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# Comparative chemical characteristics of precipitation in the Hornsund region (SW Spitsbergen) in the years 1993–1994 and 1998–1999

ABSTRACT: Certain chemical parameters such pH, specific electric conductivity (SpC) and concentrations of chloride ions (Cl-) have been analysed in samples of precipitation collected close to the Polish Polar Station at Hornsund (PPS), SW Spitsbergen. On the basis of seasonal data from years 1993-1994 and 1998-1999, some differences are apparent from the two sets. There is also a marked difference in the seasonal results, especially with respects to pH values; summer precipitation (pH of which can be as low as 3.78) is much more acidic than winter. This was particularly notable in respect of the summer of 1993, and was presumably the result of a relatively unusual atmospheric circulation and a high influx of airborne contaminants from Europe. The wide variation in specific electrical conductivity measurements is considered to be related to variations in wind direction and speed. That precipitation the highest total dissolved salts, of 11.7 mm w.e. (water equivalent), (November 1993), provided 10.7 g of salt per square metre of tundra near the Polish Polar Station. The proximity of the sea, consequently the development of marine aerosols, largely determines the chemical nature of the precipitation. Thus, variations in the chloride ion concentrations during the study periods more or less reflect the variations in the marine aerosol influences on the nature of the polluted precipitation. An analysis of the atmospheric circulation reveals that the most acid precipitation occurs most frequently in the C-8 type of circulation (cyclonic S + SW) and also, less so, for type C-3 (anticyclonic S + SW).

Key words: Arctic, Spitsbergen, Hornsund, precipitation, atmospheric circulation.

# Introduction

Hornsund is situated on the western coast of SW Spitsbergen. The precipitation is relatively high when compared with the Arctic regions as a whole. In the last de-

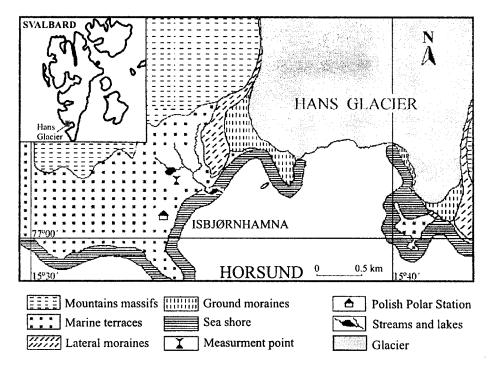


Fig. 1. Location of studies.

cade of the 20th Century, a rising trend was observed especially in summers. In the years 1990-2000, the annual average precipitation was 472.5 mm w.e. (Mietus 1990–2000) which was higher than the annual average precipitation for the years 1978–1989 by over 66.5 mm w.e. ( $\Sigma = 406$  mm). By comparison, inland meteorological stations recorded only half the amounts present on the western coast (Niedźwiedź and Ustrnul 1988). This reflects the influence of warm Gulf Stream current, which impinges on the western coast of Svalbard and creates a relatively moist climate there. In this area, the PPS staff have been working continuously since 1978 on year-long meteorological monitoring problems. There have been regular and frequent precipitation measurements and these form the basis of the present work. In 1986, it was decided to start regular monitoring of the chemical nature of the precipitation, the objective being to try to shed further light on the natural processes operating in the Polar Environment and how these are influenced by human impact. This "environmental programme" included not only issues concerning variations in the chemical composition of precipitation there, but also the chemistry of surface water in the Hornsund area. Analyses were made at the PPS; these included the measurements of pH, specific electrical conductivity and concentration of chloride ions. In 1993, the analytical programme was further extended by measurements of concentrations of heavy metals (e.g. Cu, Zn, Pb and Cd) in surface waters (Burzyk and Głowacki 1998).

A further aim of these investigations is to try to determine the amount of solid loads, which reach the ground surface along with precipitation water. It is known that excess of load (e.g. concentration of hydrogen ions) cannot be buffered by some kinds of rocks (Kulicki, Piasecki and Sobik 1994) and so may have a great influence on certain geomorphological and environmental processes.

The closeness of the ocean to Hornsund results in the presence of significant amounts of chloride ions in the air there (in the form of marine aerosols) and therefore these have a considerable influence on the chemical composition of precipitation. Thus, by systematically collecting and analysing samples of precipitation the variable amounts of chloride ions and their onshore transport can be monitored throughout the year as well as that of another ions (e.g. K<sup>+</sup>, Na<sup>+</sup>) (Marks 1978). Transport range and routes are different in various parts of the archipelago (Głowacki and Pulina 2000). Certainly, the paths taken by air flow in the Southern region of West Spitsbergen and their velocity depend on the type of circulation involved (Niedźwiedź 1987, 1993, 1997a). The data presented here are the results of measurements carried out during the 16th (1993–1994) and the 21st (1998–1999) Polar Expeditions to Hornsund (West Spitsbergen), organized annually by the Institute of Geophysics of the Polish Academy of Sciences.

## Methods

At the collecting point situated in the Fugleberget catchment, about 500 metres NE of the Station (Fig. 1), a 2 metres-high tripod carrying a precipitation funnel was deployed. By means of the funnel, samples of precipitation were collected during the summer in a 0.5 litres, polythene bottles. It was considered important to try to collect every precipitation which had a water equivalent higher than 0.5 mm. In winter, as well as in the funnel (for wet precipitation), snow samples were collected by means of a clean bowl (one cleared by distilled water). Values of pH in the rain and melt water sample were measured by means of a pH-meter (a CP-315 Elmetron model – accurate to 0.01). Specific electrical conductivity (which can inform about the mineral content of the sample) was measured using a conductivity-meter (CC-315 Elmetron model accurate to 1 µS/cm). Analysis of the concentration of chloride ions was carried out by Mohr's titration method (Krawczyk 1996). In the 1993–1994 period, 72 samples of precipitation from the Hornsund region were analysed while 43 samples were measured in the years 1998–1999. This comprises over 60% of all observed precipitation in which water equivalent was higher than 0.5 mm. Definition of "winter" and "summer" is based on temperature change. A positive average day temperature was adopted as "summer" and the converse for "winter". The duration of these periods and the average values of basic meteorological parameters are illustrated in Table 1.

Table 1	
Meteorological characteriscics during the study periods 1993–1994 and 1998–1999	
at Hornsund, Spitsbergen.	

Year		1993/1994	1998/1999	1993	1998	1993/1994	1998/1999
Expedition		Hornsund XVI	Hornsund XXI	summer	summer	winter	winter
Period	dates	01.07-30.06	01.07-30.06	04.0614.09	01.06-23.09	15.09-03.06	24.09-04.06
Number of days		365	365	103	115	262	254
	mean	-4.1	-3.2	3.2	3.6	-6.9	6.3
Average daily temperature [°C]	max.	9.3	10.8	9.3	10.8	3.4	2.7
temperature [ C]	min.	-23.2	-20.6	-1.0	-0.5	-23.2	20.6
Energy	PDD (+)	386.2	472.4	330.1	411.6	49.5	36.2
[degree-days]	NDD (-)	-1873.5	-1625.0	-4.8	-1.3	-1871.1	-1624.2
Average daily	mean	5.9	6.3	4.5	4.4	6.3	7.1
wind speed	max.	22.3	17.5	14.1	14.0	22.3	17.5
[m/s]	total	2139.4	2298.8	466.8	511.2	1661.7	1806.8
	mean	1.8	1.4	1.6	1.6	1.6	1.2
Precipitation [mm w.e.]	max.	26.8	27.1	16.8	18.7	26.8	27.1
[IIIIII w.e.]	total	431.0	350.6	76.4	83.6	317.3	225.5
Sunshine [hours]	duration	1125.7	1060.9	619.2	648.2	543.2	585.6

Table 2 pH values in precipitation in the 1993–1994 and the 1998–1999 study periods at Hornsund, Spitsbergen.

Period	Total number	Number o	f samples	Total range of values	Range of values (summer)	Ave summer	rage winter
	of samples	summer	winter	pН	pН	Нq	pН
1993-1994	72	17	55	3.78-5.81	4.38-5.55	4.86	4.64
1998-1999	43	9	34	3.88-5.84	4.18-5.61	4.79	4.95

# Chemical characteristics of precipitation

Contaminants are removed from the atmosphere by several processes. Either they are captured when raindrops or snow crystals form in a cloud or when the rain or snow actually falls (Arctic Monitoring and Assessment Programme 1997). These processes influence the physical and chemical properties of precipitation (especially in terms of their pH and SpC). However, it is far from clean to what extent marine aerosols influence the primary chemical composition of precipitation. Determination of the concentrations of chloride ions in suitable samples may help to solve this problem.

# pH determination

In some chemical processes which take place in the atmosphere hydrogen ions (H<sup>+</sup>) are released (Berner and Berner 1987). Concentration of these ions deter-

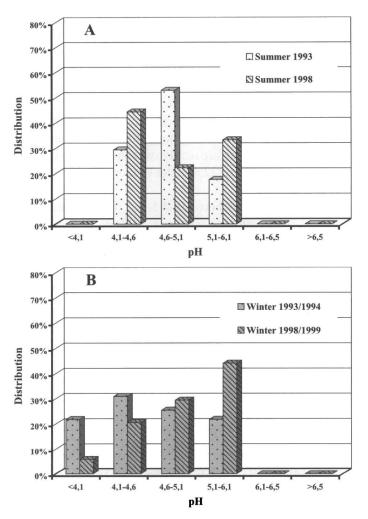


Fig. 2. Distribution of pH in Summer (A) and Winter precipitation (B) 1993–1994 and 1998–1999 in South Spitsbergen.

mines the value of the pH. A low value of pH means that the concentration of hydrogen ions is high and the water has an acid character. The values of pH measured during the years 1993–1994 and 1998–1999 indicate that precipitation was (in terms, that is, of the acidity scale used in Germany (Jansen, Block and Knaack 1988). There are no significant differences in the values of pH obtained in any of the study years (Table 2).

For corresponding seasons, the minimum value of pH was 3.78 (1993–1994) and 3.88 (1998–1999) i.e. the precipitation was very acid; – both of these values were derived from winter precipitation. The maximum values were similar (5.81 and 5.84); these were also winter measurements. In fact, these values are very close

to the natural value of pH i.e. that of non-polluted precipitation. The average values for comparable summer and winter periods varied only insignificantly  $-\pm 0.2$  of the value of pH. In the winter of 1993–1994, values of pH of precipitation was lower whereas in 1998–1999, the lower pH values characterized the summer. Their distribution was presented in the form of a histogram (Fig. 2) as recommended by Jansen and others (1988) and Leśniok (1996).

The distribution of pH values thus displayed shows certain differences between summer and winter precipitation. Among summer samples, none has a pH < 4.1 (highly acid). In winters which are nearly twice as long as summers some precipitation with pH < 4.1 took place (22% in the Winter of 1993–1994 and 6% in the Winter of 1998–1999).

Rain samples with pH values between 4.1–4.5 (considerably acid) comprise nearly 29% (summer 1993) and 45% (summer 1998) of all summer rain samples. In winter the corresponding levels are 31% and 41%.

Over half (53%) of all 1993 Summer precipitation and about 22% of all samples in the Summer 1998 are situated between pH values 4.6–5.0 (slightly acid). In Winter they comprise 25% (1993–1994) and 29% (1998–1999).

The values of pH between 5.1–6.1 (normal) are more often present in summer: 18% (1993) and 33% (1998); in winter: 5% (1993–1994) and 10% (1998–1999).

No sample above 6.1 (alkaline precipitation) has been identified in these study periods.

The cumulative loads of hydrogen ions ( $H^+$ ) which reached the ground were c. 10 mg/m<sup>2</sup> in the Winter of 1993–1994 but only 1.6 mg/m<sup>2</sup> in the Summer of 1998.

# Specific electrical conductivity (SpC)

SpC relates the quantity of dissolved substances (e.g. salts and products of their hydrolysis – acid and alkaline) in water. The measured values of SpC ( $\mu$ S/cm) have been classified temporally (Table 3).

Table 3 SpC values in precipitation in the 1993–1994 and the 1998–1999 study periods at Hornsund, Spitsbergen.

Period	Total number of samples	Number of samples		Total range of values	Range of values (summer)	Average	
						summer	winter
		summer	winter	μS/cm	μS/cm	μS/cm	μS/cm
1993-1994	72	17	55	9-2030	11-418	108	134
1998-1999	43	9	34	1-134	6-45	29	34

The SpC values of precipitation occasionally differed – the maximum value of SpC in winter 1998/1999) was 134  $\mu$ S/cm whereas it was 2030  $\mu$ S/cm for the Winter of 1993–1994. The highest SpC (2030  $\mu$ S/cm) was measured during a storm, which must have had a considerable influence on the chemical composition of the attendant rainfall.

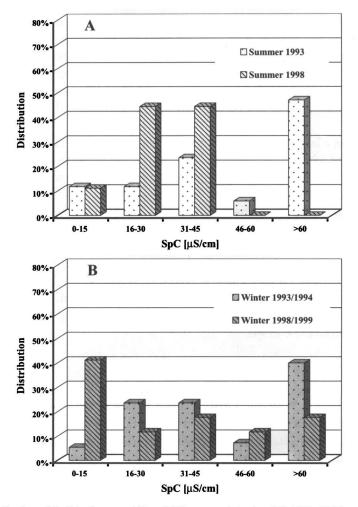


Fig. 3. Distribution of SpC in Summer (A) and Winter precipitation (B) 1993–1994 and 1998–1999 in South Spitsbergen.

As with the pH values, the SpC values were classified according to the recommendation of Jansen and others (1988) and shown in the form of a histogram (Fig. 3).

Rains containing only small amounts of dissolved salts (0–15  $\mu$ S/cm) were present in 12% of all the Summer 1993 precipitation and c. 5% of the Winter rains of 1993–1994. In 1998–1999, such water comprised 11% of Summer precipitation and c. 41% of Winter. In this case a significant difference (36%) was observed only in respect of the Winters.

Slightly higher values of SpC (16–30  $\mu$ S/cm) were noted in the years 1993–1994: 24% of all precipitation water in Winter and 12% in Summer and the converse of these figures for the years 1998–1999 – 12% in Winter and 44% in Summer. Summer rainfall of this type differ significantly – by as much as 32%.

Rainfall in which the degree of mineralization is considerable (31–45  $\mu$ S/cm) took place in a similar number of Winters. By contrast in Summer 1998, the number of such highly mineralized rainfalls doubled in the Summer of 1993.

The 1998 Summer was characterized by a lack of precipitation within the range  $46{\text -}60~\mu\text{S/cm}$  (high SpC) whereas about 6% was present in the water from the same period of 1993. The corresponding Winter had similar values of SpC in this range.

There was a large number of strongly mineralized rainfalls (over  $60 \mu S/cm$ ) in the Summer of 1993 (47%), whereas there was none in the Summer of 1998. The Winter of 1993–1994 is similarly represented (40%) whereas in the same period of 1998–1999, only 18% occurred.

The significant differences in SpC values between comparable years is also shown by the values of cumulative loads of salts which fell on an area of 1 km² in the southern region of Spitsbergen (Hornsund); 2.2 tons/km² accumulated in the Summer of 1993 but only 0.9 tons/km² in the corresponding period of 1998. The load of salts (nearly 18 tons/km²) delivered in Winter 1993–1994 was ten times higher than in the same period of 1998–1999 (only 1.7 tons/km²). It was calculated by multiplying the SpC values by a characteristic (for this region) and appropriate coefficient (Krawczyk 1994).

#### Concentration of chloride ions

Atmospheric precipitation contains chloride ions which evidently derive from several sources. The main source of chlorides is marine aerosols. Therefore, chloride ions should be a reliable indicator in the determination of the amount of Sea salt in precipitation (Berner and Berner 1987). Another source of chlorides is anthropogenic – that HCl delivered to the atmosphere by industry (Junge and Werby 1958). As precipitation collecting point was situated on a raised marine terrace, about 500 meters NE from the Polish Polar Station at Hornsund, and (500 m) to the sea shore, it is hardly surprising that rather high concentrations of chlorides (mg/dm³) are measured in precipitation samples there. Analysis of these shows that, in spite of high concentrations of chloride ions, which significantly influence the values of SpC, other ions (e.g. K<sup>+</sup>, Na<sup>+</sup>) are also present. Classified concentrations of chloride ions are shown in Table 4.

Table 4 Chloride concentration in precipitation in the 1993–1994 and the 1998–1999 study periods at Hornsund, Spitsbergen.

	Total			Total range	Range	Average		
Period	number	Number of samples		number of samples	number of samples of values of values (summ	of values (summer)	summer	winter
	of samples	summer	winter	mg/dm <sup>3</sup>	mg/dm <sup>3</sup>	mg/dm <sup>3</sup>	mg/dm <sup>3</sup>	
1993-1994	72	17	55	4–509	4–76	21	36	
1998-1999	43	9	32	1–35	4–15	10	11	

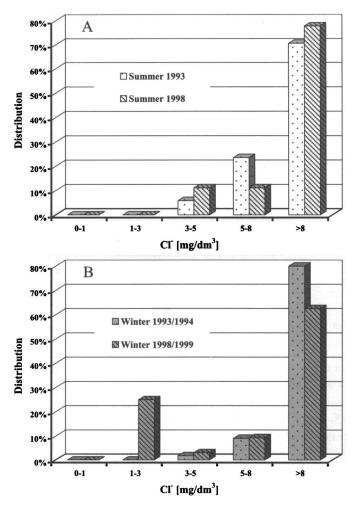


Fig.4. Distribution of chloride ion concentration in (A) and Winter precipitation (B) 1993–1994 and 1998–1999 in South Spitsbergen.

The range of measured values of chloride ions is wide – 4–509 mg/dm³ in the years 1993–1994 and 1–35 mg/dm³ in 1998–1999. A few unusually high concentrations of chlorides (181, 227, 509 mg/dm³) were directly related to specific unusual meteorological conditions. During rainfall, a strong onshore storm and high waves breaking on the coast, deliver huge amounts of marine aerosol onto the raised marine terraces. It is undoubtedly this effect which caused the significant increase of chloride ions in the precipitation.

The whole observations of changes of chloride concentrations concerning both periods (1993–1994 and 1998–1999) are shown similarly to pH and SpC in the form of comparative histogram (Fig. 4). Note that precipitation samples containing only very small concentrations of chloride ions (0–1 mg/dm<sup>3</sup>) are absent. The

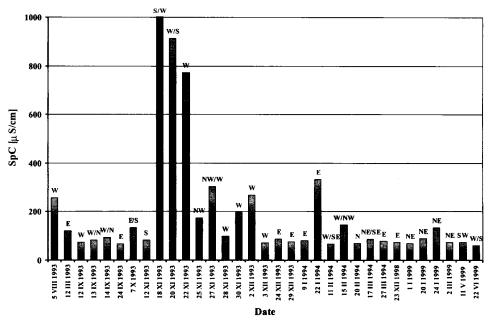


Fig. 5. Values of SpC in some high mineralizing precipitation relative to different wind direction.

slightly higher concentration (1–3 mg/dm<sup>3</sup>) is represented by only 25% in the Winter of 1998–1999. The 3–5 mg/dm<sup>3</sup> category is represented in both Winter and Summer periods, but does not exceed 10% at any time. Rather high concentrations of chlorides (5–8 mg/dm<sup>3</sup>) were observed in the Winter (about 9%) and rather more often in Summer (24%). Significantly, most of the >8 mg/dm<sup>3</sup> samples (89% in Winter and 71% in Summer) are situated in this category i.e. that in which the concentrations of chloride ions are high.

#### Chloride ion loads

By knowing the concentration of Cl<sup>-</sup> ions (mg/dm<sup>3</sup>) in any particular sample and also the amount of precipitation (mm w. e.) it is possible to calculate the loads of Cl<sup>-</sup> ions (in grams) which reaches the land and falls on any particular area (m<sup>2</sup>). Analyse of the data shows that loads delivered from the sea are clearly dependent on particular meteorological conditions, especially with respect to the level of the precipitation and the wind speed. Strong winds which blow from the W, S and, especially, the E (from the interior of the fiord) significantly increase the delivery of high loads of Cl<sup>-</sup> (Fig. 5). Storms also deliver the highest loads of chlorides; these loads are much higher than the all-year-round average. The average load of chloride ions which reached the ground in the Summer of 1993 was c. 1 g/m<sup>2</sup> but it was >10 g/m<sup>2</sup> in the Winter of 1993–1994 (6 g/m<sup>2</sup> relates to a particularly heavy rainfall on November 18<sup>th</sup>, 1993). In the Summer of 1998 the average load delivered was about 0.7 g/m<sup>2</sup> whereas it was only 1.3 g/m<sup>2</sup> in the Winter. In the 1998–1999 sea-

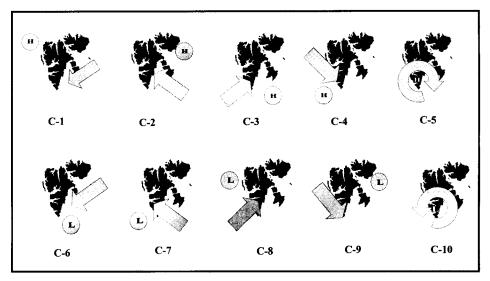


Fig. 6. Types of circulation in Spitsbergen (after Niedźwiedź 1997a): C-1 to C-5 anticyclonic situations; C-6 to C-10 cyclonic situations.

son there were no storms despite an average wind speed (6.5 m/s) being higher than that of the 1993–1994 season (5.8 m/s).

### Circulation

The influx of contaminants and aerosols into the study area must be related to atmospheric circulation in this region of the Arctic (Miętus 1996). 11 types of circulation were detailed for Spitsbergen (Niedźwiedź 1997a) (Fig. 6). The frequency of different circulation types (for the study years) is shown by histograms (Fig. 7). Anticyclonic circulations were dominant in the Summers. Two of these were predominant: C-5 (>30%) and C-2 (>20%). By contrast cyclonic circulation dominated in Winter, especially C-7 winds from the directions E+SE (25%).

The most acid precipitation is associated with cyclonic S+SW C-8 circulation (30%) and anticyclonic S+SW C-3 circulation (over 20%). The frequency of very acid precipitation is clearly related to the type of circulation what shows Fig. 8. Apparently very acid rains never occur during anticyclonic N+NE circulation.

When comparing the incidence of circulations responsible for transport of acid rains seasonally to the Spitsbergen region it is obvious that they occurred twice more often in the Summer of 1993 than in 1998. This result closely corresponds with data summarised in Table 2 and Fig. 2.

### Conclusions

For both study periods there were relatively low annual totals of precipitation (431 mm and 350.6 mm). Moreover, they are appreciably lower than the average for

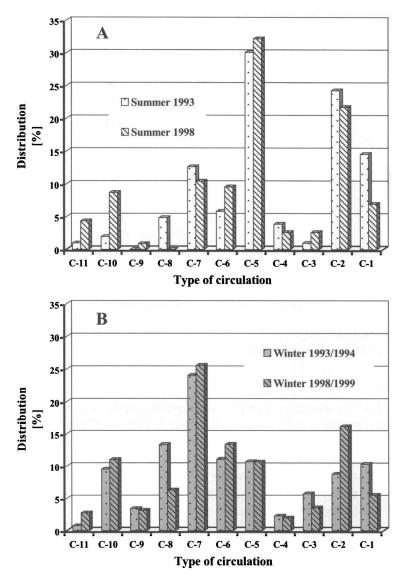


Fig. 7. Distribution of circulation in Summer (A) and Winter precipitation (B) 1993–1994 and 1998–1999 in South Spitsbergen.

the period 1990–2000 (472.5 mm). When the precipitation levels totals for polar summers (June – September) are compared, it is obvious that the study periods were the driest of all; further, the precipitation in the Summer of 1993 (76.4 mm) was the lowest in the entire decade. Therefore 1993–1994 and 1998–1999 years were atypical of the rainfall in this area. Chemical analysis of representative samples shows that:

1. In spite of the acidic character of the precipitation, the average pH for Winter precipitation slightly increased from 4.64 to 4.95 but was constant with respect the

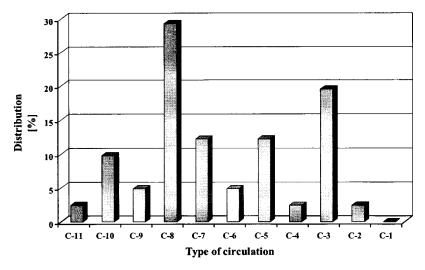


Fig. 8. Distribution of type circulation in the some very accid precipitation 1993–1994 and 1998–1999 in South Spitbergen.

Summers. Two factors appear to have influenced this – a decrease in the emission of various industrial gases in Europe; secondly the lesser tendency of air advection from the east (as suggested by some authors).

In spite of the acidic character of the precipitation, the annual cumulative load of hydrogen ions is nevertheless less than 12 mg/m²/year. Such a load still can be neutralised by the bedrock chemistry consisting, in this area, of quartzites, gneiss and amphibolites. Limestones and dolomites are able to buffer slightly higher loads.

- 2. In the case of the SpC, a significant decrease of average values was observed in all comparable periods. From 134  $\mu$ S/cm (1993–1994) to 34  $\mu$ S/cm (1998–1999) in Winters and from 108  $\mu$ S/cm to 29  $\mu$ S/cm in corresponding Summers. This means that the dissolved salt content is apparently decreasing. Consequently, a significant decrease of deposition of salts (from 20 t/km² to 2.6 t/km²) ought to be taking place.
- 3. Owing to proximity of the sea chloride ions are persistently being delivered to the raised marine terraces. Their concentrations in precipitation water could increases significantly so during storm conditions. Wind direction appears to be more important than speed in respect of the chemical composition of resulting precipitation.
- 4. The transport of contaminants to Spitsbergen apparently depends on certain types of atmospheric circulation which are periodic and of limited duration. Most frequently these occurred in winter time. Analysis of synoptic maps together with studies of air flow patterns before rainfalls shows that the precipitation with the lowest pH values (that below 4.1) comes from various parts of Europe. It is therefore impossible to attribute responsibility for the degradation of the natural environment of this part of the Arctic to particular European state.

5. Owing to the limitations of the analysis, in respect that not every single precipitation was sampled, actual amounts of cumulative loads delivered with precipitation to the area near the Polish Polar Station may be higher than those described in this paper. The discrepancy between the presented and the actual values may be of the order of 30%.

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