

THE CHEMICAL NATURE OF ACID PRECIPITATION OVER EUROPE

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ABSTRACT

A detailed analysis of the chemical data on wet precipitation for 16 European stations, for the period 1977–1980, was undertaken. The combined pattern of correlation coefficients and the stoichiometric ratios of important chemical species were employed in the interpretation. Trace-to-slight weighted average free acid levels ($\text{pH} = 5.8\text{--}4.7$) are found south of about 47°N , with the exception of northern Italy. The main acid-neutralizer in this region is alkaline calcium. Moderate or rather high free acid contents ($\text{pH} = 4.5\text{--}4.2$) exist north of this latitude where the predominant alkali, ammonia, partially neutralizes sulfur acids. The acid precipitation occurring between 47° and 55°N appears to be associated with the acidic sulfates of ammonium (probably the bisulfate) and/or sulfuric acid. Any role of nitric acid is apparent only to the north of 55°N .

INTRODUCTION

ACID precipitation has been assumed to be associated, for the most part, with sulfuric and nitric acids¹. However, ammonia, alkaline calcium, and sea-salt particles could all react with these strong acids, forming $(\text{NH}_4)_2\text{SO}_4$ ²; acidic sulfates of ammonium, ASA³; NH_4NO_3 ^{4,5}; CaSO_4 ⁶; and HCl ^{7,8}. Among these, only HCl is a strong mineral acid, while ammonium bisulfate, NH_4HSO_4 , which represents the acid in both ASA, is of lesser but considerable strength with a $\text{p}K_a$ value of ~ 1.9 for the HSO_4^- ion.

Since continental Europe is a major source of SO_2 and NH_3 ^{2,9} it is of interest to study the precipitation chemistry of the region. The WMO BAPMoN, which operates a rather dense international precipitation network over Europe, was selected as a source for the data. This paper summarizes the results obtained through an elaborate analysis of data for 16 stations that collect exclusively wet precipitation. The time period covered is 1977–1980. A more detailed version of this paper is also available¹⁰.

LIST OF STATIONS

The stations selected are shown in figure 1. In order to facilitate the discussion of results, they are grouped as follows: region I (south of 47°N): Gourdon (Gn), Kecskemet (Kt), Lazaropole (Lz), Puntijarka (Pj), Trapani Birgi (Tr) and Verona (Va); region II (47°N – 55°N): Abbeville (Ab), Chopok (Ch), Langenbrugge (Ln), Schauinsland (Sd),

Suwalki (Sk), and Witteween (Wt); region III (north of 55°N): Bredkalen (Bk), Dumfries (Df), Faero Islands (FI), and Jokioinen (Jk).

DATA SCREENING AND VALIDATION

The overall quality of the data was evaluated through the cation-to-anion ratio (I) and the calculated-to-measured conductivity ratio (k). Correctable errors were located using these ratios in conjunction with superposition of control charts for various ions or their ratios. Occasionally, errors in placement of the decimal point were located, confirmed and corrected. On the other hand, incorrectable data showing large errors were excluded in further treatment. The analyst/reporter was given the benefit of the doubt in the following special circumstance: $\text{pH} \geq 6$; $I > 1$; $k < 1$ (including the contributions to the I - and k -ratio values of $[\text{HCO}_3^-]$ deduced from pH), thus allowing for the possible presence of other unreported ions, e.g. phosphates, borates, fluoride and organic ions.

Stations reporting sulfate, nitrate, and ammonium ion concentrations in the form of SO_4^{2-} , NO_3^- , and NH_4^+ (radicals) were carefully identified, and the same data were converted to the S, N and N form. In the following text, usable data for 14 of the 16 stations which reveal satisfactory-to-good quality are treated.

SEA SALT CORRECTION

The non-sea salt (NSS) components of the SO_4^{2-} and Ca^{2+} species were determined in the usual

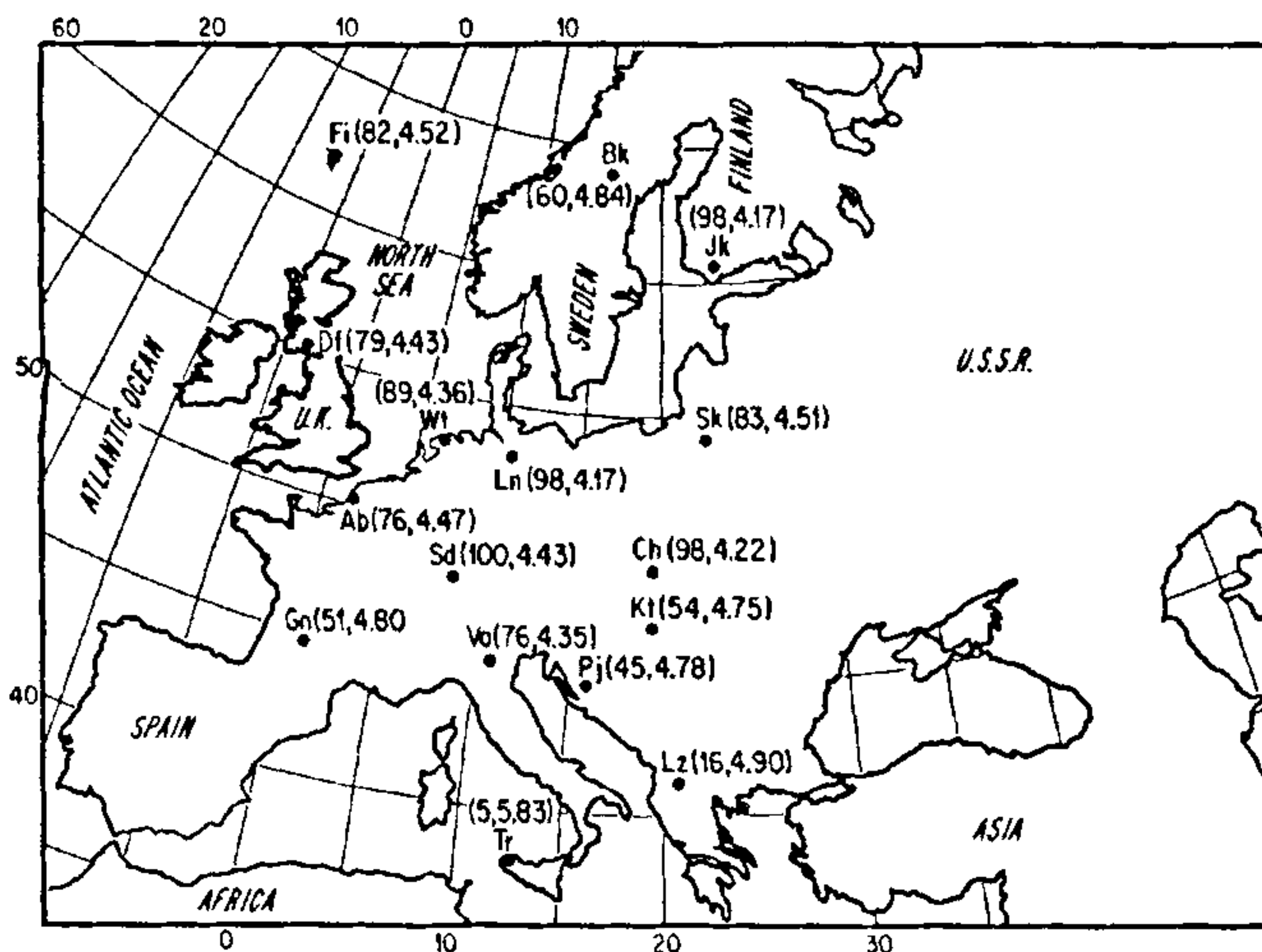


Figure 1. Selected BAPMoN stations over Europe. Figures in parantheses are, respectively, the percentage of samples with $\text{pH} \leq 5$, and the volume-weighted mean pH (pH).

manner⁵, taking care to interchange the multiplication factors in equations (3) and (4) in the above paper, which were interchanged inadvertently. When the NSS fraction (as a per cent of the total ion concentration reported) exceeded 90%, the above correction was considered unnecessary. A significant number of stations belong to this category. A general formula for calculating the NSS fraction is:

$$M(\text{NSS}\%) = \left\{ 1 - \frac{(M/\text{Na})(\text{sea water})}{(M/\text{Na})(\text{reported})} \right\} \times 100.$$

where M is any major sea salt constituent other than Na.

DATA ANALYSIS

After screening and validation of the data, and making necessary sea salt corrections for SO_4^{2-} and Ca^{2+} ions, the mass or chemical equivalent concentrations of H^+ , NH_4^+ , NSS-Ca^{2+} , NO_3^- , and NSS-SO_4^{2-} , were utilized in the analysis. The product-moment correlation, $r(X, Y)$, and the ratio of means of chemical equivalents, $[Y/X]$ (where X and Y constitute, entirely or partially the relevant cation and anion, respectively), were determined. The temporal persistence of the r -values was checked, employing "running correlations," RC, for the time periods 1977, 1977-78, 1977-79, etc. The RC values significant at the 0.01 level of confidence were

earmarked. These RCs reinforce interpretations and conclusions. For convenience, $r(\text{NH}_4^+ \cdot \text{SO}_4^{2-})$, $r(\text{H}^+ \cdot \text{SO}_4^{2-})$ and $r(\text{H}^+ \cdot \text{NO}_3^-)$ will henceforth be referred to as (A-S), (H-S) and (H-N), respectively. Only the final or terminal RCs are presented here, e.g., 1977-80, while their overall features are summarized collectively.

RESULTS AND DISCUSSION

The important results obtained are presented in table 1, and figures 1 and 2, and are discussed below. Due to the small sample size for the $\text{pH} \leq 5$ category, table 1 does not contain results for either Trapani Birgi or Lazaropole.

Region 1. With the exception of Verona in northern Italy, this region generally receives low-to-negligible volume-weighted average free acidity ($\text{pH} = 4.7 - 5.8$), as seen in figure 1, where the first number in parantheses is the percentage of samples with $\text{pH} \leq 5$, $N(5 \downarrow)$, and the second number is the pH referred to above. Ignoring Verona, the $N(5 \downarrow)$, which is the lowest at 5% for Trapani Birgi, increases systematically towards the north. This station and others in the region revealed frequent and large anion deficits for precipitation with $\text{pH} > 5$. The $[\text{HCO}_3^-]$ calculated from pH accounted, partly or fully, for these deficits. The role of alkaline Ca^{2+} in neutralization is demons-

Table 1 Coefficient of correlations, $r(X,Y)$ and ratio of means, $[\overline{Y/X}]$, for European wet precipitation with $pH \leq 5$

Region	$r(\text{NH}_4^+ \cdot \text{SO}_4^{2-})$	$[\text{SO}_4^{2-}/\text{NH}_4^+]$	$r(\text{H}^+ \cdot \text{SO}_4^{2-})$	$[\text{SO}_4^{2-}/\text{H}^+]$	$r(\text{H}^+ \cdot \text{NO}_3^-)$	$[\text{NO}_3^-/\text{H}^+]$
<i>Region I</i>						
Gourdon	0.27 (21)	2.39	0.20 (21)	2.46	-0.06 (21)	0.62
Verona	0.63*(33)	0.83	0.16 (33)	0.90	-0.05 (34)	0.65
Kecskemet	-0.09 (24)	1.08	-0.41 (23)	4.17	0.38 (24)	1.32
		0.46 ^c				0.30 ^c
<i>Region II</i>						
Abbeville	0.64*(35)	2.37	0.44*(35)	2.84	0.21 (35)	0.87
Witteween ^a	0.93*(32)	1.32	0.27 (31)	2.67	0.27 (31)	1.19
Langenbrugge	0.87*(42)	1.73	-0.16 (44)	1.82	-0.06 (47)	0.98
Schauinsland	0.69*(45)	2.59	0.72*(45)	1.56	0.39 (48)	0.59
Suwalki	0.75*(40)	1.71	0.40*(40)	3.50	0.36 (40)	1.31
Chopok	0.80*(46)	1.98	0.20 (46)	2.46	0.22 (46)	0.69
<i>Region III</i>						
Dumfries ^b	0.74*(23)	1.55	0.50 (23)	1.44	0.60*(23)	1.95
Faero Islands	0.68*(36)	10.30	0.89*(37)	1.11	0.44*(37)	0.49
Bredkalen	0.72*(29)	4.38	0.13 (29)	2.65	0.44 (29)	0.86
Jokioinen	0.45*(39)	2.30	0.41*(39)	1.91	0.62*(39)	0.68

The period of data covered is 1977–1980, with the exceptions indicated by the superscripts *a* (1977–1979) and *b* (1978–1980). The superscript *c* refers to ratio values if radical-concentrations were reported. Square brackets indicate use of ionic equivalent concentrations. The numbers in parentheses show sample sizes. SO_4^{2-} represents the non-sea salt portion. Correlations with an asterisk indicate significance at the 0.01 level of confidence.

trated by the following interesting set of RC values of $r(\text{Ca}^{2+} \cdot \text{H}^+)$ for samples with $pH > 5$ whose sample size is indicated by $N(5 \uparrow)$. The periods in order are: 1977, 1977–78, 1978–79 and 1977–80. The results are:

Trapani Birgi: -0.56, -0.52, -0.56,
-0.52* $N(5 \uparrow) = 36$,
Gourdon: -0.85, -0.44, -0.56, -0.48,
 $N(5 \uparrow) = 20$.

Larger values of the RCs were not expected because the Ca^{2+} vs H^+ relation is a nonlinear one⁵ and the probable arid, calcareous dust transport¹⁰ does not occur throughout the year.

Region II. The percentage of $N(5 \downarrow)$ is quite large at all stations east of 5°E, i.e. for five of the six members (figure 1). The results in table 1 and figure 2 might, at first glance, tempt one to believe that the ASA—especially NH_4HSO_4 —are the main acids. However, a predominant contribution to the free $[\text{H}^+]$ from the ASA, vis-a-vis the HSO_4^- dissociation, would also require (among other constraints), statis-

tically significant (H.S) values in tandem with the (A.S). Thus, a major contribution to free acidity by the ASA is possible only in the case of Abbeville.

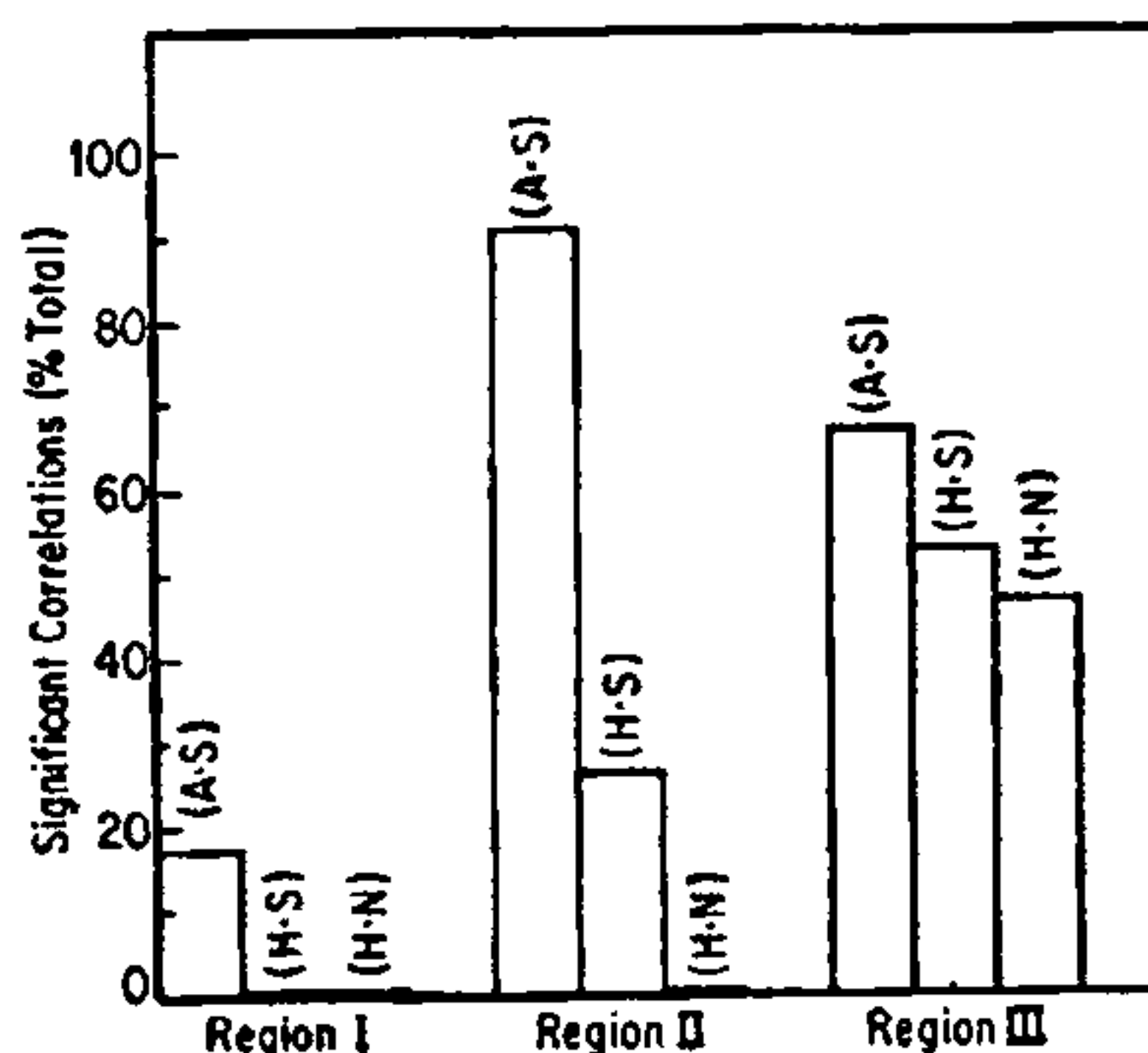


Figure 2. Percentage of “running correlations,” RC, significant at the 0.01 level. The total in the ordinate refers only to the fraction of significant correlation coefficients for a given cation-anion (X-Y) pair.

Schauinsland and Suwalki. Unneutralized H_2SO_4 must be considered as the major acidifier at the remaining three locations, despite the poor (H.S) value. This is reasonable as long as HNO_3 is unimportant; the $[\text{SO}_4^{2-}/\text{NH}_4^+]$ ratio value is well over 1.0; and $[\text{SO}_4^{2-}/\text{H}^+] > 1.0$ (cf. table 1). Such ratios for region II would then suggest that a significant fraction of the NSS-SO_4^{2-} is associated with neutral $(\text{NH}_4)_2\text{SO}_4$, which suppresses the (H.S) and simultaneously yields an artifact $[\text{SO}_4^{2-}/\text{NH}_4^+]$ ratio that appears to correspond to one of the ASA.

Region III. Although the pattern of r -values in table 1 is confusing, a brief discussion on the individual stations in this region is possible and is offered below.

(a) Bredkalen, Sweden. The $\text{pH} = 4.84$ is anomalously low for a typical Swedish station. Frequently, large concentrations of Ca^{2+} were reported. The Ca^{2+} appeared to have been present originally as a mixture of CaCO_3 and some neutral species, most likely CaSO_4 [since $r(\text{Ca}^{2+} \cdot \text{H}^+)$, was found to be weak but negative in sign for the most part¹⁰]. Anthropogenic sources, such as aerial liming of acid lakes, quarry operations, etc., may be responsible for such Ca^{2+} levels. However, for samples with $\text{pH} \leq 5$, unneutralized H_2SO_4 could be the main acid, according to the arguments just presented for region II. The role of HNO_3 , if any, may be much less important than that of H_2SO_4 , since none of the RCs for (H.N) were found to be statistically significant¹⁰.

(b) Dumfries, Scotland. The individual RCs for (H.N) were found to be most persistent despite the presence of a considerable fraction of non-acidic nitrate ($\text{NO}_3^-/\text{H}^+ = 1.95$), on the average, suggesting a primary role of HNO_3 (cf. table 1).

(c) Faero Islands, N. Atlantic. Although all the correlations presented in table 1 are significant, the stoichiometric ratios support the role of H_2SO_4 as the predominant acid. Further, all four RCs obtained for (H.S) were uniformly high and significant¹⁰.

(d) Jokioinen, Finland. Unlike Bredkalen, fairly high free acidity ($\text{pH} = 4.36$) is present at Jokioinen. The overall correlations in table 1 and other available information (not presented here) do not suggest a dominance of one acid over the other.

In short, the present data are insufficient for making general conclusions on acid precipitation chemistry to the north of 55°N , except that there is evidence of considerable importance of HNO_3 in acidification in some cases. More data from the United Kingdom, Scandinavia, and their adjacent seas are needed for such an assessment.

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