On the relation between pH and the chemical composition in atmospheric precipitation

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ABSTRACT

Based on chemical analyses of some 2 000 rainwater samples, the relation between the pH and the total amount of acid or of base respectively is studied. Considering the carbon dioxide–water system the theoretical relation between pH and total amount of acid or bicarbonate is calculated. A regular deviation is observed between the empirically found and theoretically calculated relation. Starting from chemical analyses of the most important compounds in atmospheric precipitation, a quantitative hypothesis is formulated of how these compounds originally were associated with acids or bases. It is further assumed that these have netralized each other and that the system has come to an equilibrium with the carbon dioxide pressure of the atmosphere. Good agreement is obtained between the predicted amount of acid or base and the measured one, and this is taken as a clear indication of the validity of the model. This model on the stoichiometric relation between acids and bases turns out to be a useful tool both for an interpretation of the amount of acid found in precipitation and in estimating future deposition of acid by precipitation.

1. Introduction

In the study of the continuing acidification of precipitation, which is especially marked in the southern and western parts of Scandinavia, the question arises if there exists a simple relation between the pH of precipitation and its chemical composition, especially in relation to the sulphate concentration. A substantial amount of data are available to try to anser such a question and some 2 000 samples have been used in this study.

The first step has been to relate measured pH to the amount of acid or base (alkalinity) obtained by titration. A very clear and "smooth" relation was then obtained, though small but significant deviations existed between measured values and those obtained theoretically with due regard taken to prevailing concentrations and equilibrium constants.

The following model forms the basis for this study. Starting from chemical analyses of several important compounds in precipitation a quantitative hypothesis is adopted of how these compounds originally were associated with acids or bases in a stoichiometric sense. It is then assumed that acids and bases have neutralized each other and that the system has come to an equilibrium with the carbon dioxide pressure of the atmosphere. A good agreement between measured and predicted alkalinity is then obtained.

2. Chemical composition of atmospheric precipitation

Table 1 shows the chemical components that have been used for the calculations and gives also the typical composition of precipitation in different parts of Europe. Data are taken from the so-called European Atmospheric Chemistry Network (sometimes referred to as the IMI-network—International Meteorological Institute, Stockholm). A map of the stations is shown in Fig. 1. For further information about this network see for instance Eriksson (1960), Eriksson (1970), and Granat (1972). In the last reference the laboratories which have been running this station network are listed.

Fig. 1. Location of the sampling stations. Stations mentioned in Table 1 are indicated by circles. Map indicates both stations in use 1969 and stations used before where sampling have now ceased (filled and open circles respectively).

The term alkalinity is often used in this report. If bicarbonate is present (in detectable quantities) alkalinity is numerically equal to the amount of bicarbonate. Otherwise the alkalinity is the titrated amount of acid—with a negative sign.

Of course the elements given in Table 1 are only a few of those present in precipitation in amounts that are possible to analyse. Table 2 gives some additional information. One can see that the analytical programme presented in Table 1 and which is used for the following calculations includes the quantitatively most important components—at least with respect to soluble inorganic material. The following fact is a further proof of this statement. Using the whole data material for calculation, no significant difference is obtained between calculated and measured conductivity nor between the sum of positive and the sum of negative ions in one sample. This must mean that there are no other ions in precipitation in concentrations comparable to those given in Table 1.

However, there is organic material and thus presumably also weak acids and bases. Of course there is also insoluble material of inorganic nature. Some of these compounds may very well take part in acid–base reactions but the importance of such substances is at present difficult to estimate and has been ignored in the following. A small interference is also suspected from iron and aluminium ions. By pointing out their possible importance the desirability of making direct measurements of them or their sum is indicated.

Table 1. *Average composition of precipitation*

Data from some of the stations in The European Atmospheric Chemistry Network. The analytical programme covers the main part of the dissolved inorganic matter in precipitation. The values are arithmetic averages from about 180 samples from each station

	2 Ki N Sweden	23 Pl SW Sweden	526 U Belgium	703 LM France
SO_4^{2-}, μmol/l	21	51	63	29
Cl^-, μmol/l	11	98	55	60
NO_3^-, μmol/l	5	32	36	32
NH_3, μmol/l	6	48	25	15
Na^+, μmol/l	13	85	42	40
K^+, μmol/l	5	7	6	4
Mg^{2+}, μmol/l	5	15	15	16
Ca^{2+}, μmol/l	16	21	33	17
H^{+a}, μmol/l	—	22	38	16
$HCO_3^{\,b}$, μmol/l	21	—	—	—
Conduct., $10^{-6}\ \Omega^{-1}\ cm^{-1}$	12	45	37	19
Precip., mm/month	30	54	68	63

[a] Calculated as the difference between total amount of hydrogen ion (taken from pH measurements) and bicarbonate ion over total amount of precipitation.

[b] As *a* but reversed (difference taken between bicarbonate and hydrogen ions).

Table 2. *Trace elements in precipitation* (μ*mol/l*)

(1), (2) Typical value and range respectively, here summarized from reported measurements in the European part of the USSR—75 samples (Drozdova & Makhonko, 1970). (3) Data from Quillayute, Washington, USA—2 samples (Rancitelli & Perkins, 1970). (4) Unpublished data—Int. Met. Inst., Stockholm, 3 samples, except for mercury where we have 30 samples

Please note that the data given are not strictly quoted but have been extracted from the papers indicated only to show orders of magnitude of concentrations

	(1)	(2)	(3)	(4)
Ag			0.009	
As			0.02	
Al				0.4
Au			< 0.0001	
Br			0.03	
Cd				0.01
Co			0.0007	< 0.1
Cr			< 0.04	< 0.1
Cs			0.0005	
Cu			0.05	0.1
Fe	0.7	0.05 – 4.	0.4	0.2
Hg			< 0.005	0.001
Mo				< 0.05
Mn	0.2	0.02–0.8	0.05	0.07
Ni	0.07	0.02 – 0.3		< 0.1
Pb	0.03	0.005 – 0.2		0.02
Rb			0.02	
Sb			0.001	
Sc			0.00004	
Se			0.001	
Zn			0.3	

3. Model hypotheses regarding acids and bases

The basic idea in establishing a relation between the amount of alkalinity (acid or base) and the elements in precipitation is, that some of the elements present at the moment of collection (or analysis) orginally were corresponding ions to hydrogen ions or base-ions. When being included in cloud or rain droplets the acids and bases have neutralized each other more or less. The reasoning is purely stoichiometric and is not affected by the way in which these reactions have proceeded in reality. This is presented in some detail below.

Sulphate

Sulphate in precipitation is added to the atmosphere as anthropogenic emissions (mainly as SO_2), as hydrogen sulphide formed in nature by biological action, and as sea spray (Eriksson, 1960; Robinson, & Robbins, 1970; and many others). For this study the sulphate from sea spray is irrelevant (neutral sulphate). The amount can be estimated roughly by a comparison with sodium which comes almost exclusively from the sea. When sea spray is formed, some elements are often enriched in the aerosol phase, but according to a discussion by Granat (1972) such an enrichment is not present at those coastal stations where the correction for sea-salt must be applied to give suitable entry data for this study. The remaining sulphur can be considered to come from sulphur dioxide and hydrogen sulphide emissions. These substances are eventually oxidated to sulfuric acid (at least in a stochiometric sense) before they are more or less neutralized. We can now start our summation of the amount of acids and bases, and assume that for each mole of sulphate remaining after deduction of sea-salt, 2 moles of hydrogen ions were originally available.

Nitrate

Among the nitrogen oxides which are emitted into the atmosphere, mainly through the action of bacteria in the ground but also through oxidation of nitrogen by combustion (Robinsson & Robbins, (1970) and others) NO, NO_2 will eventually end up as nitrate in the precipitation. At present there seems to be no other mechanism through which an appreciable part of nitrate in precipitation could emanate but from oxides of nitrogen. The principle reaction is given as $3\ NO_2 + H_2O \rightarrow 2\ HNO_3 + NO$ and we assume therefore that for each mole of nitrate in the precipitation one mole of hydrogen ions was originally available.

Chloride

The predominant source of chloride in precipitation is sea spray. A small part comes from anthropogenic emissions i.e. hydrochloric acid. Data on the latter are sparse but indicate that the anthropogenic emissions are negligible compared with the natural ones. We therefore assume that chloride does not indicate an addition of acids or bases.

Ammonium

Ammonium in precipitation emanates from ammonia created by the action of baceria on nitrogen compounds in the ground, perhaps mainly from urine (Healy, T. V., McKay, H. A. C., Pilbeam, A. & Scargill, D. (1970)). We therefore assume that each mole of ammonium in precipitation originally has been ammonia and bonded one mole of hydrogen ions. This is true at pH-values that are found in precipitation.

Sodium

Sodium in precipitation has sea-water as its source and has been emitted into the atmosphere as sea-spray. Sea-water has a pH of about 8.5 and thus contains some bases, and the presence of sodium in precipitation indicates that some alkali is present. This is not included in the present calculations. The amount is small, however. We assume therefore that sodium in precipitation does not indicate the addition of acid or base.

Potassium, magnesium, calcium

Compounds containing these metals are added to the atmosphere by soil erosion, by sea-spray and by anthropogenic emission. From what we know about the lifetime of particles in the atmosphere we have to consider most of Europe and northern Africa as possible source areas for the dust that is found in the precipitation collected at the stations used for this study.

Considering briefly the composition of the soils in these areas it seems possible to summarize the result for soluble materials in the following simplified way. Magnesium and calcium are bonded to carbonates and sulphates, while chlorides seem to be of little importance quantitatively. Possibly this also holds true for the potassium compounds. The model used does not pretend to reveal whether an amount of, for instance, calcium sulphate in precipitation was originally supplied to the atmosphere as calcium sulphate aerosol, or whether it was formed by the reaction between sulphuric acid (from SO_2) and a calcium compound, i.e. calcium carbonate.

The quantity of potassium, magnesium and calcium that comes from the sea is (in the same way as for sulphur) irrelevant in this investigation because they are mainly bonded to chloride (the small amount of bicarbonate in sea water has been considered when discussing sodium). These quantities of potassium, magnesium and calcium have therefore been estimated by comparison with sodium and have been deducted.

Examples of anthropogenic emissions of potassium, magnesium and calcium are ash from burning of coal or oil and exhausts from processing industries. The calcium content of oil is about 5 ppm and its content of sulphur about 2 %. Since most of the sulphur in precipitation comes from fossil fuels, one would have a calcium-to-sulphur relation of about 1/4 000 if oil were the source of calcium. In reality this ratio is 1:3 to 1:2 (cf. Table 1).

Based on the considerations above and the results of some studies of the areal distribution of the deposition on a rather small scale (i.e. Andersson, 1969; Rodhe, 1970) one can conclude that anthropogenic emissions are of considerable importance for the amount of these elements in precipitation in some (urban) areas, but of little importance compared with natural emissions for the total deposition of calcium, magnesium and potassium compounds in the area covered by the station network.

We assume that each mole of potassium, magnesium and calcium in the precipitation, remaining after deduction of sea salt, was originally associated with carbonate, potassium with one half, magnesium and calcium with one mole, in a stoichiometric sense.

The sum of hydrogen ion and carbonate

From the discussion above we can sum up the amount of available acid:

$$a = 2\left([SO_4^{2-}] - [Na^+]\frac{27.6}{457}\right) + [NO_3^-] - [NH_4^+]$$

and the amount of carbonate available:

$$b = \frac{1}{2}\left([K^+] - [Na^+]\cdot\frac{9.7}{457}\right) + \left([Mg^{2+}] - [Na^+]\frac{55.6}{457}\right) + \left([Ca^{2+}] - [Na^+]\frac{10.0}{457}\right)$$

where a square bracket means concentrations of the component in mole/l as found in the precipitation.

4. The pH in a solution of acid and carbonate

Let a system of a moles of hydrogen and b moles of carbonate in 1 litre of water come to equilibrium with the carbon dioxide pressure of the atmosphere by which process x moles of carbon dioxide are introduced or expelled. Put

$$e = a - 2b$$

where e is positive or negative.

The following equations are generally applicable.

$$\frac{[H_2CO_3]}{P_{CO_2}} = K_0 \tag{1}$$

or

$$[H_2CO_3] = K_1 = P_{CO_2} \cdot K_0 \tag{1 a}$$

$$\frac{[HCO_3^-][H^+]}{[H_2CO_3]} = K_2 \tag{2}$$

$$\frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} = K_3 \tag{3}$$

$$[H^+][OH^-] = K_V \tag{4}$$

where

P_{CO_2}	3.20×10^{-4} atm		
	5°C	20°C	25°C
K_0	64	39	34
K_2	3.0×10^{-7}	4.2×10^{-7}	4.5×10^{-7}
K_3	2.7×10^{-11}	4.2×10^{-11}	4.7×10^{-11}
K_V	0.2×10^{-14}	0.7×10^{-14}	1.0×10^{-14}

According to the rules of the electroneutrality equation we have

$$2[H_2CO_3] + [HCO_3^-] + [H^+] - [OH^-] = a + 2x \tag{5}$$

and for the "total carbonate content"

$$[H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] = b + x \tag{6}$$

From (5) and (6) one obtains

$$[HCO_3^-] = [H^+] - [OH^-] - 2[CO_3^{2-}] - e \tag{7}$$

and from (2) and (3) that

$$[CO_3^{2-}] = \frac{K_1 K_2 K_3}{[H^+]^2} \tag{8}$$

The combination of (7), (1a), (2), (4), (8), and simplifications gives

$$-e = \frac{K_1 K_2}{[H^+]}\left(1 + \frac{2K_3}{[H^+]} + \frac{K_V}{K_1 K_2}\right) - [H^+] \tag{9}$$

which for all normal precipitation samples (pH < 8) can be simplified to

$$-e = \frac{K_1 K_2}{[H^+]} - [H^+] \tag{9 a}$$

where $e = a - 2b$

5. Evaluation

5.1. *A relation between measured pH and alkalinity*

All the samples from the network have been analysed for pH and bicarbonate (titration). In

Table 3*a*. *Relation between pH and measured alkalinity for samples in group a*

For each pH-class the corresponding alkalinity is calculated according to eq. (9*a*) ($\log k_1k_2 = -11.2$). Measured alkalinity is given at mean value and median value together with standard deviation and number of samples for each pH-class. Group *a* constitutes samples where alkalinity is reported either as acid or bicarbonate

	Alkalinity, μmol/l				
pH	Calc. from pH	Measured mean value	Median value	Standard dev.	No. of samples
3.8	−160	−108	−100	11	2
3.9	−126	−101	−113	36	7
4.0	−100	− 83	− 82	25	27
4.1	− 79	− 53	− 56	40	31
4.2	− 63	− 47	− 52	37	51
4.3	− 50	− 40	− 37	29	60
4.4	− 39	− 28	− 33	28	70
4.5	− 31	− 28	− 30	25	65
4.6 4.7	− 22	− 18	− 16	29	110
4.8 4.9	− 15	− 1	− 2	33	57
5.0 5.1	− 9	− 0.3	4	15	36
5.2 5.3	− 4	15	8	25	33
5.4 5.5	− 2	32	17	65	40
5.6 5.7	+ 1	36	25	50	30
5.8 5.9	3	48	29	69	35
6.0	5	35	37	28	14
6.1	7	45	49	28	13
6.2	9	71	63	46	12
6.3	13	73	70	32	10
6.4	16	101	74	88	14
6.5	20	59	33	55	3
6.6	25	159	124	125	8
6.7	32	322	559	273	4
6.8	40	119	125	60	4
6.9	50	295	317	130	7
7.0	63	288	202	170	3
7.1	79	—	—	—	0
7.2	100	361	361	70	2
7.3	126	843	499	888	5

addition acid samples (with no bicarbonate) have been titrated for acid at IMI since 1967.

The samples were subdivided into classes according to the pH-value, class broadness being either 0.1 or 0.2 units. For each pH-class the mean, median and standard deviation of the alkalinity were calculated and the result is given in Tables 3*a* and 3*b*.

The data material was grouped according to the difference in analyses performed. Group *a* thus contains samples where the alkalinity determinations have been made at all pH-values. That is samples from stations in Sweden, Norway, Denmark, Iceland, Austria and station 114 (Germany) since and including 1967.

Group *b* contains samples where alkalinity is reported only when bicarbonate is found (no titration of acid is performed), i.e. samples from all stations except those in group *a* and samples from stations in group *a* but before 1967. In group *b* all samples with pH less than 5.2 (arbitrary chosen) *and* bicarbonate equal to 0 were excluded.

The relation between alkalinity and pH is shown in Fig. 2*a* and Fig. 2*b*. The median value for each pH-class has been plotted against pH both for data in group *a* and group *b* and compared with the relation according to eq. (9*a*). In Fig. 2*b* (the logarithm of the alkalinity versus pH) eq. (9*a*) is simplified to a straight line relationship. This is a very convenient way to show the relation between alkalinity and

Table 3*b*. *Relation between pH and measured alkalinity for samples in group b*

For each pH class the alkalinity is calculated according to eq. (9a) (with $\log k_1k_2 = -11.2$). Measured alkalinity is given as mean and median value together with standard deviation and numbers of samples for each pH class. Group *b* constitutes samples where alkalinity is reported only when bicarbonate is present. A very large amount of acid samples are therefore excluded in the table

	Alkalinity, μmol/l				
pH	Calc. from pH	Measured mean value	Median value	Standard dev.	No. of samples
5.2 5.3	−4	0	0	0	101
5.4 5.5	−2	1	0	5	92
5.6 5.7	+1	11	7	20	79
5.8 5.9	3	29	16	57	93
6.0	5	36	20	48	44
6.1	7	26	22	17	26
6.2	9	41	28	49	43
6.3	13	53	42	51	42
6.4	16	54	50	33	39
6.5	20	89	81	81	33
6.6	25	86	86	44	35
6.7	32	146	126	125	26
6.8	40	120	106	58	26
6.9	50	172	119	125	26
7.0	63	248	200	255	8
7.1	79	207	183	108	17
7.2	100	349	134	374	3
7.3	126	1 345	998	1 239	36

pH. However, alkalinity values between −10 and +10 μmol/l must be excluded because the straight line relationship is not valid here.

We find that there is evidently a relation between the pH and the alkalinity in precipitation, but that the spread is appreciable especially when the pH is larger than about 6.2.

The relation between pH and alkalinity based on eq. (9*a*) can be compared with the empirically found relation in Fig. 2*a* or 2*b*. When *e* is larger than 8 or less than −7 μmol/l one obtains

$$\mathrm{pH} = -\log e \quad (e > 8 \times 10^{-6}\ \mathrm{mol/l})$$

and

$$\mathrm{pH} = \log(-e) - \log k_1k_2 \quad (e < -7 \times 10^{-6}\ \mathrm{mol/l})$$

We shall interpret the deviations in some details and try some explanations. Fig. 2*a* suggests an equivalence point of 5.2. Put $e = 0$ in eq. (9*a*). We then obtain $\mathrm{pH} = \frac{1}{2}\log k_1 k_2$ and if the assumptions in chapter 4 are valid we must then have that

$$\log k_1 k_2 = -2 \times 5.2$$

The left hand side of this equation is dependent on the temperature, the carbon dioxide pressure and, to a small extent, the ion strength. The results when varying these are shown in Table 4.

To obtain $\log k_1 k_2 = -10.4$ at ordinary laboratory conditions and ordinary precipitation water one has to assume $P_{CO_2} = 15 \times 10^{-4}$ atm compared to the normal 3.2×10^{-4} in nature and about 6×10^{-4} in laboratory air.

A similar deviation could of course be explained by postulating no equilibrium with air but a substantial oversaturation of carbon dioxide. This is stoichiometrically possible since there is often enough carbonate present in the precipitation even to maintain the sufficient carbon dioxide overpressure in the bottles where the rain-

Table 4. *Calculated values of log* K_1K_2 *at some temperatures and* CO_2*-pressures*

Temp. (°C)	P_{CO_2} (atm × 10^6)	$\log k_1 k_2$
25	325	−11.2
25	600	−11.0
5	600	−10.7

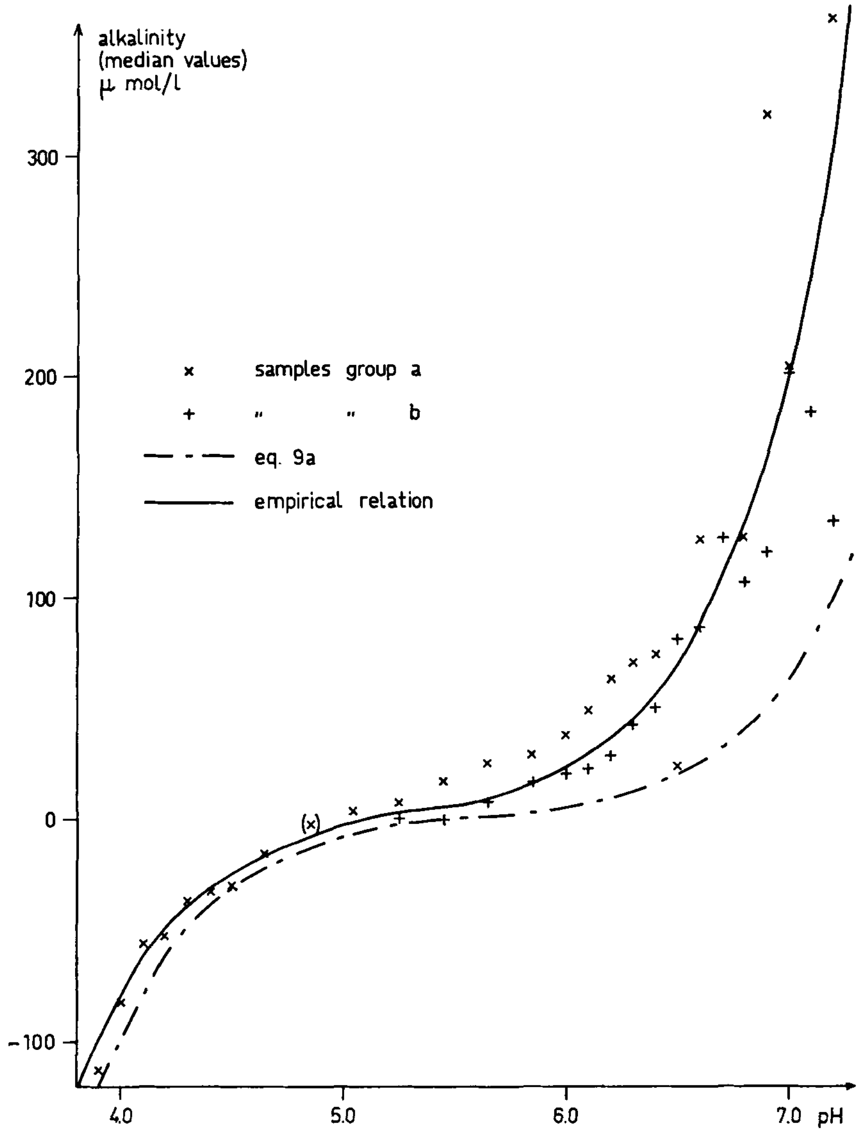

Fig. 2a. Calculated and measured relation between pH and alkalinity. The figure is based on data in Tables 4*a* and 4*b*. Median values have been plotted against each pH-class. The relation according to eq. (9a) (with $\log k_1k_2 = -11.2$) is shown. An empirical relation is also indicated.

water is transported to the laboratory. However, the mechanical treatment in the laboratory makes it less likely that the water can remain oversaturated.

Tests where bicarbonate solutions (0.01 mM to 0.2 mM) were equilibrated with laboratory air gave results that were in good agreement with calculated values (with $\log k_1k_2 = -11.2$).

It seems unlikely that the observed deviations could be explained by analytical errors.

Taking into consideration the average composition of precipitation in the region of interest, the rather good agreement—on the average—between sum of negative and positive ions as well as the agreement, also on the average, between calculated and estimated conductivity

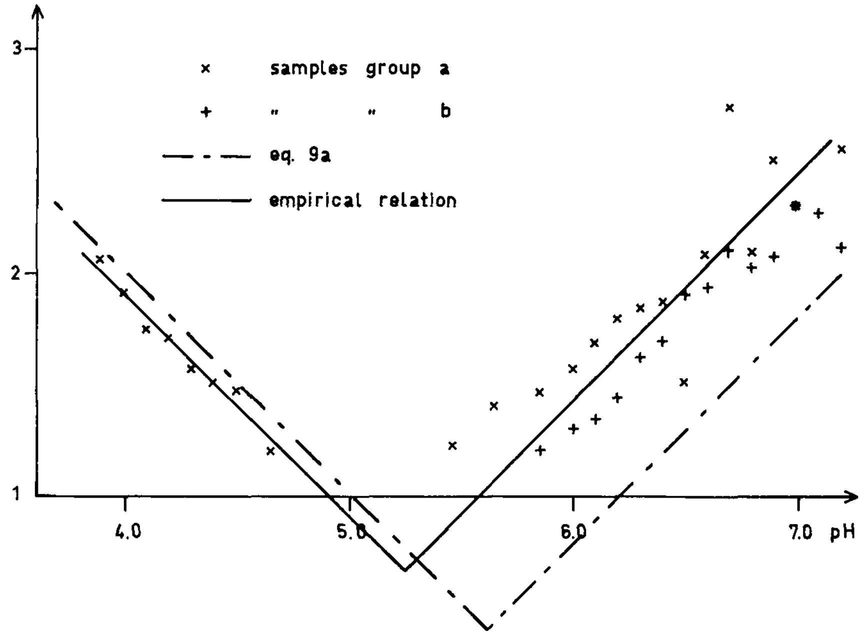

Fig. 2b. The figure is based on data in Tables 4*a* and 4*b* but samples with alkalinity between −10 and +10 μmol/l have been excluded. The relation according to eq. (9*a*) is shown. An empirical relation is also indicated.

it seems as if this discrepancy could be interpreted as "buffer capacity" emanating from undissolved "earth" material in the precipitation.

For the same reasons as above it may be concluded that these "earth" particles have such a composition that they give some of the ions in Table 1 after dissolution.

The most likely one, calcium carbonate is however soluble at all pH found in rainwater. However, there may well be a compound that is sufficient insoluble at higher pH but soluble at pH at about 5.6—a pre-requisite for acting as a buffer under the assumed conditions. (Alkalinity determination is made in two steps. Sample is first titrated to pH 4.0, then brought to equilibrium with normal carbon dioxide pressure in air and finally titrated to pH 5.6.)

We can thus also explain the very large and irregular deviation at higher pH-values between alkalinity calculated from pH and measured alkalinity as the result of various amount of buffer—which amount can of course vary independent of pH-value.

It should be pointed out that the amount of samples with pH larger than for instance 6.2 is very small compared to the total number.

On the acid side there is a deviation of 0.1–0.15 pH units. Unfortunately only one laboratory (IMI) has made both pH-determinations and titrations in this case. The deviation may be explained by errors in the pH determinations and there is also some evidence for this. In the most acid samples one could observe a discrepancy between measured and calculated conductivity which almost vanishes if the hydrogen concentration entering the calculations is reduced with an amount equal to 0.15 pH-units (when calculating the conductivity the hydrogen ion concentration is taken from the pH value and not from the titration).

We thus arrive at a semi-empirical relation between pH and alkalinity where the shape of the curve is the predicted one and with rather good agreement for pH-values below about 5.6, but with deviations between measured and theoretical values that have not yet been completely explained.

5.2. *Comparison between measured and calculated alkalinity*

From the assumptions in section 3 about the relation between some of the components in precipitation and acids and bases the obtained

Table 5. *Alkalinity calculated according to model hypothesis and compared with measured values*

	Alkalinity, µmol/l			
pH	Measured	Calc.	Difference[a]	No. of samples
3.8	-128	-113	-15	7
3.9	-110	-99	-11	13
4.0	-93	-71	-22	37
4.1	-61	-54	-7	53
4.2	-56	-46	-10	76
4.3	-43	-40	-3	90
4.4	-37	-26	-3	97
4.5	-30	-27	-3	81
4.6	-30	-21	-9	78
4.7	-19	-15	-4	58
4.8 4.9	-11	-0	-11	88
5.0 5.1	-8	1	-9	90
5.2 5.3	-3	11	-14	55
5.4 5.5	1	22	-21	54
5.6 5.7	17	28	-11	46
5.8 5.9	15	29	-14	50
6.0 6.1	23	27	-4	41
6.2	44	77	-33	22
6.3	63	60	3	13
6.4	77	80	-3	15
6.5	57	76	-19	13
6.6	39	72	-33	7
6.7	147	154	-7	5
6.8	84	120	-35	4
6.9	256	260	-3	6
7.0	200	259	-59	3
189				

[a] Difference between measured and calculated alkalinity.

alkalinity (net acid or net bicarbonate) was calculated for a large number of samples.

In order to have an overlook of the result the material was grouped in classes according to pH-value and for each such class (0.1 or 0.2 unit broad) the mean value of the composition and some other properties were calculated. Samples both from group *a* and group *b* have been used. The results of these calculations are summarized in Table 5. Calculated alkalinity may either be compared with the measured one or the alkalinity obtained from measured pH through eq. (9a).

From Table 5 it can be seen that alkalinity calculated according to the model hypothesis, agrees very well with the measured one. Up to pH 6.4 the deviation is often less than 10 µmol/l and if the calculated values are compared to alkalinity obtained from pH through the relation in section 5.1 the deviation is even smaller. When judging these results one must remember that values are obtained as differences between larger numbers and thus are very sensitive to errors of the order of the sensitivity level of the analytical method.

The pH in precipitation is thus determined by several compounds of different origin. It is thus not surprising that the relation between one element (sulphate) and pH has a correlation coefficient which is not significantly different from zero.

6. Discussion

A model has been formulated to try to explain primarily from where different acids and bases are emanating, and secondly to clarify the order of magnitude of the amounts of acids and bases supplied to the atmosphere. The good agreement between predicted and measured alkalinity indicates that this model is approximately valid. From this model we can draw several interesting conclusions concerning the acidification of precipitation.

To begin with we see that sulphur emitted into the atmosphere by natural processes (H_2S) certainly creates sulphuric acid but that this is neutralized when found in the precipitation. However, if the emissions of acid-forming compounds are increased above a certain level and other emissions kept constant, the precipitation will become acid. At such a balance point (which is the situation for large parts of Scandinavia) a small percentage increase of the emitted amounts of sulphur (as SO_2) can give a large increase in the depositon of acid.

If looking for a relation between anthropogenic sulphur emissions and the acid content of precipitation one will not usually find a clear relation, unless several other components are being considered. Sulfur (sulfuric acid) is the dominating factor for the acidification of the precipitation, but nitric acid created from nitrogen oxides is not unimportant. Data from the atmospheric chemistry network show an increasing concentration in precipitation of both sulfate and nitrate (Granat, L. 1972). An acidification can also be brought about, if the emissions of bases are reduced, for instance by dust removal from exhaust gases. One thus can think about dust removal that mainly cuts down the alkaline substances or a replacement of coal with oil as fuel as causes for acidification of the precipitation. However, an inspection of the precipitation chemistry data rather shows a small increase of alkali emissions, indicated by for instance an increase of calcium in precipitation, although the picture is quite variable.

To predict further depositions of acid with precipitation one needs good estimates of future emissions of both acid-forming and neutralizing substances. There is, however, only some such information available for sulfur.

A reasonable prediction is probably obtained, if the sum of the emissions of the other acid and neutralizing substances is assumed to be constant and that the sulphur emissions are increased according to a prognosis for the oil and coal consumption. Since the precipitation on the average does not contain any neutralizing capacity, all additional sulphur emissions to the atmosphere will reach the ground as sulphuric acid. With a knowledge about the atmosphere as a transporter one is able to predict where this additional acid will reach the ground.

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О СВЯЗИ МЕЖДУ ЗНАЧЕНИЕМ pH И ХИМИЧЕСКИМ СОСТАВОМ В ОСАДКАХ

На основе анализа 2 000 проб дождя изучается соотношение между значением pH и полным содержанием кислот или оснований, соответственно. При рассмотрении системы двуокись углерода — вода вычисляется теоретическое соотношение между pH и полным количеством кислоты или бикарбоната. Наблюдается регулярное отклонение эмпирически установленного соотношения от теоретического. На основе химического анализа наиболее важных компонент в атмосферных осадках формулируется количественная гипотеза о том, как эти компоненты были первоначально связаны с кислотами или основаниями. Предполагается далее, что они нейтрализовали друг друга и что система пришла к равновесию с давлением углекислого газа в атмосфере. Получается хорошее согласие между предсказанными и измеренными значениями концентраций кислот или оснований, что представляется ясным указанием на справедливость модели. Эта модель стехиометрической связи между кислотами и основаниями оказывается полезным инструментом как для интерпретации значений концентрации кислот, найденных в осадках, так и для оценок будущих отложений кислот осадками.