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On the composition of precipitation water and its acidity

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ABSTRACT

The aim of this paper is to calculate the pH from the mean ionic composition of precipitation water published by several workers in the literature and to provide some characteristics of regional and source differences in rainwater. The calculated pH is compared to the "measured" mean pH based on precipitation-weighted hydrogen ion concentrations. Deviations are related to gaps in the anion-cation-balance. It has been found that in areas with high basic soil, particulate contribution to the atmosphere bicarbonate in rainwater plays an important rôle. In the vicinity of lignite-fired power plants, further basic contributors like oxides of Fe and Al seem to be of importance in the control of pH. Furthermore, some regional particularities in neutralizing capacity has been found. The percentage of basic species in European precipitation is twice as high as in North America, whereas no differences are found between eastern and western Europe. However, the nitrate share in eastern Europe in rainwater is ⅓ less than in western Europe.

1. Introduction

The pH value of precipitation water is a result of the acid-base balance of chemical constituents arising from the incorporation of atmospheric gases and aerosols by in-cloud and sub-cloud scavenging. One can distinguish between 5 sources of atmospheric chemical species: volcanic eruptions and exhalations, biogenic release, seaspray, soil dust, and man-made emissions. Components emitted by these sources can be found in precipitation water. The pH of the "natural" rainwater in remote areas far from industrial countries varies between less than 5 (Galloway et al., 1982) and more than 7 (Sequeira, 1982) depending on the region regarded. Today it is a well-known fact that the value of pH = 5.6 is not appropriate as a reference value for rainwater without human influences (Charlson and Rodhe, 1982).

Man-made activities disrupt global balances between the oxidation and reduction rates in the direction of higher oxidation combined with a greater proton supply in the atmosphere (Stumm et al., 1983). The results of man-made emission estimates (Logan, 1983, Möller, 1984b) show that the global acid input from SO_2 and NO_x amounts at present to 6–7 Teq year^{-1}, 20–25% of which is due to NO_x emissions. On the other hand, the base input from anthropogenic NH_3 emissions (Möller and Schieferdecker, 1982) is only 1.5–2.5 Teq year^{-1}. Other man-made basic species are Ca, Mg and Fe components contained in fly ash from lignite-fired power stations. Lignite mining and combustion, however, are limited to a few regions of the world. As a result of man-made excess acidity, the pH value in industrial areas often ranges between 4 and 5 (Georgii, 1981). However, great regional differences can be observed as a function of the type and distribution of anthropogenic (especially the fuel base) and natural emission sources (especially soil dust).

It is often not clear which ions control the hydrogen ion concentration in rainwater and which sources are responsible for the rainwater components. Knowledge of the inter-relationship between rainwater components, pH and their origin is

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indispensable for computation, especially for prediction of the acidity from emission data which can vary as a function of space and time. The aim of this paper is to evaluate from a theoretical point of view the pH from the ionic composition of precipitation water samples published in the literature and to compare the pH calculated with the pH measured. On the basis of these calculations, regional particularities and differences will be given.

2. Data analysis

The hydrogen ion concentration of rainwater can theoretically be determined from the ionic balance on the basis of the condition of electric neutrality:

$$[H^+] = \sum [\text{anions}] - \sum [\text{cations without } H^+]. \quad (1)$$

However, generally not all ions are analysed in order to establish the ionic balance. The experience gained has shown that nearly 100% of the total composition (without H^+ and HCO_3^-) is given by the following main components:

SO_4^{2-}, NO_3^-, Cl^-, NH_4^+,
Ca^{2+}, Mg^{2+}, Na^+, K^+.

One approach to evaluate $[H^+]$ from the rainwater composition is based on stepwise regression using the general equation

$$[H^+] = a + b[SO_4^{2-}] + c[NO_3^-] + d[Cl^-] + e[Ca^{2+}] + f[Mg^{2+}] + g[Na^+] + h[K^+] + i[NH_4^+] \quad (2)$$

(Hakkarinen, 1983). From the North American Precipitation Network, Hakkarinen has found considerable variations in the coefficients for different stations. Other regression equations, partly more simplified, were published by Bowersox and de Pena (1980), McNaughton (1981), Asman et al. (1981), MAP3S (1982). Based on eq. (1), the theoretical hydrogen ion concentration will be as follows (see e.g. Granat, 1972; Hakkarinen, 1983; Liljestrand, 1985):

$$[H^+] - [HCO_3^-] = c_A - c_B = [\text{acidity}] \quad (3)$$

where $c_A = 2[SO_4^{2-}] + [NO_3^-] + [Cl^{-1}]$ and $c_B = 2[Ca^{2+}] + 2[Mg^{2+}] + [K^+] + [NH_4^+] + [Na^+]$ as concerns the main components listed above. With $[HCO_3^-] = K_1 Hp/[H^+] \approx 4.41 \cdot 10^{-12}$ mol^{-2} l^{-2} (298 K) where K_1 is the equilibrium constant of the $(CO_2)_{aq}$ protolyse, H the Henry constant and p the atmospheric CO_2 partial pressure, we obtain from eq. (3)

$$[H^+]^2 - [H^+](c_A - c_B) - 4.41 \cdot 10^{-12} = 0. \quad (4)$$

In these equations, we neglect the bases CO_3^{2-} and OH^- because their contribution is significant only for pH > 8. The mean hydrogen ion concentration has to be estimated according to eq. (5) or (6), resulting as a solution of eq. (4):

$$\overline{[H^+]}_{meas} = \tfrac{1}{2}A + \sqrt{\tfrac{1}{4}A^2 + 4.41 \cdot 10^{-12}}, \quad (5)$$

where

$$A = \sum_j P_j([H^+]_j - K_1 Hp/[H^+]_j) / \sum_j P_j;$$

j indicates the single sample, P is the precipitation amount;

$$\overline{[H^+]}_{calc} = \tfrac{1}{2}\overline{(c_A - c_B)} + \sqrt{\tfrac{1}{4}\overline{(c_A - c_B)}^2 + 4.41 \cdot 10^{-12}}, \quad (6)$$

where

$$\overline{(c_A - c_B)} = \sum_{i,j} c_i P_j / \sum_j P_j,$$

the precipitation-weighted mean composition. Eq. (6) has been used in this work to calculate the theoretical mean $[H^+]$ from the mean ionic composition of rainwater and to compare the pH calculated with the pH_{pwm} given in the literature based on precipitation-weighted mean hydrogen ion concentration $[H^+]_{pwm} = \sum_j P_j[H^+]_j / \sum P_j$. Liljestrand (1985) has shown that this mean hydrogen ion concentration is inappropriate, since $[H^+]$ is a non-conservative quantity upon mixing of samples. Both values correspond only if pH < 5. In Table 1, the stations used for analysis by eq. (6) are listed. At these stations, wet-only precipitation samples were taken during a longer time period (at least 1 year).

The problem of data quality and comparability of data obtained at different stations is widely known (e.g. Hakkarinen, 1983; de Pena et al., 1980; Horvath, 1980; Pack and Shephard, 1983). Without discussing this problem in more detail, we mention that in this paper, only mean values from long-time period are taken into account to exclude random variations. The accuracy of measured pH values depends on the pH range and is about ±0.15 pH units in the range between pH 4 and 5 (Marquardt et al., 1984). On the other hand, the

Table 1. *Selected measuring stations of precipitation for analysis in this paper*

No.	Station	Characteristics	Time period	Sampling	Reference
1	GDR	background	1982–84	each event	Marquardt et al. (1984)
2	Czechoslovakia	rural clean, altitude 545 m	1977–79	monthly	Moldan (1980)
3	Czechoslovakia	ind. area with power plants	1977–79	monthly	Moldan (1980)
4	Hungary	average from 6 stations	1977–80	monthly, daily	Horvath (1981)
5	Poland, Suwalki	rural in NE, Mazuren	1980–82	monthly	EMEP (1984)
6	Yugoslavia, Puntijarka	rural area, altitude 988 m	1978–82	monthly	EMEP (1984)
7	Holland, Den Helder	coastal station from 8 parallel samplers; maritime periods only	1979–80	episodes of 2 to 3 days	Asman and Slanina (1980)
8	Holland, Den Helder	as No. 7 but continental periods only			Asman and Slanina (1980)
9	Holland, Witteven	WMO background station	1978–82	monthly	EMEP (1984)
10	England	rural site, NW	1979–81	daily	Harrison and Pio (1983)
11	Norway, Birkenes	maritime influenced background, SW	1978–82	month	EMEP (1984)
12	Norway, Jergul	inland station in Finnmark, NE	1978–82	monthly	EMEP (1984)
13	Norway, Bjørnøya	island in North Atlantic	1978–82	monthly	EMEP (1984)
14	Norway, Kårvatu	maritime influenced remote area, N	1978–82	monthly	EMEP (1984)
15	USA, Minnesota	mixed forest-agricultural, average from 3 stations	1978–79	each event	Munger (1982)
16	USA, NE-Minnesota	forested area in vicinity of coal-fired power plant, average from 3 stat.	1981	148 events	Pratt et al. (1984)
17	USA, S-Minnesota	agricultural area in vicinity of man-made emitters, average from 4 stat.	1981	263 events	Pratt et al. (1984)
18	USA, Illinois	agricultural area near Champaign	1979–81	each event	Gatz (1984)
19	USA, California	Pasadena, industrial region			Liljestrand and Morgan (1978)
20	USA, New York	maritime influenced city			Feely and Larsen (1979)
21	USA, Florida	remote area			Hendry and Brezonik (1980)
22	USA, Alaska	Poker Flat, yukon taiga	1979–81	each event	Galloway et al. (1982)
23	Canada, Ontario	industrial region			Scheider et al. (1979)
24	Bermuda, St. George	subtropical oceanic island	1979–81	each event	Galloway et al. (1982)
25	Australia, Katherine	tropical savannah	1979–81	each event	Galloway et al. (1982)

analytical accuracy is generally within 10%. However, the absolute accuracy of analysis is a function of the concentration. The results for some stations with low values of rainwater composition (total concentration below 50 μmol l^{-1}) have to be considered with caution (nos. 12–14, 22, 25). Besides, calculations in the pH range $5 < pH < 8$ according to formulae based on eq. (1) are

extremely questionable (Liljestrand and Morgan, 1979). Moreover, it should also be noted that the mean results from event, daily or monthly sampling and analysis can significantly differ due to the concentration changes during the storage. Dramatic changes as well as no systematic alteration has been reported in the literature (e.g., Marquardt et al., 1984). Owing to these problems, one has to interpret and compare data for different stations only with caution.

3. Results and discussion

3.1. Controlling factors of precipitation water composition and acidity

It is the aim of this subsection to discuss briefly the different sources and factors controlling the composition and acidity of precipitation water. Besides seasalt, such factors can be biogenic, volcanic, soil and man-made emissions. Concerning the relation between biogenic and man-made emissions, the biogenic natural contribution (especially for sulfate and nitrate) seems to be negligible in industrial areas of the northern hemisphere (Möller, 1983, 1984a, b). An inverse situation has been found for tropical areas with high primary bioproductivity excluding any anthropogenic emitters resulting in comparable rainwater content to industrialized regions (Servant et al., 1984). In the regions regarded in this paper, the volcanic contribution to the rainwater sulfate is negligible due to the probably low global annual SO_2 emission by volcanoes (Möller, 1983). However, it seems that soil particulate matter plays an important rôle in the precipitation chemistry. Moreover, there are wide differences in the soil composition and in the emission capacity in various areas and regions. The main contributors to rainwater from soil dust are carbonates of Ca and Mg. They may dissolve in atmospheric liquid water in the presence of carbonic acid (CO_2-saturated water); cf. Mészáros (1966):

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca^{2+} + 2\,HCO_3^- . \quad (7)$$

Acidic water droplets may, however, also incorporate carbonates according to the equation below:

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^- . \quad (8)$$

The bicarbonate ion is involved in a protolytic equilibrium depending on the hydrogen ion concentration:

$$HCO_3^- + H^+ \rightleftharpoons H_2CO_3 . \quad (9)$$

The second protolytic step ($HCO_3^- \rightleftharpoons H^+ + CO_3^-$) in rainwater with pH <8 is negligible. Furthermore, Ca and Mg are originated from fly ash as sulfate and different oxides. In this latter case, the following reactions are possible:

$$CaO + 2\,CO_2 + H_2O \rightarrow Ca^{2+} + 2\,HCO_3^- , \quad (10)$$

$$CaO + CO_2 + H^+ \rightarrow Ca^{2+} + HCO_3^- , \quad (11)$$

$$CaO + 2H^+ \rightarrow Ca^{2+} + H_2O . \quad (12)$$

Due to these reactions, the neutralization capacity of Ca compounds ranges between 0 and 2 equivalents. In Table 2 is listed the $\overline{pH}$ calculated according to eq. (6). For 14 Stations, a surprisingly good agreement is found between pH values based on measurements and calculations. For the stations where the agreement is good, the mean difference is 0.08 pH units, while the range of the variation is 0.0–0.21. However, for some stations, the deviation is much more important. The reasons can be summarized as follows.

Case 1: $pH_{pwm} > \overline{pH}_{cal}$.

The high measured pH in the GDR (no. 1) and Yugoslavia (no. 6) is probably due to the fact that besides Ca and Mg, there are further base-forming components in fly ash (e.g., oxides of Fe and Al), in rainwater which have not been measured systematically until now. The gap in the anion-cation-balance resulting from eq. (1) can be closed if we take into account an additive term of basic species in this equation. The Ca/Fe ratio in fly ash in GDR lignite-fired power stations is 1.8 (1 to 3) on an average. If this concentration ratio were also valid for rainwater, a pH value of about 4.5 would be calculated according to eq. (6) for station no. 1, provided that other concentrations remained the same (see Table 2). This new value is in agreement with pH_{pwm}.

Case 2: $pH_{pwm} < \overline{pH}_{calc}$.

This situation exists at the Hungarian stations (no. 4) and at the north America central stations (nos. 15 to 17, and 23). This can be explained if we assume that in both areas, soil dust plays an important rôle, since according to eqs. (7) and (8),

Table 2. *Results of analysis of rainwater composition.*

No.	c_A (μeq l^{-1})	c_B (μeq l^{-1})	[Na^+] (μeq l^{-1})	pH_{pwm}	$\overline{pH}_{calc}$	Relative contribution of excess components in eq–%* SO_4^{2-}	NO_3^-	NH_4^+	($NH_4^+ + Ca^{2+} + Mg^{2+} + K^+$)
1	312	246	50	4.5	4.2	39	9	23	44
2	189	109	8	4.31	4.1	45	18	22	36
3	332	234	13	4.14	4.01	46	12	23	40
4	173	210	21	4.5	6.9	31	12	22	56
5	200	150	17	4.42	4.3	42	14	27	41
6	232	159	17	4.70	4.14	48	5	15	39
7	376	314	191	4.25	4.21	39	21	29	40
8	337	231	47	4.08	3.97	39	24	22	37
9	207	183	78	4.48	4.62	37	21	34	42
10	196	166	57	4.47	4.52	36	13	25	45
11	179	113	48	4.16	4.18	42	24	25	30
12	43	25	9	4.53	4.74	54	17	17	29
13	1090	1372	921	4.99	7.8	41	12	25	47
14	80	75	52	4.85	5.2	44	16	22	35
15	57†	101‡	9	4.95	7.0	22	17	25	61
16	56	68	18	4.67	6.4	36	15	24	49
17	76	98	10	4.83	6.7	30	15	29	55
18	98	37	3	4.18	4.21	37	32	22	30
19	164	76	25	4.06	4.06	32	42	19	26
20	207	78	36	3.92	3.89	63	20	6	16
21	85	61	19	4.53	4.62	42	15	7	37
22	12	3	1	4.96	5.03	64	18	9	18
23	106	98	17	4.00	5.07	58	27	3	15
24	217	199	147	4.79	4.73	48	14	10	25
25	22	14	7	4.78	5.07	38	25	12	38

For explanation of c_A and c_B see text (eq. (3)), pH_{pwm} = precipitation-weighted mean based on measurements, $\overline{pH}_{calc}$ = calculated mean according to the acidity conception.

* 100 eq–% = sum of ions listed in text according to eq. (3) with $[Na^+]_* = 0$.

† Without Cl^-.

‡ Without Na^+.

significant contribution of bicarbonate have to be expected. The contribution of soil dust originated components (Ca, Mg, K) to rainwater content at these stations is significantly higher in comparison with other stations listed and ranges from 26 to 36 eq-%. In earlier measurements in Hungary, Mészáros (1966) has found that 53 (17 to 100)% of total Ca is present as bicarbonate, on average. In spite of the high uncertainty of this figure due to very low number of cases (Mészáros, 1966), this is in relatively good agreement with our estimate of 46% using eq. (3).

Case 3: $pH_{pwm} \neq \overline{pH}_{calc}$.

No good agreement has been found for stations where the total ionic concentrations of excess components in rainwater are very low (nos. 12 to 14, and 25). At these stations, the relative error of measurement will be so high that the calculation of pH from the concentration of rainwater components is not meaningful. Besides, for stations nos. 22 and 25, organic acids must probably be taken into account to balance the proton supply (Galloway et al., 1982).

3.2. *Regional differences*

In spite of the limited number of stations analysed here, some regional characteristics can be derived from the precipitation chemistry data by comparing them qualitatively to the emission pattern. From the data in Table 2, we evaluate a neutralization share of $NH_4^+ + K_*^+ + 2(Ca_*^{2+} +$

Mg^{2+}_{*}) in eq-% (the asterisk means that these components are corrected from seasalt contribution):

middle Europe 41 (33 to 45)

north America 22 (15 to 29).

There is no difference between eastern and western Europe. However, for northern Europe, this share may be less than for other parts of Europe and amounts to about 30 eq-%. The variations in north America are more important than in Europe. It seems that in north Central US, the neutralization share is significantly higher (about 36 eq-%) than in other parts of north America. It follows from Table 2, that the contribution of nitrate to the acidity in terms of 100 $(NO_3^-/(NO_3^- + SO_4^{2-})$ is also different for different parts of the world:

eastern Europe 24 (19 to 29)

western Europe 34 (26 to 38)

north America 36 (24 to 57).

These figures reflect the relationship between man-made SO_2 and NO_X emissions. The significantly lower ratio for eastern Europe is caused by high SO_2 emission from lignite combustion and from relatively low NO_x emissions owing to lower traffic density related to western Europe.

Similarly, a difference is observed in the NO_3^-/NH_4^+ ratio between different parts of the world:

eastern Europe 0.5 (0.3 to 1.0)

western Europe 0.7 (0.5 to 1.1)

north America 1.1 (0.5 to 10).

The difference between eastern and western Europe can be explained by the difference in nitrate contribution as already discussed (the ratio of nitrate concentration is 1.4 between western and eastern Europe). The difference between western Europe and north America as a whole is somewhat higher because the ammonium contribution in north America is considerably lower (by a factor of more than 2). The situation is different for north central US with a NO_3^-/NH_4^+ ratio comparable to western Europe in spite of the fact that the absolute concentrations of NO_3^- and NH_4^+ are significantly lower in north central US (this ratio amounts 21/37 $\approx$ 0.6 for both stations nos. 16 and 17). In this way, the same ratio can reflect rather different situations, e.g., (in μmol l^{-1}), the ratio of NO_3^-/NH_4^+ is equal to 98/135 = 0.7 for an industrial-agricultural area (no. 8) and is the same (5/7 = 0.7) for remote area (no. 14).

4. Conclusions

According to the material presented in this paper, important differences in neutralizing capacity in atmospheric precipitation can be found as a function of the emission pattern of the region considered. Thus, it is proposed that this must be taken into consideration by interpreting the results of calculations of pH on the basis of an anion-cation-balance. This implies that the composition of precipitation water reflects the influences of regional and even national air pollution.

The results discussed also show that in areas where the atmospheric concentration of soil dust is high, the bicarbonate ions play an important rôle in the control of pH. Therefore, the idea of acidity to estimate mean hydrogen ion concentrations according to eq. (5) should be used.

It is probable that at places influenced by emissions from lignite-fired power plants, compounds of Fe and Al also control the acid-base balance.

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