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Acidification and chemistry of stream water on the example of the Waksmudzki and Miętusi Streams in the Tatra Mountains (southern Poland)

Małgorzata GRODZIŃSKA-JURCZAK

Jagiellonian University, Institute of Environmental Biology, ul. Ingardena 6, 30–060 Kraków, Poland

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Abstract – A three-year study (1991–1993) on the chemistry of streams was carried out in two valleys of different bedrock in the Polish Tatra Mountains. Significant seasonal fluctuations in the concentration of most of the studied elements of the granitic Waksmundzki and carbonate Miętusi Streams were observed. The chemistry of the Miętusi Stream was dominated by calcium and magnesium ions and the Waksmundzki Stream by sulphate ions. The drawing of general conclusions on changes in the stream chemistry over the last 30 years is impossible because of the different analytical methods used and only a single samplings of the stream water taken by the investigation carried out in the 60's.

Key words: acid rain, stream acidification, mountain ecosystems.

Zakwaszenie i chemizm wody potoków na przykładzie Potoku Waksmundzkiego i Miętusiego w Tatrach (południowa Polska). Przeprowadzono 3-letnie (1991–1993) badania hydrochemiczne w dwóch dolinach różniących się typem podłoża geologicznego. W granitowym Potoku Waksmundzkim i wapiennym Potoku Miętusim stwierdzono istotne zmiany sezonowe w stężeniu większości badanych pierwiastków. Chemizm wody Potoku Miętusiego był zdominowany przez jony wapniowe i magnezowe, a Potoku Waksmundzkiego przez jony siarczanowe. Wyciągnięcie ogólnych wniosków na temat zmian hydrochemicznych w ciągu ostatnich 30 lat nie jest możliwe, ponieważ badania przeprowadzone w latach 60-tych były wykonane innymi metodami i zostały oparte na pojedynczych próbach.

1. Introduction

The effect of acid rain on the chemistry and biology of surface and ground waters is widely documented. Close relations between the bedrock geology, soil cover, and calcium and magnesium carbonate content in the water overlap the sensitivity to acidification of the aquatic with the soil ecosystems (Wróbel 1988, Bricker and Rice 1989). Alkalinity (acidic and neutral carbonate content) is leached by sulphates, decreasing alkalinity to the calcium and magnesium ion ratio, raising the ratio of sulphate to magnesium and calcium ions. In the water sensitive to acidification the content of carbonate is non-significant, hence the input of acidic precipitation increases its acidity (Schindler 1988). In acidified water, besides hydrogen ions, there was also found a high concentration of aluminium and manganese ions. Such elements mainly originate from the soil covering the catchment (Renberg and Wik 1985, Wróbel 1988). In Poland most of the mountain, depleted, and degraded soils are of low alkalinity and therefore sensitive to acidification. High acidity and the concentration of aluminium in the water affect its biological life manifested in a reduction in both the number of species and individuals in each species.

Studies on the chemistry of atmospheric precipitation and its effect on water chemistry changes have been carried out in Poland. The investigations mainly covered industrial areas while the sites most endangered by acidification were situated far away from large agglomerations (Turzański 1991). The most acidified streams and lakes were found chiefly in the mountain regions — highly exposed to air pollution (particularly sulphur and nitrogen substances) — and of low buffering capacity (Szczęsny 1989, Wróbel 1989). Experiments in the Karkonosze Mountains (south-western Poland) suggested an increase in a stream acidity and soil degradation (Wasilewski 1989), and a fall in the organic matter decomposition rate (Fischer and Kidawa 1993) which might be connected with a forest decline in that region (Godzik and Sienkiewicz 1990) In the Tatra Mountains a non-significant acidity increase in large lakes was detected while greater pH changes were apparent in small ponds (Wojtan 1989, Krywult 1990).

It seemed worthwhile to carry out more complex investigations in the Tatra Mountains, including the chemistry of atmospheric precipitation and running water combined with an estimation of forest health. In the current work only a part of the collected data is discussed, the remaining results being published in another paper (Grodzińska-Jurczak 1996). The aims of this work were: 1) to learn the chemistry, mainly the acidification, of streams in two valleys built of granite and carbonate rocks, 2) to analyze the effect of atmospheric precipitation on the stream chemistry, 3) to observe changes in the stream chemistry according to climatic seasonality and the altitude of each of the valleys, 4) to compare the chemistry of the streams with that found in the 60's. The choice of valleys and streams representing different bedrock geology should make it possible to show how the different ecosystems are affected by atmospheric precipitation of similar acidity.

2. Study area

The studies were carried out in two Tatra valleys (fig. 1). The Waksmundzka Valley (49°15' N, 20°04' E) is situated in the High Tatra and built of crystalline rocks, mainly granite, or covered by morainic and alluvial deposits of the same material (Gieysztor 1961). In the lower part a podzolic and brown soil is present (Oleksynowa and Komornicki 1964, Trafas 1985). The Waksmundzki Stream (6.2 km long), with the steepest stream declivity in the Tatra Mts (184 m km^{-1}), beginnings at altitude 1865 m as a seasonal runoff from melting snow, then as a brook from the spring, flows along the valley and finally falls into the River Białka (alt. 987 m) (Gieysztor 1961). Plant communities are vertically zoned, the following being present: a lower zone with fir-spruce forest (*Abieti-Piceetum montanum* (Szafer, Pawł. et Kulcz.) J. Mat.), a higher zone with Carpathian spruce forest (*Plagiothecio-Piceetum tatricum* (Szafer, Pawł. et Kulcz.) J. Mat.), and dwarf pine (*Pinus mughus* Scop.) zone. Three sampling stations were established along the stream at the following altitudes: Station 1 at 1950 m, Station 2 at 1650 m, and Station 3 at 1350 m.

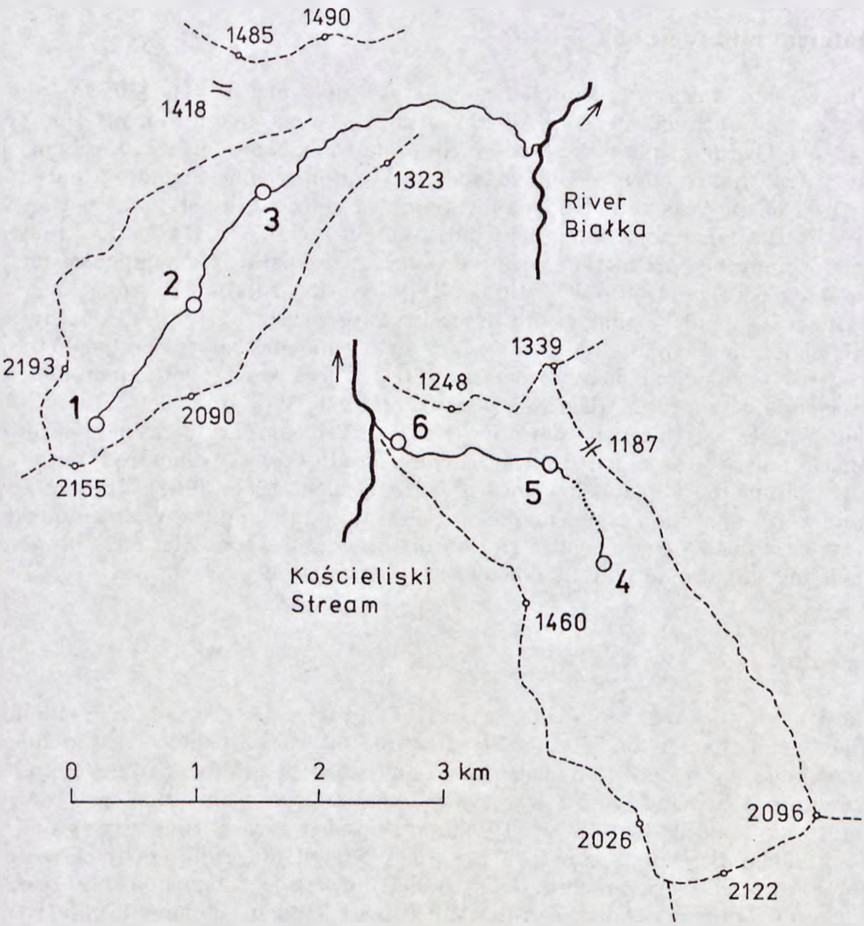

Fig 1. Localization of the investigated stations in the Waksmundzka (1–3) and Miętusia (4–6) valleys: broken line — main mountain ranges with selected peaks and passes.

The Miętusia Valley (49°15' N, 19°53' E) is situated in the Western Tatra Mts. built of limestone, marls, and glacial and alluvial deposits (Trafas 1985). The soils are gleys and brown soils The Miętusi Stream begins at altitude 1200 m and flows into the Kościeliski Stream. Carpathian spruce forest (*Polysticho-Piceetum* (Szafer, Pawł. et Kulcz.) J.Mat.) is present in the higher zone, the lower one being dominated by fir-spruce forest (*Galio-Piceetum carpaticum* J.Mat.). Seminatural meadow association (*Gladiolo-Agrostietum* (Br.-Bl.) Pawł. et Wal.) is also characteristic of that region (Trafas 1985). Three sampling stations were established along the Miętusi Stream: Station 4 at altitude 1200 m, Station 5 at 1100 m, and Station 6 at 950 m.

3. Material and methods

The stream water was sampled at monthly intervals, at least 20 cm from the banks at a depth of 40 cm. All the samples were taken during the period 1991–1993. Owing to the risk of avalanches and thick snow cover in the upper part of the Tatra Mts. from November to April the sampling was carried out only in the lower part of the Waksmundzka Valley. Samples collected in polythene bottles were filtered in the laboratory using a Buchner funnel. Acidity (pH) was determined by a microcomputer pH-meter with automatic temperature compensation and combined electrode; NO_3^-, PO_4^{3-} and NH_4^+ ions by colorimetry analysis (Specol analyzer); SO_4^{2-} nephelometrically (Specol analyzer), Na^+, K^+, Ca^{2+} ions by flame atomic emission (Flapho 4); Mg^{2+} and Zn^{2+} by atomic absorption spectrophotometry (Varian BQ 20); and heavy metals (Pb^{2+}, Cd^{2+}, Cu^{2+}) voltamperometrically (microcomputer analyzer) (Hermanowicz et al. 1976, Williams 1985).

The values of the two main indicators of stream acidification — pH and sulphate ions — obtained in the current studies were compared with those available from the 60's (Oleksynowa and Komornicki 1958, 1964). They measured pH and SO_4^{2-} of stream water at the stations situated along the Waksmundzki and Miętusi Streams. A detailed description of the stations from the 60's allowed the present investigator to pair the results of the two studies.

4. Results

Acidity of the Waksmundzki Stream at stations 1–3 varied from 4.5 to 5.9 (Table I) and that of the Miętusi Stream from 6.7 to 8.3 (Table II). Calcium and magnesium ion concentrations were much higher in the Miętusi Stream than in the Waksmundzki Stream. In the case of Ca^{2+} the mean concentration in the Miętusi Stream was 31.0 mg dm^{-3} (SD = 11.87) and exceeded several times its value in the Waksmundzki Stream (mean 0.72 mg dm^{-3}, SD = 0.48). Differences between the streams for Mg^{2+} were smaller — ca. 10-fold. In both streams the concentration of Ca^{2+} significantly depended on the month, increasing in summer (Table III), but for Mg^{2+} such a dependence was noted only in the Miętusi Stream (Table II).

Concentration of sodium ions did not differ significantly between the two streams (Tables I and II). In both of them sodium concentration depended significantly on the season (Table III). In the case of the Waksmundzki Stream it also depended on the altitude, increasing with height. The concentration of potassium ions in the Miętusi Stream (Table II) was higher than in the Waksmundzki Stream (Table I), where its concentration differed between the stations. Only in the Waksmundzki Stream was a significant seasonal dependence of potassium ions observed (Table III).

In both streams the concentration of ammonium ions was low (Waksmundzki Stream: mean 0.09 mg dm^{-3}, SD = 0.25; Miętusi Stream: mean 0.11 mg dm^{-3}, SD = 0.25) (Tables I and II). In the Miętusi Stream the concentration of ammonium ions depended significantly on the season (Table III). In both streams the concentration of sulphate ions varied significantly between the seasons. In the Waksmundzki Stream the highest values were measured in August 1992 (3.88 mg dm^{-3}) and the lowest in September 1991 (0.45 mg dm^{-3}) (Table I). The concentration of sulphate ions in the Miętusi Stream was much higher, varying from 1.22 mg dm^{-3} in September 1993 to 11.82 mg dm^{-3} in April 1992 (Table II). In both streams the concentration of sulphate ions depended significantly on the season (Table III).

Table I. Concentration of the studied elements (mg dm^{-3}) and pH in the Waksmundzki Stream (mean value of Stations 1–3).

Month	pH	Ca	Mg	Na	K	NH_4	SO_4	NO_3	PO_4	Cd	Pb	Cu	Zn
1991													
May	5.1	1.24	0.19	0.31	0.29	0.64	1.77	0.33	0.0011	0.0019	0.0152	0.0178	0.0724
June	4.7	1.09	0.02	0.30	0.17	0.07	0.72	0.35	0.0020	0.0012	0.0036	0.0085	0.0176
July	5.2	1.28	0.19	0.58	0.31	0.14	0.97	0.52	0.0016	0.0006	0.0186	0.0042	0.0277
August	5.9	1.38	0.24	0.56	0.45	0.01	0.54	0.40	0.0578	0.0005	0.0020	0.0012	0.0179
September	5.2	1.11	0.18	0.45	0.77	0.45	0.45	0.50	0.0016	0.0018	0.0074	0.0054	0.1019
October	5.3	1.11	0.24	0.54	0.51	0.01	0.92	2.01	0.0902	0.0019	0.0073	0.0067	0.0912
1992													
May	5.1	0.88	0.19	0.42	0.39	0	3.54	0.13	0	0.0004	0.0012	0.0019	0.0300
June	5.3	0.75	0.15	0.46	0.33	0	1.66	0.08	0	0.0020	0.0045	0.0034	0.0450
July	5.6	0.55	0.12	0.28	0.52	0	1.37	0.26	0.0033	0.0006	0.0017	0.0030	0.0467
August	4.8	0.62	0.14	1.00	0.50	0	3.88	0.47	0.4500	0.0012	0.0038	0.0042	0.0300
September	4.9	0.30	0.14	0.28	0.21	0.17	2.17	1.90	0.0067	0.0008	0.0066	0.0103	0.0300
October	4.5	0.30	0.21	0.39	0.44	0	1.80	0.54	0	0.0010	0.0023	0.0040	0.0350
1993													
May	4.9	0.37	0.09	0.21	0.26	0	0.97	0.40	0	0.0099	0.0010	0.0042	0.0313
June	5.2	0.18	0.06	0.45	0.23	0	2.71	0.46	0	0.0042	0.0013	0.0044	0.0550
July	5.3	0.14	0.10	0.49	0.15	0	3.38	0.56	0	0.0006	0.0038	0.0018	0.0120
August	5.5	0.31	0.03	0.72	0.53	0	2.26	0.28	0.0578	0.0001	0.0056	0.0056	0.0140
September	4.7	0.40	0.04	0.32	0.11	0.04	1.60	0.37	0	0.0001	0.0045	0.0009	0.0087
Mean	5.2	0.72	0.16	0.44	0.35	0.09	1.76	0.59	0.0326	0.0018	0.0055	0.0053	0.0403
SD	0.4	0.48	0.06	0.23	0.23	0.25	1.16	0.67	0.1049	0.0027	0.0075	0.0055	0.0411

Table II. Concentration of the studied elements (mg dm^{-3}) and pH in the Miętusi Stream (mean value of Stations 4–6).

Month	pH	Ca	Mg	Na	K	NH_4	SO_4	NO_3	PO_4	Cd	Pb	Cu	Zn
1991													
September	7.9	21.7	5.4	0.35	1.30	0.68	2.85	0.41	0.0016	0.0006	0.0078	0.0047	0.0318
October	7.7	29.4	20.7	0.59	0.73	0.21	3.11	0.70	0.0016	0.0004	0.0046	0.0085	0.0313
November	7.9	31.1	10.5	0.72	0.97	0.04	3.18	0.98	0.0021	0.0041	0.0051	0.0065	0.0205
December	7.8	28.6	12.1	0.51	0.29	0	3.47	0.70	0.0029	0.0018	0.0088	0.0053	0.0320
1992													
January	7.4	31.4	14.6	0.58	0.61	0.04	2.28	0.48	0.0029	0.0010	0.0127	0.0083	0.0568
March	7.8	21.8	9.4	0.53	0.51	0.17	4.89	0.19	0.0029	0.0009	0.0074	0.0181	0.0333
April	7.6	18.7	10.1	0.50	0.51	0.02	11.82	0.47	0	0.0007	0.0054	0.0088	0.0233
May	7.9	28.7	10.8	0.49	0.41	0	5.50	0.79	0	0.0003	0.0040	0.0072	0.0200
June	7.3	30.0	5.7	0.58	0.47	0	8.66	0.99	0	0.0003	0.0056	0.0065	0.0150
July	8.3	34.9	11.9	1.09	1.81	0.09	8.68	0.67	0.6800	0.0004	0.0038	0.0074	0.0200
August	7.7	28.5	11.2	0.40	0.41	0	7.26	0.61	0.9100	0.0073	0.0050	0.0134	0.0200
September	7.8	33.4	10.3	0.42	0.41	0.32	2.80	0.53	0.1267	0.0007	0.0065	0.0105	0.0367
October	7.1	49.8	10.2	0.42	0.41	0	5.63	0.63	0	0.0005	0.0008	0.0015	0.0200
November	7.5	41.8	10.8	0.45	0.38	0	8.19	1.36	0	0.0002	0.0026	0.0065	0.0250
December	6.7	28.3	11.2	1.16	0.42	0	8.22	1.42	0	0	0.0007	0.0037	0.0123
1993													
January	6.9	17.4	10.1	0.82	0.38	0	6.47	1.48	0	0	0.0002	0.0218	0
February	7.3	22.2	11.8	0.43	0.44	0	7.52	0.84	0	0.0013	0.0031	0.0062	0.0100
March	7.7	52.3	12.6	0.54	0.51	0.63	3.22	1.06	0.2058	0	0.0002	0.0037	0.0200
April	7.5	51.5	10.1	0.44	0.44	0.08	5.34	1.41	0.0015	0	0.0034	0.0046	0.0140
May	7.7	51.5	10.1	0.96	0.63	0	6.96	1.33	0	0	0.0013	0.0445	0.0093
June	7.6	20.3	11.1	0.79	0.50	0	6.59	1.25	0	0	0.0005	0.0043	0.0217
July	7.6	18.1	13.2	0.62	0.67	0.17	7.19	1.10	0	0.0003	0.0020	0.0037	0.0093
August	7.5	21.7	10.2	0.63	0.30	0	4.81	0.55	0.0536	0.0003	0.0067	0.0060	0.0063
September	7.4	23.7	10.1	0.60	0.30	0	1.22	0.68	0	0	0.0048	0.0085	0
Mean	7.6	31.0	11.1	0.61	0.57	0.11	5.66	0.85	0.0700	0.0008	0.0043	0.0900	0.0205
SD	0.4	11.8	5.1	0.30	0.47	0.25	2.98	0.46	0.2600	0.0016	0.0049	0.0160	0.0155

Table III. Statistical significance of the differences between the mean concentrations of the investigated elements in successive months in 1991–1993 (two-way ANOVA): *F* — test statistics, *P* — significance level.

Parameter	Waksmundzki Stream		Miętusi Stream	
	F	*P*	*F*	*P*
pH	4.948	0.0001	8.310	0.0001
Ca	3.450	0.0002	14.894	0.0001
Mg		ns	2.171	0.0126
Na	3.472	0.0001	1.810	0.0488
K	2.056	0.0169		ns
NH_4		ns	2.415	0.0072
SO_4	3.587	0.0001	7.799	0.0001
NO_3	4.060	0.0001	3.936	0.0001
PO_4	4.606	0.0001	6.521	0.0001
Cd	4.118	0.0001	10.350	0.0001
Pb	1.771	0.0473		ns
Cu	2.185	0.0108		ns
Zn	2.264	0.0097	4.303	0.0001

ns — statistically non-significant dependence

Only in the Miętusi Stream did the concentration of sulphate ions depend significantly on the altitude, reaching its highest values at higher situated stations. Acidity and sulphate concentration of the two streams from the current studies were compared with the data available from the 60's (Oleksynowa and Komornicki 1958, 1964). In neither stream at successive stations did values of pH from the 60's differ from the current findings. In the Waksmundzki Stream at all stations except Station 3 sulphate ion concentration measured in the 60's exceeded the current results. Such differences were much greater at all stations in the Miętusi Stream.

The concentration of nitrate ions was similar in the two streams (Waksmundzki Stream: mean 0.59 mg dm^{-3}; Miętusi Stream: mean 0.85 mg dm^{-3}) (Tables I and II). In both streams the concentration of ions significantly depended on the season (Table III). The concentration of phosphate ions in the Waksmundzki and Miętusi streams was distinctly low (Tables I and II). Statistical analysis showed that in both streams the concentration of phosphate ions depended on the season (Table III).

The concentration of heavy metals in both streams was decidedly low, depending significantly on the season and/or altitude (the higher the altitude the higher the concentration of metal) (Tables I–III). The concentration of cadmium and lead depended on the season and the altitude, copper only on the season, while zinc ion concentration depended significantly on the altitude (Table III).

5. Discussion

In the case of several elements their concentrations depended significantly on the altitude — the higher the altitude the higher their concentration. The concentration of the elements also showed a dependence on the season, in most cases rising to higher values in the summer months. Alkalinity is an indicator of stream water sensitivity to acidification (Bricker and Rice 1989), and on account of this the Waksmundzki Stream is very sensitive (average alkalinity 0.05 mval dm^{-3}), while the Miętusi Stream is more resistant (0.36 mval dm^{-3}). Stream water in the valley with a granitic bedrock is more acidic (pH 4.5–6.9) than that of the carbonate one (6.7–8.3). The concentration of most of the studied elements varied seasonally in both valleys. The chemistry of both streams is dominated by sulphate ions, whose concentration was much higher in the Miętusi Stream. It was in accordance with the total precipitation and chemical fallout, also dominated by sulphate ions in both valleys (M. Grodzinska-Jurczak unpubl.). Although sulphate deposition in the Miętusia Valley was greater than in the Waksmundzka Valley, it did not significantly reduce the pH of the Miętusi Stream. This is connected with the bedrock of the valley. In the Miętusi Stream the concentration of neutralising acidic substances (Ca^{2+}, Mg^{2+}) was 5 times higher than in the Waksmundzki Stream (Kram and Hruska 1993).

In both streams the concentration of nitrate ions was distinctly low. American studies showed similar results — even in the areas with high nitrate deposition its concentration in stream water was also low (Probst et al. 1990). Only during times of high water (spring melting period and autumn rains) was the nitrate concentration in streams and lakes raised. Nitrates are important nutrients and in many cases might be reduced by plants in the catchment ecosystem (Probst et al. 1990). The concentrations of ammonium ions did not differ significantly between the streams. This would be in agreement with the observations of Probst et al. (1990).

The concentration of hydrogen ions differed significantly between the stations. In the upper parts of both valleys this might result from the type of water supply to the streams. The Waksmundzki Stream receives mainly snow meltwater flowing directly on the rocks and therefore not buffered (Krywult 1990). In the lower parts of the valleys the water flowing in the streams does not originate directly from the melting snow patches. Before entering the stream it percolates through the soil layers where it is exchanged and mixed with the meltwater. The variation of hydrogen ion concentration between the subsequent stations in the Miętusi Stream may be connected with a better buffering ability of acids in the water feeding the stream owing to thicker soil layers (C.P. Driscoll, N.M. Johnson, G.E. Likens and M.C. Seller unpubl.). However, the best buffering is at the lowest station where the soil is mostly well developed and contains a large amount of alkaline cations.

Differences in the concentration of heavy metals (Cd^{2+}, Pb^{2+}, Zn^{2+}, Cu^{2+}) between the stations in the Waksmundzki Stream may be explained by the thick snow cover of long duration mainly in the upper part of the valley. Jeffries (1990) found a significantly higher concentration of heavy metals in snow cover than in atmospheric precipitation and streams. However, the water entering the stream in its upper course was more contaminated with heavy metals than in its lower course where the snow cover was of shorter duration. Additionally, the heavy metal concentration is 5–10 times higher in the earliest melting snow than in the remaining cover (Jeffries 1990). Sampling was always scheduled for the beginning of the melting period because of the change in the stream water chemistry during melting.

In the Miętusi Stream the concentration of sulphate ions depends significantly on the altitude of the station, increasing at the head of the valley. This might be connected with the irregular spruce forest coverage. The upper part of the valley is sparsely wooded, dry deposition of acidic substances to the needle and twig floor is therefore smaller there (Probst 1987).

Seasonal variation in the concentration of elements (mainly acidic substances) in the stream is connected with the analogous seasonal differences in deposition of acidic substances from the atmosphere (Hornbeck et al. 1976). Particularly in the

Waksmundzka Valley the duration of snow cover should be considered. The reaction of snow is usually higher (less acidic) than that of atmospheric precipitation. The older the snow the higher its pH, and the first melting snow (ca. 20% of the cover) is the most acidic. In the longer lying snow chemical exchange reactions take place between the hydrogen ions and other cations originating from organic materials (hulls of cones, seeds, needles, twigs) carried by with the wind (Hornbeck et al. 1976).

Seasonal variation in the concentration of elements in the streams may also be connected with the length of time the precipitation is held in the soil. The successive soil layers are of different acidity. The change in precipitation chemistry before entering the stream would depend on the ion exchange reactions taking place in the soil. These reactions are closely connected with the chemistry of particular soil layers (e.g. alkaline saturation) (Hornbeck et al. 1976). The type of snow also affects the chemistry of stream water. Snow is less effective than rain in trapping pollutants from the atmosphere (e.g. sulphur compounds). The season and type of atmospheric precipitation dictates the amount of air pollutants entering the stream.

In connection with the investigated changes in the acidity of the Waksmundzki and the Miętusi Streams caused by atmospheric precipitation, the pH and sulphate concentration of both streams from the current studies were compared with the data from the 60's (Oleksynowa and Komornicki 1958, 1964). It was hypothesized that acid rain would cause acidification of the stream water, mainly on the granitic, low buffered bedrock. Since single samplings (August 1957 in the Waksmundzki Stream and 1960 in the Miętusi Stream) do not permit the comparison of data with the current results statistically, graphical methods were used instead. Stream acidity at all stations in the two valleys did not differ from the results from the 60's while the sulphate concentration of the streams was higher. Single samplings and different analytical methods prevent the drawing of general conclusions concerning changes in the water pH as well as the sulphate concentration in the two streams over the last 30 years. In the 60's pH was measured colorimetrically (Hellig colorimeter), while in the current study a more sensitive, potentiometric, method was used. Sulphate concentration was measured nephelometrically (Hermanowicz et al. 1976), while 30 years ago the investigators calculated it from the difference between total and carbonate water hardness, which is the sum of chloride, sulphate, and nitrate ions. Oleksynowa and Komornicki (1958, 1964) did not include in their calculations nitrate and chloride content, assigning the obtained values to sulphate concentration. Such results exaggerated the real ones.

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