EVIDENCE OF SPRINGWATER ACIDIFICATION IN THE VOSGES MOUNTAINS (NORTH-EAST OF FRANCE): INFLUENCE OF BEDROCK BUFFERING CAPACITY

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Abstract. Investigations on springwater acidity were carried out in the Vosges mountains (north-eastern France). Acid or poorly buffered spring and streamwaters were detected in the same area. The proportion of acid springwaters ($pH < 5.6$) is about 20% among 220 springs. The springwater pH on granite are equally spread between 5.0 and 6.8 whereas on sandstone a majority of springs is in the range 5.6 to 6.2. As a whole, but mainly on sandstone, from the 1960's to 1990's, the shape of the pH distributions shifts toward greater acidity. In the sandstone area, trends in pH, alkalinity, total hardness (corresponding to divalent cations), sulfate and nitrate were considered over the 30 yr period (1963-1996) in relation to the bedrock chemical composition. Kendall seasonal tau coefficients indicate that decreasing trends were significant for the first three parameters. Linear regression on the smoothed mean value revealed 18 and 90% decrease for pH and alkalinity respectively, for springwaters draining poor-base cation sandstone whereas only 8 and 30% decrease respectively, was observed on clay-enriched sandstone. On silica-enriched sandstone, alkalinity began to decrease in the early 70's as well as pH. Loss of alkalinity only occurred in the early 80's for springs draining clay enriched sandstone. This can be interpreted as a titration process by acid atmospheric inputs of the buffering capacity of weathering and exchange processes in the soils and the catchment bedrock. The nitrate presents an increasing step in the early seventies but possibly as a result of change in analytical technics and/or increase in atmospheric inputs mainly resulting from increase in fertiliser inputs in agricultural areas or in car traffic. Surprisingly no change in sulfate was noticed in any groups of springs probably as a result of the adsorption/mobilisation in the soils. These long-term trends in spring waters (1963–1996) confirmed the soil and streamwater acidification trends already mentioned in this region, in relation to acid atmospheric inputs since no climate nor forestry practice changes have been detected over the period. Moreover, in spite of acid atmospheric input reductions, no recovery can presently be detected.

Keywords: acidification trends, granite, Northeast of France, sandstone, sensitive areas, springwater

1. Introduction

In industrialised countries, atmospheric pollution has been identified as being partly responsible for forest soil, stream water and lake acidification. Direct demonstrations were provided by vegetation records, comparison of soil pH and exchangeable nutrient at different time intervals, or by some long-term data time series on spring, stream or lake water (Wright, 1977; Wright *et al.*, 1994; Tamm and Hallbäcken, 1986, 1988; Falkengren-Grerup *et al.*, 1987; Thimonier *et al.*, 1992; Zulla and Billett, 1994; Sverdrup *et al.*, 1995). However, pre-industrial data are often lacking. Sometimes, chemical data records for springs supplying drinking water are available. Historical data sets allow then to relate geochemical characteristics of freshwater to changes in atmospheric inputs with time (Von Brömsen, 1985; Maxe *et al.*, 1995; Skjelkvåle and Henriksen, 1995; Lång and Swedberg, 1995; Swedberg, 1995) and to the buffering capacity of the catchment bedrock (Peters and Driscoll, 1987).

In France, acidity of stream waters was mainly identified and mapped in the Vosges mountains located in the north-eastern part (Massabuau *et al.*, 1987; Probst *et al.*, 1990; Party *et al.*, 1997). This region not only represents one of the most sensitive areas but also receives the highest atmospheric inputs of acid in the country (up to 0.4 to 1.0 kmol ha^{-1} a^{-1} of H^+ and 10 to 15 kg ha^{-1} a^{-1} of S; Dambrine *et al.*, 1995). The acidity of streamwaters was clearly related to the presence of quartz-enriched sandstone and acid granite regions covered by coniferous (Party *et al.*, 1995; Probst *et al.*, 1995). Like in many other places in Europe, pre-industrial lake and streamwater pH has been tentatively reconstructed and compared to present-day data using either empirical models (see Henriksen *et al.*, 1988; Probst *et al.*, 1995) or diatom data for lake sediments (Battarbee *et al.*, 1993; Kreiser *et al.*, 1995), indicating in this region of France an acidification process since the last century. But these data remain very scarce. In this region, chemical analysis for springs supplying drinking water were recorded regularly (sometimes for 30 yr) by the Ministry of Health. These data were used in order to check directly if there was any acidification/recovery trend in spring waters.

In this respect, this paper presents (i) the extent of springwater acidity compared to that of streamwater; (ii) the long-term trends in springwater pH, alkalinity, Total Hardness, sulfate and nitrate over a 10–30 yr period; (iii) the link with bedrock characteristics. Finally, the results will be discussed in relation to the trends in acid atmospheric inputs in Europe over the period.

2. Materials and Methods

2.1. LOCATION OF THE STUDY AREA

The Vosges Massif, located in the north-eastern part of France (Figure 1) covers 6000 km^2, and lays along the Rhine valley close to the German boarder. The altitude ranges from 350 m to 1427 m a.s.l. The slope facing the east is steep whereas the western side slopes gently to the Lorraine plateau. The climate is oceanic mountainous. This mountain receives the highest atmospheric acid load

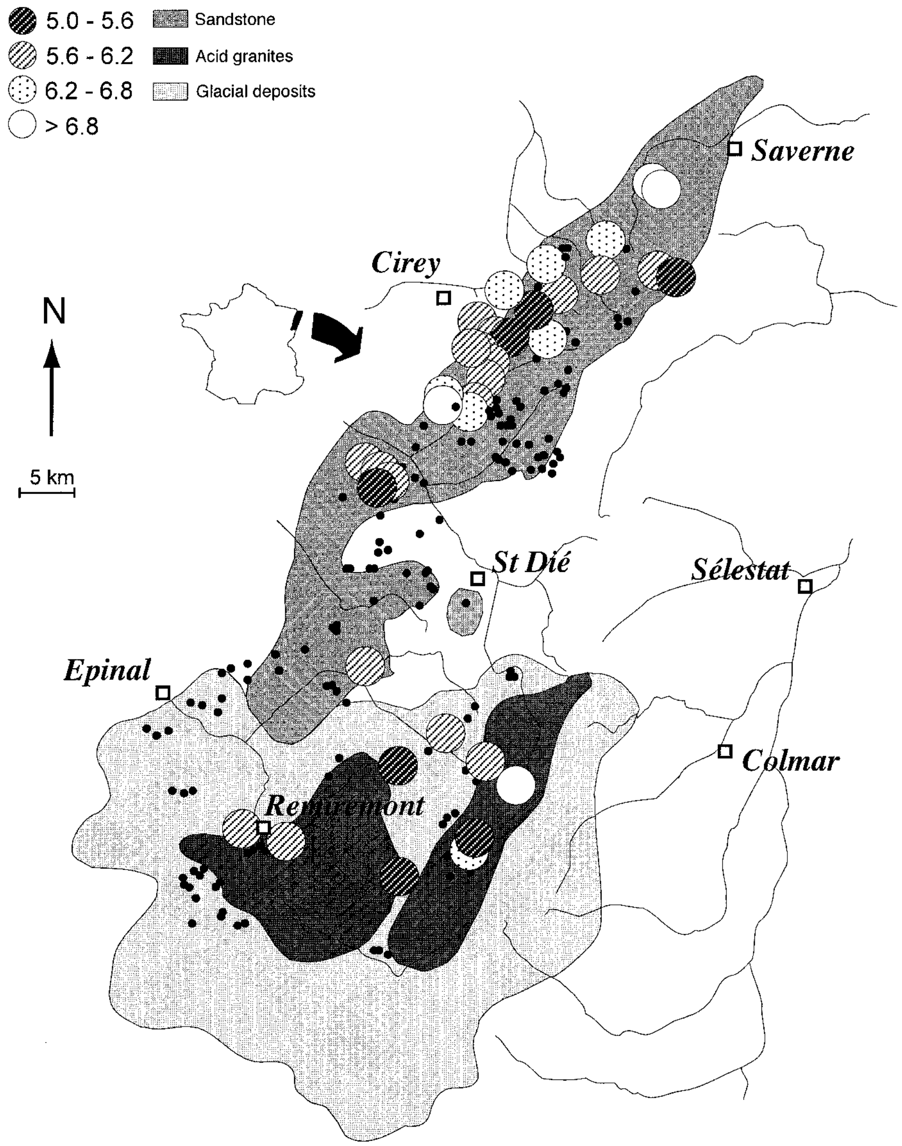

Figure 1. Location map of the study area and of studied springs. Mean pH of springwaters considered for long-term trends analysis (n = 36, among 220 studied springs) are indicated.

in France (Dambrine *et al*., 1995) in the two main areas where acid streams have been detected, particularly sensitive to acid atmospheric inputs: the northwestern part, composed of sandstones, and the central part mainly underlain by acid granites (Probst *et al*., 1995). Moreover, in the central part, these bedrocks are often covered by cemented glacial deposits that may increase catchment sensibility to acidification (Party *et al*., 1995). Mixed stands of silver-fir (*Abies alba Mill.*) and beech (*Fagus sylvatica* L.) represent the natural forest but silver fir, norway spruce (*Picea abies* Karst) and silver pine (*Pinus sylvestris* L.) forest are now dominant.

2.2. DATA BASE

Chemical data for some 550 springs supplying drinking water in the Vosges Mountains are achieved at the Health and Environment Department of the Health Ministry. Springs have been repeatedly sampled over a 30 yr time period (1963–1996), generally twice a yr, during both low and high flow periods and analysed for pH, alkalinity, NO_3^-, SO_4^{2-}, Total Hardness (TH, assimilated to $Ca^{2+} + Mg^{2+}$). These springs are mainly from the sensitive regions to acidity of the Vosges mountains (Figure 1) on the western side as indicated by a streamwater pH map previously drawn on the basis of a survey of pH and alkalinity of 800 unpolluted small catchments investigated in 1992 (Party *et al*., 1995, 1997). A subset of 220 springs was selected on the basis of catchments where both pH of streamwater and springwater were measured in 1992. Moreover, the selected drainage catchments were geographically located and the underlying bedrock geochemistry identified. Hence the distribution of spring and streamwater pH as well as chemical trends could be related to geochemical characteristics of the catchment bedrock. However, due to some lack of data, long-term chemical trends could only be considered for 36 springs. This selection only took into consideration series with at least 10 yr of records. This subset of data concerns 26 springs draining sandstones (silica dominant and clay-enriched) located on the north-western side of the Vosges mountains (Party *et al*., 1995) and 10 springs on granite in the central part. However, these latter only concern series with 10 yr of records only and the data are less frequently recorded to conclude about any trends. Hence, statistical trends will mainly be discussed for a 30 yr time series of the north-western region on sandstone. They are representative of the proportion of considered streams in these areas (118 streams draining sandstone).

2.3. ANALYTICAL METHODS

Since the beginning of the chemical records, analytical work was done in 3 different laboratories in Nancy and Strasbourg using the same techniques. pH was measured with a pH meter and alkalinity by acid titration with helianthin or methyl orange as indicators. Total Hardness (TH) was analysed by complexometric method using EDTA. Total Hardness and alkalinity were measured manually in the sixties and automatically from the seventies but the technique never changed. Sulfate was analysed using barium precipitation by manual gravimetric or nephelometric methods then by colorimetry (technicon apparatus). Nitrate was detected using brucine in the sixties and automatic colorimetry (technicon apparatus) using cadmium or hydrazine reduction, from the seventies.

As analytical methods for pH, alkalinity and total hardness did not change during the studied period and are similar between laboratories, the analytical bias on observed trends are very unlikely. However, in the seventies the generalisation of automatic colorimetry for sulfate and nitrate analysis could have influenced changes in trends.

2.4. STATISTICS

Trends over time were assessed using a statistical software (SYSSTAT). Normality of the distributions was checked. Because of its robustness, Kendall seasonal (Tau) non-parameteric correlation was used (Hirsch *et al.*, 1982; Hirsch and Slack, 1984). Mean data were transformed using smoothing procedure on mean time series analysis according to Cleveland’s lowess algorithm which was preferred to running mean smoothing procedure because of non-Gaussian data. Regressions were then applied and trends evaluated using student t and analysis of variance (as usually done in the literature Etchanchu and Probst, 1988; Driscoll *et al.*, 1995).

3. Results

3.1. SPRING WATER ACIDITY DISTRIBUTION

Springwaters and streamwaters have been arranged in Table I according to their pH values in 1992. Classes of springwater pH correspond to those previously chosen for streamwaters (Party *et al.*, 1995). The results indicate that most (60%) of the 220 selected springs (representing 40% of the 550 springs) present a $\mathrm{pH} < 6.2$ and that 22% are acidic ($\mathrm{pH} < 5.6$). In the same area, among 150 small upper streams (which represent 31% of the 481 streams for which pH and alkalinity were measured all over the Vosges mountains), 50% have a $\mathrm{pH} < 6.2$ and 22% are acidic. Figure 1 indicates both the spatial distribution of springwater considered in this study and the distribution of the springwater pH for which long-term trend analysis was performed. Acid streams and acid springs are located in the same area (Probst *et al.*, 1990; Party *et al.*, 1995) but the median of pH (Table I) for springwaters is between 5.6 to 6.2 whereas it is between 6.2 to 6.8 for streamwaters. The percentage of acid springs is also greater. This might indicate that as a whole in the same area spring waters are less buffered than streamwaters.

The pH data from this subset of 220 springs have been related to the drainage bedrock area (Table I, Figure 1). The majority of springs draining the sandstone region are characterised by a pH in the range 5.6–6.2 whereas springs draining granite are equally spread between the three ranges of pH from 5.0 to 6.8.

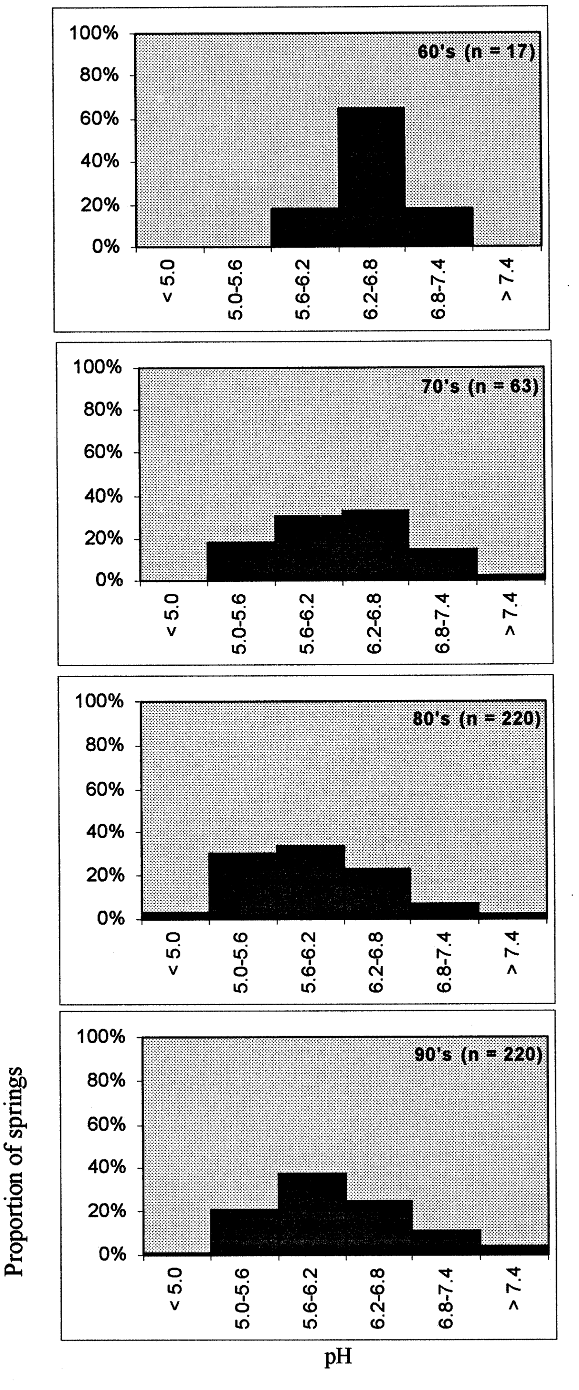

Figure 2. Distribution of mean pH of springwaters of the Vosges mountains by decades for the 1963–1995 period.

TABLE I

Distribution of springwater pH according to the drainage bedrock and comparison with streamwater pH on the western side of the Vosges mountains. The percentages in italic represent the proportions of springs (n=220) and streams (n=150) relative to the initial sets (n=550 and n=481, respectively).

Region		Selected set	pH in 1992				
			< 5.0	5.0–5.6	5.6–6.2	6.2–6.8	> 6.8
Springwaters							
Sandstones	n	162	2	31	65	38	26
	%	*30*	1	19	40	24	16
Acid Granites	n	58	0	15	19	17	7
	%	*10*	–	26	33	29	12
Total	n	220	2	46	84	55	33
	%	*40*	1	21	38	25	15
Streamwaters							
Total	n	150	9	25	42	62	13
	%	*31*	6	16	28	41	9

Mean pH of springwaters were calculated by decades since the 1960’s. The pH distributions are shown in Figure 2. In the 1960’s all springs had a pH > 5.6, whereas in the 1970’s only about 70% had a pH > 5.6. The percentage of springs with a pH > 6.2 was also greater in the 1960’s and 1970’s, than in the eighties and nineties. No acidic springs (pH < 5.6) were detected in the 1960’s, whereas some slightly acidic springs (5.0 < pH < 5.6) appeared in the 1970’s and very acidic springs in the eighties (pH < 5.0). More generally, this means that the shape of the pH distribution moves overtime from mostly higher pH values (6.2 < pH < 7.4) to mostly lower pH values (5.0 < pH < 6.2) between the sixties and the eighties. No real changes occurred between the eighties and the nineties. However, one can observe that the number of springs was not the same in the different decades. This could have biased the result. But all the observed springs in the sixties and the seventies are still present later on and if we consider these springs alone, the shape of the pH distribution moves also clearly from higher to lower pH between the sixties and the eighties.

3.2. SPRINGWATER CHEMICAL TRENDS

Mean values for each parameter (pH, TH, alkalinity, sulfate and nitrate) of 26 springwaters draining sandstones have been calculated since 1963. Mean values and their standard deviations as well as the smoothed curve on mean data were

TABLE II

Chemical compositions of the different sandstones: (I) siliceous sandstone (after Millot *et al.*, 1967), (II) conglomerate (after Perriaux, 1961), (III) clay-enriched sandstone (after Millot *et al.*, 1967).

%	SiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	Tio_2	P_2O_5	L.I.
I	94.90	3.64	1.00	–	< 0.01	0.07	< 0.01	0.02	2.45	0.05	–	0.69
II	91.19	3.75	0.69	0.53	0.02	0.66	–	0.20	1.30	0.16	0.02	1.33
III	81.30	7.06	1.60	–	0.01	0.30	0.87	0.21	4.40	0.41	–	3.20

L. I.: Loss on ignition.

plotted on Figures 3a to 3e for springs draining three types of sandstone. The first set of springs (I) corresponds to 10 springs draining siliceous sandstone, the second (II) to 7 springs on siliceous sandstone and conglomerate and the last set (III) to 9 springs draining clay-enriched sandstone. As an indication the chemical composition of each type of sandstone is given in Table II.

3.2.1. *pH, Alkalinity and Base Cations*

Trends in pH, alkalinity and TH (representing Ca + Mg) were investigated over the 1960 to 1990's period (Figure 3a, 3b and 3c). As seen on Figure 3a, mean pH ranges are as follows: 5.1 to 7.0, 4.9 to 7.4 and 5.9 to 7.5 for the first group (I), the second (II) and the third (III), respectively. Alkalinity of springwaters from group I and II are in the same range (540 to 0 μeq L^{-1}) whereas alkalinity from group III ranges in between 890 and 190 μeq L^{-1} (Figure 3b). TH varies in between 1030 and 220 μeq L^{-1} in the two first groups and between 1170 and 360 μeq L^{-1} in the third one (Figure 3c). For the different parameters, the smoothed curves indicate clearly different ranges and trends particularly between springs from groups (I, II) and (III).

As shown on Table III, the KS tau coefficients indicate a significant decrease of pH over the period for springs belonging to group I and II and a less significant decrease for pH of springs from group III. The linear regressions calculated on each mean smoothed curves indicate the same relatively steep negative slope for group I and II and a less significant negative slope for group III (Table IV). The percentages of mean declines have been calculated on each trend. The results indicate 18% of decrease for spring water pH in group I and II and only 8% decrease for pH in group III (Table IV).

Kendall Tau coefficients indicate comparable trends for alkalinity with a significant decline in group I and II (Table III). The linear regressions between mean trends in alkalinity and time indicate steep decline for group I and II with a significant negative slope in group I whereas alkalinity decline in group III was less obvious. The percentages of decline were very important and indicate about 90% of alkalinity loss (groups I and II, Table IV). This confirms previous results obtained

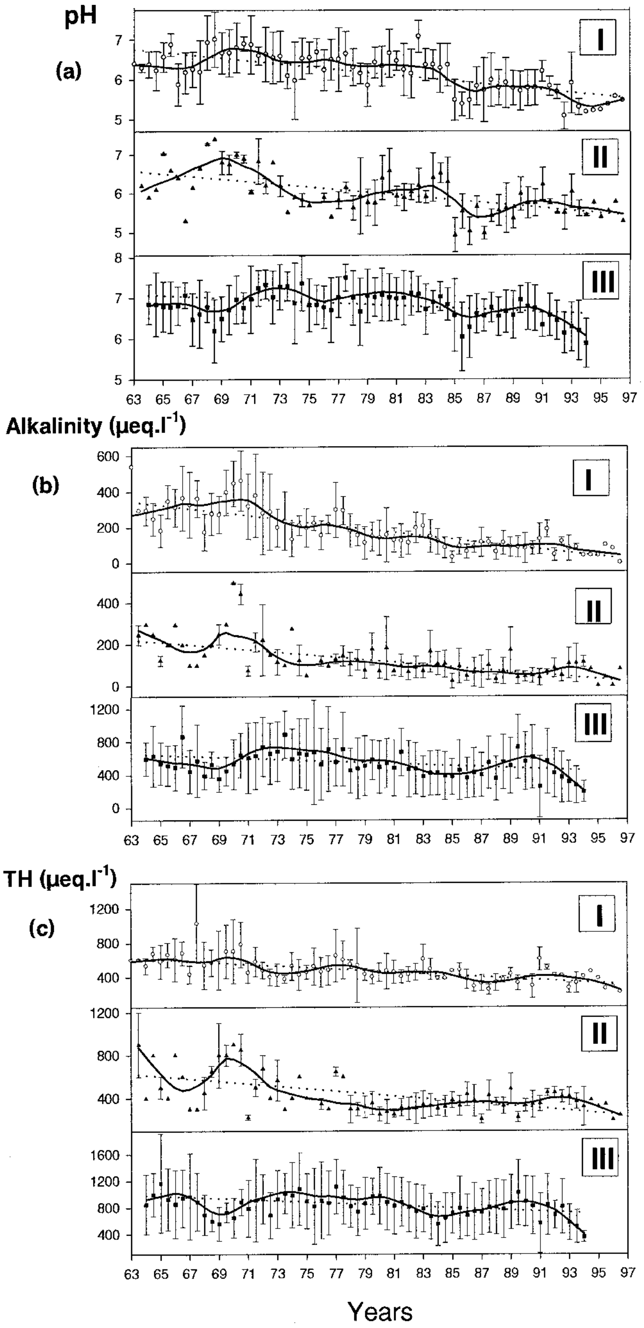
pH
(a)
I
II
III
7
6
5
8
Alkalinity (µeq.l-1)
(b)
600
400
200
0
1200
800
TH (µeq.l-1)
(c)
1600
63 65 67 69 71 73 75 77 79 81 83 85 87 89 91 93 95 97
Years

Figure 3a–c.

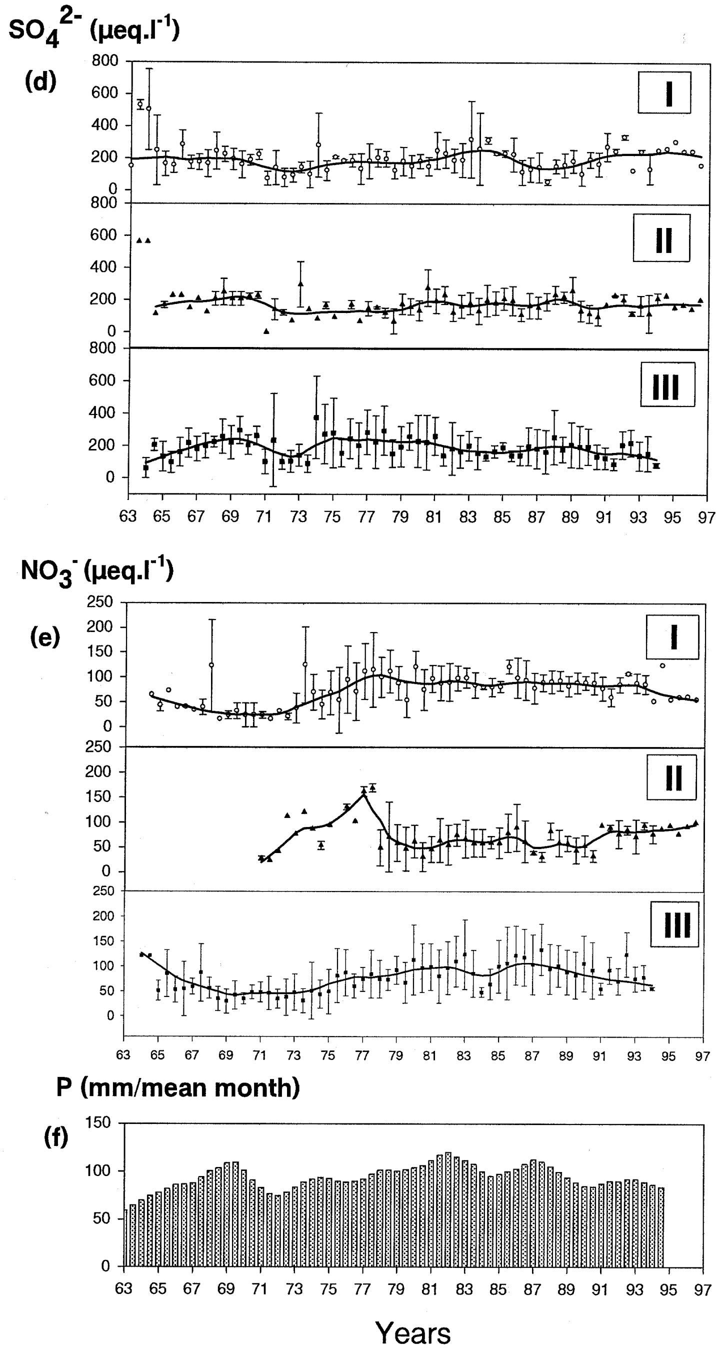

Figure 3a–f. Long-term trends in pH (a), alkalinity (b), Total hardness (c), nitrate (d) sulfate (e) and precipitation amount (f) (represented as a mean month by six-month periods). Mean value, standard deviation, smoothed curve and linear regression (dashed line, when significant) are noticed.

TABLE III

Kendall seasonal tau coefficients between chemical parameters (pH, alkalinity, Total hardness, sulfate and nitrate) and time (period 1963–1995) for groups of springwaters draining each type of sandstone (I, II, III). Each data point is the mean ± Std (n=10 for group I; n=7 for group II; n=9 for group III).

	Kendall correlation		
	Tau	p	n
pH-I	–0.530	***	68
pH-II	–0.403	***	66
pH-III	–0.272	**	61
Alk-I	–0.678	***	68
Alk-II	–0.503	***	66
Alk-III	–0.316	**	61
TH-I	–0.517	***	68
TH-II	–0.263	**	66
TH-III	–0.279	**	61
NO_3-I	0.230	*	65
NO_3-II	0.111	NS	51
NO_3-III	0.325	**	61
SO_4-I	0.068	NS	68
SO_4-II	0.040	NS	66
SO_4-III	0.122	NS	61

I – Siliceous sandstone / II – Conglomeratic sandstone / III – Clay-enriched sandstone. Significance threshold (p): **** < 0.0001; *** < 0.001; ** < 0.01; < 0.05; NS non significant.

using independent data and methods on some lakes of the Vosges located in the same area (Kreiser *et al*., 1995). Similar behaviour can be detected on divalent cation concentration (TH, Tables III and IV). TH decline was highly significant for groups I and II whereas in the last group, decline was detected but the slope was lower. The percentage of base cation decline was 50% and was less important for the springs from the third group.

Looking at the trend curves (Figure 3a and 3c), it appears that pH, alkalinity and TH began to decline obviously in the 1970’s period for springs belonging to groups I and II and only at the beginning of the 1980’s for pH in group III whereas alkalinity also began to decrease in the 70’s like in the other groups. According to

TABLE IV

Linear regression parameters between smoothed chemical parameters (pH, alkalinity, Total Hardness, sulfate and nitrate) and time (period 1963–1995) for groups of springwaters draining each type of sandstone (I, II, III). Percentage of change with time for each smoothed parameter, student t-test on slope and analysis of variance on the regression are indicated

	Linear regression				Student t-test		Fisher F-test	
	b	a	r^2	% decline	t	p	F	p
pH-I	6.77	–0.018	0.74	–18.0	–13.6	****	185.3	****
pH-II	6.59	–0.017	0.62	–17.5	–10.4	****	107.3	****
pH-III	7.10	–0.008	0.28	– 7.5	–4.8	****	23.1	***
Alk-I	349	–4.77	0.88	–93.0	–21.9	****	479.5	****
Alk-II	224	–2.95	0.79	–89.0	–15.5	****	241.1	****
Alk-III	654	–3.22	0.25	–33.0	–4.5	****	20.0	***
TH-I	625	–4.59	0.83	–50.0	–18.6	****	344.4	****
TH-II	632	–5.68	0.55	–61.0	–9.0	****	81.4	****
TH-III	997	–4.38	0.32	–30.0	–5.3	***	27.8	***
NO_3-I	41.4	0.78	0.34	–	5.8	****	33.1	***
NO_3-II	75.3	–0.03	NS	–	–	–	–	–
NO_3-III	53.3	0.71	0.10	–	2.5	*	6.3	*
SO_4-I	165.9	0.65	0.13	–	3.1	**	10.0	**
$SO_4$0II	162.3	0.12	NS	–	–	–	–	–
SO_4-III	203.7	–0.45	NS	–	–	–		–

I – Siliceous sandstone / II – Conglomeratic sandstone / III – Clay-enriched sandstone. Significance threshold (p): **** < 0.0001; *** < 0.001; ** < 0.01; * < 0.05; NS non significant.

all the parameters, the decline seems to be enhanced in the nineties specially for group III even if it is already possible to confirm this trend.

As shown on Figure 3f, the precipitation amount has not changed significantly over the studied period. Only mid-term trends in chemical parameters can be linked to climatic effect. For each parameter where decline was observed, a multiple regression analysis confirmed that time was the only highly significant factor in explaining the observed trends.

3.2.2. *Particular Case of Nitrates and Sulfates*

Trends were also performed on sulfate and nitrate (Figure 3d and 3e), but no significant trends could be detected whatever the groups. Concerning nitrate, in the three groups, no general significant long-term trends were observed. In all groups of springs, we observed a steep increase in nitrate concentrations in the mid-seventies, but the nitrate concentrations still remain lower than 15 mg L^{-1}.

4. Discussion

The investigations of springwater chemistry in the Vosges mountains have detected poorly buffered and acid springs in the area where acid streams have been previously found. This shows that in this area, waters draining deep soil layers are no more buffered and drinking water supply can finally be affected. Probst *et al.* (1995) and Party *et al.* (1995) has related the distribution of acid streams to that of sensitive silicate drainage bedrock, cemented glacial soil layers and the presence of coniferous trees. Springwater acidity can then obviously be related to the same environmental factors. The observed trends on spring water chemistry give unique interesting data for France to know if this acidity is natural, recent or if it appeared several years ago like in other parts of industrialised areas. The mean pH distribution for the last four decades on sandstone indicates that a more important number of poorly buffered and acid springs occur in the eighties compared to the sixties. The long-term trends for pH, alkalinity and base cations indicated a general obvious decline for 30 yr in this area of the Vosges mountains. However, the acidification process which led to pH and alkalinity decrease was not of the same intensity between the three groups of springs. The groups I and II of springs draining silica-enriched sandstone with a poor buffering capacity revealed an important decline in alkalinity and almost simultaneously in pH, whereas springs from group III which drain clay-enriched sandstone, show a less important decrease in alkalinity and a delayed decrease in pH. The declining trends in pH and alkalinity began in the early 70's for the two first groups draining the poorest bedrock base cation whereas in group III, the alkalinity first began to decrease only in the eighties followed by the pH some years later. The intensity and the occurrence of the declines in pH, alkalinity and TH are different in relation to the buffering capacities of the bedrocks. The clay-enriched sandstone has a higher base cation content than the other sandstones (Table II). Hence the different observed patterns between groups of springs can be interpreted as a natural titration process at a region scale regarding acid atmospheric inputs. Weathering and exchange processes in soils on this type of bedrock were able to buffer inputs till the buffering capacity would be exhausted. These results are consistent with intensive catchment studies in the Vosges where acidification of soils and waters on a poorly buffered granite has been pointed out (Probst *et al.*, 1992; Dambrine *et al.*, 1997). Similar results have also been observed in catchments and lakes from U.S.A (Driscoll *et al.*, 1995). However, only few studies deal with groundwater chemical patterns, similar observations have been set up for groundwater in nordic countries such as Swedberg (1995) and Knutson *et al.* (1995). From 1960, no real change in precipitation amount nor in forestry practices occurred and only short-term trends can be interpreted as climate effect.

Indeed, the beginning in springwater pH and alkalinity decline corresponds to the peak of atmospheric emissions of SO_2 in France (Canh, 1991; Ulrich and Willot, 1993). An important increase of SO_2 emissions began at the end of the 1950's and reached a first maximum in 1973 (1st oil crisis). Then, the emissions decreased till 1975, after which a new increase occurred and a new maximum was reached in 1980 (2nd oil crisis). Since that time, SO_2 emissions have decreased regularly to reach nearly the values measured in the 1950's.

The delay between the maximum SO_2 emissions and the beginning of perceived acidification process in the catchments correspond to the titration process according to the relative buffering capacities of the different sites. The hydrogeologic control of surface water chemistry has been mentioned in many other places (Peters and Driscoll, 1987). However, in spite of significant reduction of pollutant emissions and consequently of acid inputs to catchments over Northern Europe, no recovery can yet be observed in the Vosges region.

Unlike in many sites, following the decrease in atmospheric inputs in northern Europe over these last decades, the sulfate concentration in spring waters did not change in either of the three groups, as it could be expected. This can be the result of mobilisation and release of adsorbed sulfate previously stored during several decades of important inputs to soils, as observed in a nearby intensive studied catchment (Probst *et al*., 1992). These processes probably delay the recovery of surface water acidification. Such observations were also done by Jeffries *et al*. (1995) in Canadian lakes.

The increasing step of nitrate observed in the three groups of springs in the early seventies can not be obviously interpreted. It may correspond to change in analytical techniques (however the increase seems progressive) and/or to the consequences of increase in atmospheric inputs mainly reflecting the beginning of both the intensive use of fertilisers in agriculture and car trafic by that time.

5. Conclusion

Springwater chemical investigations in the Vosges mountains (N-E of France) reveal the occurrence of acid springs where acid streamwater were detected. This means that ground water is no more buffered in some catchments, potentially leading in some places to significant changes for drinking water supplies and ecosystem equilibrium. The percentage of less buffered springs seems more important than streams in the same area and acid springs occurred more frequently in the granitic area. As a mean, the distribution of spring pH moves from the sixties to the eighties, from dominant well buffered pH to circumneutral pH with the occurrence of acid spring at the beginning of the eighties.

Long-term mean trends in pH, alkalinity and base cations of springwater gathered in three groups according to the type of drainage sandstone, indicate significant decreases. However, the decrease was more important for spring draining base-poor sandstones than for springs on clay-enriched sandstone: 18 and 8% for pH, 90 and 30% for alkalinity, 50 and 30% for base cations, respectively. The decline for both pH and alkalinity began in the early seventies for all springs except those draining clay-enriched sandstone the pH of which decrease only by the early eighties. Since no climate and forestry practices changed, and particularly no relationship was found with precipitation amount, these trends could be related to acid atmospheric input influence. The difference in the trends can be interpreted as the result of the buffering capacity of the various types of sandstones regarding acid atmospheric input titration by weathering and exchange processes.

The increasing step of nitrate in the seventies is difficult to interpret and the sulfate presents no changes over the period meanwhile decreasing atmospheric inputs, probably as a result of adsorption – mobilisation processes in the soils. This could contribute to delay the recovery regarding acidification process in this region.

These long-term trends are the only available reliable data in France which allow to reconstruct the trends in springwater chemistry that result from climate or pollution climate changes. They clearly show that together with other investigations in this region, surface water chemistry has been changing over time since the sixties. Thanks to the buffering capacity of exchange and weathering processes, drinking water supplies have not been immediately concerned by acidity. However, the observed trends must lead to abatement strategies of atmospheric pollutant together with different forest management practices since coniferous forest plantations have clearly been involved in increasing acid atmospheric inputs capture (Landmann and Bonneau (eds), 1995). This is a minimum safeguard to ensure drinking water supplies for the future generations, particularly in these sensitive mountainous areas.

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