + 2(Mg⁺⁺) + (Na⁺) + (K⁺) + (NH₄⁺) - 2(SO₄⁻) - (NO₃⁻) - (Cl⁻)

** NH₄⁺ → NO₃⁻

June which did not contain dust particles and to the freshly fallen snow of September 1984, yearly deposition rates (table 4) can be inferred: $0.53 \text{ g m}^{-2} \text{ SO}_4^{2-} - \text{S}$, $0.25 \text{ g m}^{-2} \text{ NO}_3^- - \text{N}$, $0.19 \text{ g m}^{-2} \text{ NH}_4^+ - \text{N}$ and $0.024 \text{ g m}^{-2} \text{ H}^+$. The deposition of inorganic nitrogen equals that of sulphate on an equivalence basis. On a weight basis, the same amount of total dissolved nitrogen and sulphate-sulphur ($0.53 \text{ g m}^{-2} \text{ yr}^{-1}$) is deposited.

4. DISCUSSION

4.1 CORRELATION BETWEEN SINGLE PARAMETERS

The best positive linear correlation of proton activity (for $\text{pH} \leq 5.7$ only) exists with NO_3^- , SO_4^{2-} and DN (fig. 6, table 5). A good correlation can also be found between NH_4^+ and SO_4^{2-} ($r=0.84$) but not between SO_4^{2-} and NO_3^- ($r=0.56$) or between NH_4^+ and NO_3^- ($r=0.63$). Correlation coefficients are best ($r=0.97$) between $(\text{Ca}^{++}, \text{Mg}^{++})$ and HCO_3^- . Chloride shows only low correlation with Na^+ , Ca^{++} and Mg^{++} . Total dissolved phosphorus does not seem to be correlated with any other parameter.

Table 5: Correlation coefficients (linear regression) between different ions, DN and DP ($n=37$)

	Ca^{++}	Mg^{++}	Na^+	K^+	NH_4^+	NO_3^-	SO_4^{2-}	Cl^-	HCO_3^-	DN	DP
H^+	-0.39*	-0.37*	-0.39*	-0.32*	0.65**	0.81*	0.75**	0.06**	-0.44	0.78**	0.26
Ca^{++}		0.97*	0.74*	0.52*	0.41*	0.05*	0.64*	0.51*	0.97*	0.22*	0.17*
Mg^{++}			0.75*	0.55*	0.39*	0.04*	0.54*	0.44*	0.97*	0.21*	0.21*
Na^+				0.85*	0.20*	0.14*	0.33*	0.53*	0.71*	0.23*	0.16*
K^+					0.14*	0.07*	0.24*	0.39*	0.53*	0.17*	0.24*
NH_4^+						0.63	0.84	0.24	0.26	***	0.00
NO_3^-							0.56	0.20	0.03	***	0.02
SO_4^{2-}								0.35	0.42	0.72	0.09
Cl^-									0.41	0.24	0.05
HCO_3^-										0.10	0.20
DN											0.08

* $n=34$

** $\text{pH} \leq 5.7$ $n=23$

*** not determined

4.2 IMPORTANCE OF NO_3^- AND SO_4^{2-} FOR THE ACIDITY OF PRECIPITATION

To answer the question whether the precipitation's acidity at high mountain altitudes is more affected by nitric or sulphuric acid, a multiple linear regression was calculated between the parameters H^+ , NO_3^- and SO_4^{2-} . Proton activity could be best approximated by the following equation, based on equivalence values:

$$(\text{H}^+) = 2.3 + 0.6 (\text{NO}_3^-) + 0.3 (\text{SO}_4^{2-}) \quad (1)$$

with a correlation coefficient of $r=0.87$ ($n=23$).

Galloway and Dillon (1983) called attention to the constantly increasing importance of nitric acid for the acidity of precipitation in the USA. It is made evident by the equivalent ratio of NO_x/SO_2 for emissions (0.5 to 0.6 in 1980) showing upward tend-

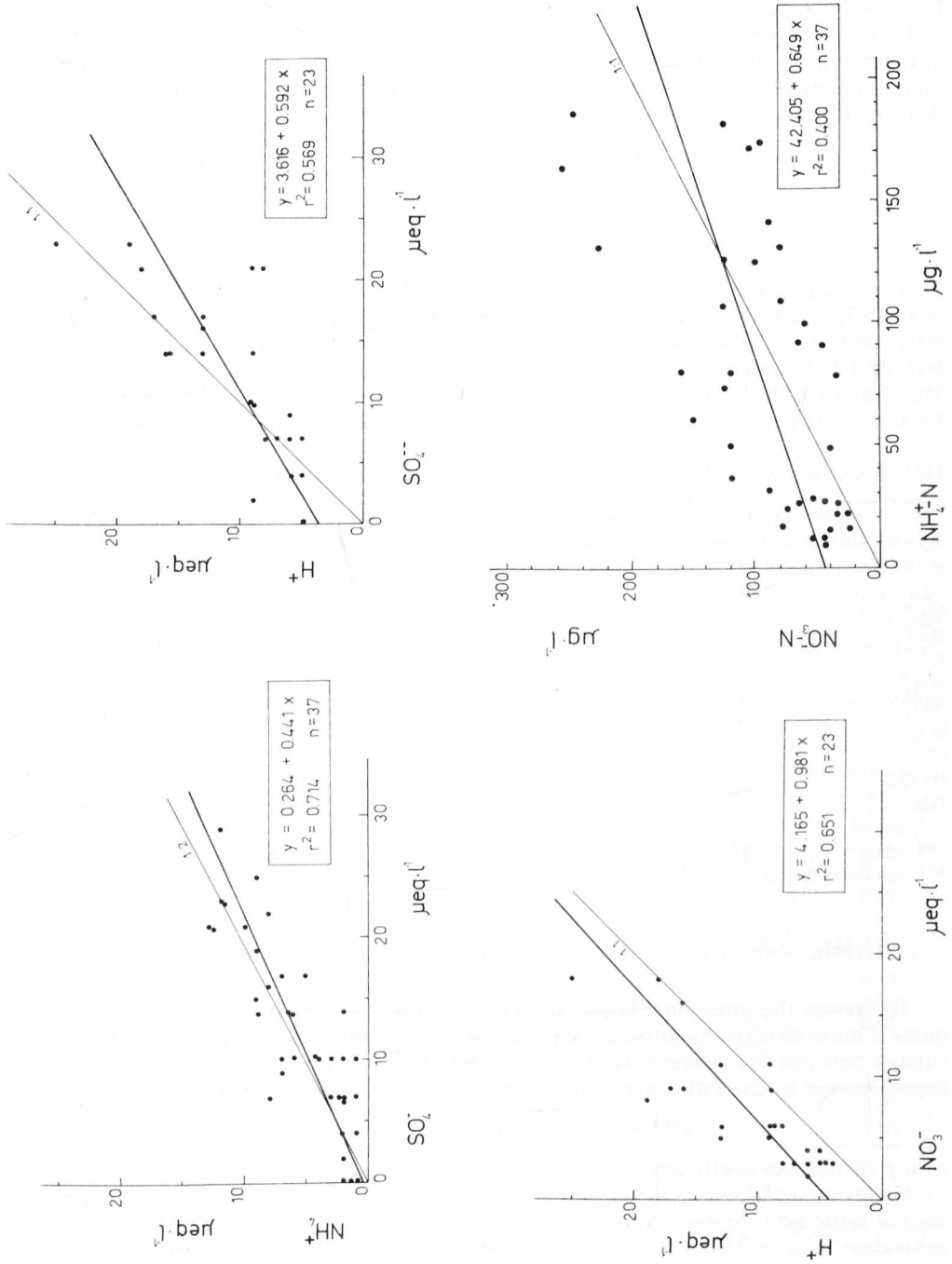


Fig. 6: Linear regression between proton, sulphate, nitrate and ammonium concentrations, and determination coefficients (r^2). Badeis and Teufelseck, 13 Juni 1984

ency as well as the ratios NO_3^-/H^+ and $\text{SO}_4^{2-}/\text{H}^+$. In 1961 the corresponding numbers were 0.32 and 0.98, changing till 1980 to 0.46 and 0.66. The sum of the 2 ratios is generally greater than 1.

Mosello et al. (1985) showed that sulphate concentrations in bulk desposition at lake Maggiore (Italy) decreased by 15 % during the last decade. In the same period (1975–84) nitrate increased by 60 %.

Schotterer et al. (1984) found a similar trend taking firn-samples at Colle Gnifetti (Monte Rosa, Switzerland). Between 1963 and 1977 the ratio $\text{NO}_3^-/\text{SO}_4^{2-}$ amounted to approximately 0.30 and changed into 0.63 from 1977 to 1981, which corresponds quite well to the results of Hintereisferner.

Comparable measurements in Tyrol are available from Puxbaum et al. (1985). The ratios between H^+ , NO_3^- , SO_4^{2-} , Cl^- and NH_4^+ can be seen in table 6. For sulphate, nitrate and protons the differences between Hintereisferner and the lower situated stations of Kufstein, Reutte and Achenkirch are small. At Hintereisferner the $\text{Cl}^-/\text{SO}_4^{2-}$ ratio is approximately 4 times higher, the $\text{NH}_4^+/\text{SO}_4^{2-}$ ratio twice lower than at Kufstein, Reutte and Achenkirch.

Table 6: Comparison of sulphate, nitrate, proton, chloride and ammonium ratios from lower situated (wet only) stations in Tyrol (Kufstein, Reutte, Achenkirch) (from Puxbaum et al. 1985) with Hintereisferner

	Kufstein	Reutte	Achenkirch	Hintereisferner	
				all samples	for $[\text{H}^+] \geq 5 \mu\text{eq l}^{-1}$
$\text{SO}_4^{2-}/\text{H}^+$	1.34	1.38	2.14	1.63	1.14
NO_3^-/H^+	0.85	0.85	1.28	0.90	0.67
$\text{NO}_3^-/\text{SO}_4^{2-}$	0.64	0.63	0.60	0.56	0.63
$\text{Cl}^-/\text{SO}_4^{2-}$	0.12	0.17	—	0.56	—
$\text{NH}_4^+/\text{SO}_4^{2-}$	0.93	0.77	0.95	0.43	—

If we compare the mean annual concentrations at these stations with those at Hintereisferner, the corresponding numbers are:

	valley/glacier
SO_4^{2-}	4
NO_3^-	4
Cl^-	1
NH_4^+	10
H^+	4

If we assume that all chloride in precipitation originates from sea spray, the marine part of sulfate accounts for 17 % of SO_4^{2-} .

As already mentioned above, Galloway and Dillon (1983) found that in most cases the sum of NO_3^-/H^+ and $\text{SO}_4^{2-}/\text{H}^+$ was greater than 1. At Hintereisferner, however, this sum reaches a value of 2.5 (or 1.8 for $[\text{H}^+] \geq 5 \mu\text{eq l}^{-1}$), respectively. This might be explained by the fact that approximately 50 % of the sulfuric acid is buffered by ammonia (fig. 6). This is similarly valid for the stations of Schönberg and Innsbruck (both Tyrol, not yet published).

Schnoor et al. (1983) mention that H_2SO_4 can react with NH_3 to form NH_4HSO_4 or $(\text{NH}_4)_2\text{SO}_4$ aerosols. In addition, the NH_4NO_3 aerosols are in equilibrium with $\text{NH}_3(\text{gas})$ and $\text{HNO}_3(\text{gas})$.

4.3 EFFECTIVE ACIDITY

According to Schaug and Semb (1976) it should be realized that $(\text{NH}_4)_2\text{SO}_4$ may act as a strong acid in a natural ecosystem. They found that in southern Norway the proportion of NH_4^+ to SO_4^{2-} increases in air masses of continental origin. The authors pointed out that precipitation acidity (free H^+ at $\text{pH} \leq 5$) was generally determined by the following equation:

$$(\text{H}^+) = 2(\text{SO}_4^{2-}) + (\text{NO}_3^-) - (\text{NH}_4^+) \quad (2)$$

We found, based on equivalence values, the following relationship:

$$(\text{H}^+) = 2.1 + 0.8(\text{NO}_3^-) + 0.5((\text{SO}_4^{2-}) - (\text{NH}_4^+)) \quad (3)$$

with a correlation coefficient of $r = 0.87$ ($n = 23$).

Galloway and Dillon (1983) pointed out that in terrestrial ecosystems considerable amounts of ammonium are retained. Therefore it must be regarded as a potential acid. Oxidation to nitrate produces 2, adsorption by plants 1 equivalent of acidity. A comparison of 50 high mountain lakes in Tyrol with the precipitation in that area suggested that approximately 80% of ammonium is oxidized to nitrate. Average lake water had only $\frac{1}{5}$ of the mean ammonium concentration of precipitation but more than twice the concentration of nitrate (Psenner, Zapf, Nickus and Arzet 1986). By assuming that all NH_4^+ oxidizes to NO_3^- , an annual deposition of approximately 30 meq m^{-2} of mineral acidity results (table 4).

4.4 COMPARISON WITH OTHER HIGH MOUNTAIN STATIONS

The volume-weighted average pH of the whole snow cover at Hintereisferner was 5.1 at Badeeis and 5.2 at Teufelseck. The median of all samples was pH 5.2. Since the variations in snow chemistry from year to year and between nearby situated stations do not seem to be very great (table 7), the estimation of an "average" precipitation for high altitude stations in Tyrol is possible within certain limits of time and distance. It is characterized by a pH value of 5.2, an ammonium concentration of $5 \mu\text{eq l}^{-1}$, a nitrate concentration of $8 \mu\text{eq l}^{-1}$ and a sulphate concentration of $12 \mu\text{eq l}^{-1}$.

Table 7: Precipitation chemistry of Hintereisferner and Kühtai (Stubai Alps) in 1984 and 1985

Station	Altitude m a. s. l.	Sampling Period	Number of samples	pH	H^+	NH_4^+	NO_3^-	SO_4^{2-}	Cl^-	DN	DON	DP
					$\mu\text{eq l}^{-1}$							
Hintereis- ferner	3070 m	Oct. 83—June 84	14	5.18	7	6	8	13	9	239	50	3
	3150 m	Oct. 83—June 84	23	5.06	9	5	6	12	7	192	34	3
	3150 m	Oct. 84—May 85	21	5.15	7	5	8	10	6	237	50	1
Kühtai	2415— 2500 m	Nov. 84—Apr. 85	30	5.16	7	3	8	13	4	190	36	2

Tripet and Wiederkehr (1983) assumed a mean pH of approximately 5.0 for high mountain regions in the inner part of Switzerland, whereas typical swiss rain water has a pH of 4.3 (Zobrist and Stumm 1983). In ice cores taken at Monte Rosa (Switzerland), the range of pH values, nitrate and sulphate concentrations were similar to those at Hintereisferner. Schotterer et al. (1984) also pointed out the enormous influence of dust fall from the Sahara desert on the chemistry of precipitation. On Hintereisferner, one single event of dust fall is able to neutralize the mineral acidity of the whole snow pack.

The mean concentration of cations and anions at Hintereisferner is comparable to that at high mountain stations in Switzerland (table 8). Apart from Ca^{++} , Mg^{++} (both heavily affected by dust fall) and Cl^- , the chemical composition of snow equalled that at Colle Gnifetti. Mosello and Tartari (1982) measured pH values of 4.8 to 5.5 in higher regions of the Piedmont Alps (Italy), whereas in the discharge area of Lake Maggiore, precipitation was significantly more acidic with a pH from 4.3 to 4.5. Such values are typical for (wet only) stations in Tyrol and Salzburg (Austria) at altitudes between 500 and 1000 m a. s. l. (Puxbaum et al. 1985, Rassaerts et al. 1985).

Table 8: Average concentration of cations and anions in precipitation at Jungfrauoch, Colle Gnifetti (both Switzerland; from Zobrist 1983) and at Hintereisferner

	Jungfrauoch 3570 m mg l^{-1}	Colle Gnifetti* 4450 m mg l^{-1}	Hintereisferner 3150 m mg l^{-1}
Ca^{++}	0.69	0.086	0.320
Mg^{++}	0.06	0.010	0.028
Na^+	0.24	0.050	0.055
K^+	0.20	0.060	0.030
$\text{NH}_4^+ - \text{N}$	0.19	0.085	0.071
$\text{SO}_4^- - \text{S}$	0.38	0.160	0.195
Cl^-	0.42	0.079	0.252
$\text{NO}_3^- - \text{N}$	0.14	0.068	0.087
pH	5.4	5.4	5.1

* without dust layers

In 1982/83 the yearly average pH of 3 stations situated at 2000–2200 m a. s. l. in the Italian Alps was 4.8, 5.1 and 5.3, respectively (Gruppo di Studio 1985). The concentration of sulphate, nitrate and ammonium, however, was distinctly (more than 3 times) higher than at Hintereisferner. In Ticino (Switzerland) Stumm and Righetti (1982) observed a mean pH of 4.5 in snow at 2000 m a. s. l. Smidt (1985) found that in Zillertal (Tyrol) nitrate and sulphate deposition decreased with increasing altitude, but proton deposition increased from $5 \text{ mg m}^{-2} \text{ yr}^{-1}$ at 600 m a. s. l. to $20 \text{ mg m}^{-2} \text{ yr}^{-1}$ at 1720 m a. s. l. In Switzerland, Zobrist (1983) observed a significant decrease in concentrations only above 3600 m a. s. l.

The precipitation on Hintereisferner is very similar to that of background areas in Norway and Canada (Wright 1983). Actual concentrations of sulphate and nitrate in snow from South Greenland are both approximately five times lower, i. e. $2 \mu\text{eq l}^{-1}$ (Neffel et al. 1985).

Little information exists on dissolved organic nitrogen (DON) concentrations and

depositions. At high mountain stations in Tyrol it was between 34 and 50 $\mu\text{g l}^{-1}$ (table 7). Timperley et al. (1985) give a world-wide reference list of DON deposition values which range from 0.10 to 1.05 $\text{g m}^{-2} \text{yr}^{-1}$. The DON deposition at Hintereisferner was at the lower end of this scale (0.08 $\text{g m}^{-2} \text{yr}^{-1}$).

A direct comparison of concentrations of dissolved substances in snow and rain is significant for stations with similar annual precipitation levels. In other cases it is better to compare yearly deposition rates. Nevertheless, the differences between intensity and capacity factors should be taken into consideration. The proton deposition of 0.024 g m^{-2} at Hintereisferner corresponds to that of lower situated stations in Tyrol with a mean pH of 4.4 to 4.6.

In the future more attention should be paid to the analysis of distance-height-profiles, the meteorological conditions during single events and the interactions between precipitation, melting water, soils and lakes.

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