

Discrepancies between conductivity and pH values measured in acid humic waters – How can this published data be explained?

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Sammendrag

Artikkelen diskuterer publiserte og upubliserte målinger av konduktivitet og pH i surt humusvann. Dataene viser feilaktive korresponderende verdier. Det vil si at verdiene ikke er i samsvar med hverandre relatert til velkjent hydrokjemi. Et viktig spørsmål i denne forbindelse er om målingene er korrekte og hvis ikke, hvilken av dem er feilaktige, pH, konduktiviteten eller begge? Vurdering av publiserte og egne data, på grunnlag av beregnede og målte konduktivitetsverdier, indikerer primært feilaktige pH-målinger. Dette gjør de vitenskapelige publikasjonene, som er basert på disse merkelige resultatene, delvis av tvilsom verdi. Konduktiviteten bør generelt benyttes som en kontrollerende faktor

selv om den også kan ha sine mindre feilkilder.

Summary

Published data of pH and conductivity in some acid humic waters have shown erroneous corresponding values. This means that the values were not consistent with each other according to well-recognized hydrochemistry. A main questions was arised in this connection. Were the measurements correct and if not which of them were wrong, pH, conductivity or both? Assessment on basis of calculated and measured conductivity values, by using published data and own measurements, indicate primarily erroneous pH measurements. This makes the scientific papers which are based on

these remarkable results partly of questionable value. Conductivity should generally act as a controlling parameter even if the latter also could have some uncertainties.

Introduction

pH measurements are of great importance in water quality assessment and especially in water pollution research connected to acidification. As these measurements are considered to be quite simple, fast and easy to perform, relatively few reliability investigations have been done. This has, however, produced some remarkable and doubtful results which consequently may have given questionable or weaken conclusions.

On basis of long time experience we mean that pH is a quite complicated and difficult measurement to carry out and accordingly to achieve reliable values, particularly in humic waters poor in electrolytes. Bates (1964), Grøterud (1971, 1972), Blakar and Digernes (1984) and Bye (1997) are some of the relatively few papers which have dwelt on complications and uncertainties of pH determinations and tried to discuss how to become aware of potential faults.

This paper is partly based on an oral presentation at the 28. World Congress for limnologists in Australia 2001. The idea of that presentation was conceived by reading a paper in the scientific journal *Nordic Hydrology* (Rueslåtten and Jørgensen 1978), which showed remarkable values of pH and conductivity which consequently could not be consistent

with each other according to well-recognized hydrochemistry. This again has led to examination of some other published papers which dealt with acid humic waters and had measured both pH and conductivity (Walker 1990, Rosenqvist 1981). In addition the authors have made their own measurements to get more closely into the phenomenon.

Methods

Unfortunately, no completely description of the equipments and methods connected to conductivity and pH measurements, taken from the published paper, have been given. This make it difficult to compare the two parameters in question, but in spite of this problem it will nevertheless be possible to give a rough picture of the discrepancies. The authors' measurements have been done in the following way: pH with a portable Radiometer pH meter 80 with a combined electrode GK 2401 C and conductivity with a WTW conductivity meter.

The pH meter was calibrated with two buffer solutions (pH 4.00 and 7.00) at the same temperature as the water samples. At some cases, when the electrode did not show the perfect respons (59 mV/pH), the instrument was adjusted by the buffer solution around the expected recorded value, i. e. pH 4.00. The conductivity meter was calibrated by KCl solutions at regular intervals with concentrations of 0.0001 – 0.0005 M which correspondingly mean 14.94 – 73.90 $\mu\text{S}/\text{cm}$ at 25°C (Golterman 1969). The conductivity meter has shown good

stability during long experience. To calculate the theoretical conductivity values at 20°C in the water samples, the equivalent conductivity of major ions in $\mu\text{S}/\text{cm}$ at 18 and 25°C according to Golterman (1969) were used. To determine the concentrations of Ca, Mg, Na and K atomic absorption photometry were used. Cl was determined by potentiometric titration according to the American Public Health Association (1962) and SO_4 was found as the difference between the concentration of total strong acid anions and chloride (sometimes also nitrate). Total strong acid anions were determined by ion-exchange procedure according to Mackereth (1963). Water colour was observed by a B.D.H. Lovibond Nessleriser and recorded as mg Pt/L.

As this paper is very much focusing on the H^+ ion and its equivalent conductivity according to the pH, the table below may be of practical utility. The values are given at 20°C.

For example, a measured pH of 4.1 together with a conductivity of 19.2 would give an immediate signal of something wrong with the measurements. It is also of importance whether a wrong pH is measured too low or too high, owing to the logarithmic scale as seen in the table above. If the measurement gives 0.3 pH unit too low value, the relative error regarding H^+ is about 100%.

Compared with the same pH unit measured too high values gives about 50 % relative error (Bye 1997). This applies also to the calculated conductivity based on pH. This again may play a key role, as the pH values in acid soft water very often were determined too low, as will be demonstrated in the next section.

The questionable data to discuss

Conductivity is an useful parameter to keep a check on the concentration of the ions analysed in a water sample. By good experience with water analyses the measured conductivity can sometimes immediately reveal that something must be wrong with the concentration of the ions analysed. This applies especially to acid soft water. The sum of ions may be too high or too low according to the conductivity measured. This again can be controlled more closely by calculating the conductivity by using the equivalent conductivity for the analysed ions. Generally, the calculated conductivity is very often higher than the measured one in soft water (Grøterud 1972). This can be related to the analytical procedure. For example, it may be possible that adsorbed or absorbed cations could be released during the analyses. Then the ionic balance also will be affected, i. e. the cations could be in excess of the anions. Finally, the conductivity

pH	5.0	4.9	4.8	4.7	4.6	4.5	4.4	4.3	4.2	4.1	4.0	3.9
$\mu\text{S}/\text{cm}$	3.2	4.1	5.2	6.5	8.1	10.2	12.9	16.2	20.4	25.7	32.4	41.0

Table 1. pH and equivalent conductivity at 20°C.

values indicates that there may have been analysed too many ions (Grøterud 1972). The pH values were often determined in the field (or in situ) and generally increase during the time before other measurements in the laboratory (Grøterud 1971). It is therefore important to make all measurements at the same time Grøterud (1972).

Neutral soft water laks from North-Eastern Norway

Data from Bøyum (1970) were used to exemplifying the difference between measured and calculated conductivity from lakes in North-Eastern Norway as shown in the table below. The lake waters were relatively poor in electrolytes and roughly neutral with respect to pH. The calculated values are done by the authors.

All lakes show higher calculated than measured conductivity, the discrepancies were 2.8 - 7.1 $\mu\text{S}/\text{cm}$ or 7.7 - 32.5 %. The majority of the lakes have a slightly excess of analysed cations compared with anions, and Bøyum (1970) explained this with analytical errors and that organic colloids or complex colloids, negatively charged, could balance some cations. The latter statement is considered to be somewhat questionable as there are too many analysed ions (cations). A better suggestion is that cations have been released from particles or colloids during the analytical process.

Acid humic meltwaters from Oslo region

The above mentioned example of using the calculated conductivity as a controlling aid, is a basis for the

	Cond.meas. $\mu\text{S}/\text{cm}, 18^\circ\text{C}$	Cond.calc. $\mu\text{S}/\text{cm}, 18^\circ\text{C}$	Difference $\mu\text{S}/\text{cm}$	Difference %
Lake no. 1	36.4	39.2	2.8	7.7
" " 2	31.9	34.8	2.9	9.1
" " 3	31.3	33.8	2.5	8.0
" " 4	40.0	43.0	3.0	7.5
" " 5	40.7	47.3	6.6	16.2
" " 6	22.4	28.1	5.7	25.4
" " 7	15.7	20.8	5.1	32.5
" " 8	20.2	25.7	5.5	27.2
" " 9	26.8	33.1	6.3	23.5
" " 10	31.0	37.1	7.1	22.9
" " 11	24.8	31.4	6.6	26.6
" " 12	25.6	31.3	5.7	22.3

Table 2. Difference between measured and calculated conductivity from lakes in North-Eastern Norway.

following example of data which will be given a critical analysis. These data are from two localities (Ø and N) near Oslo city (Rueslåtten and Jørgensen 1978). Meltwater samples collected at the edge of, and at increasing distance from, the snow patches were analysed and should reveal that the water composition changed radically during flow across the bedrock surface, event at low temperatures (0-2°C). A rapid increase in the hydronium content occurred while the water was flowing along the bedrock/humus interface, was reported. By comparing some of the pH (hydronium) values with the corresponding conductivity values, obvious discrepancies were revealed. This was confirmed by calculating the conductivity and are given below.

Unfortunately, the anions were not analysed in the paper referred to. Therefore the calculated conductivity had to be made by using the following rough assumptions:

1) $[Cl] = [Na]$; $[SO_4] = \Sigma [Ca, Mg, K]$;

- 2) Organic anions $[OA] = [H^+]$; $[NO_2] = 0$ (not measured);
- 3) Conductivity of $[OA] > 0$ (not known).

Calculated conductivity = Σ conductivity of $[Ca] + [Mg] + [K] + [Na] + [Cl] + [SO_4] + [NO_3] + [H^+] + [OA]$.

Owing to this necessary simplification, the differences of the conductivities shown in the table were considered to be a minimum. This was the reason for using the symbol for greater than (>) in the table. The calculated conductivities were significantly higher than the measured values, differences from 18.9 to 37.2 $\mu S/cm$ or 94.5 to 204.4 % were found. In addition, the calculated contribution from the hydronium ions were from 16.2 to 40.8 $\mu S/cm$ and that these values were nearly the same or higher alone than the measured ones. This bear witness, as already mentioned, to something wrong with the

Samples	Cond.meas. $\mu S/cm$	Cond.calc. $\mu S/cm$	Difference		Cond. $[H^+]$ $\mu S/cm$
			$\mu S/cm$	%	
Ø3	20.0	>38.9	>18.9	>94.5	16.2
Ø4	18.2	>55.4	>37.2	>204.4	40.8
N2	20.5	>44.6	>24.1	>117.6	20.4
N3	22.5	>56.1	>33.6	>149.3	40.8
N4	22.2	>46.2	>24.0	>108.1	25.7

Table 3. Data from two localities (Ø and N) near Oslo city. Measured and calculated conductivity.

water analyses. But it is complicated and difficult to point out what is wrong because of insufficient description of the methods used. However, many of the pH measurements are dramatically low in relation to the conductivity values, and this discrepancies should have been discovered or reflected by the responsible scientists. By experience, pH is the most sensitive measurement, especially in these acid humic waters.

It seems therefore probably that the pH values were the most uncertain measurements, even if the measure of conductivity also could have some uncertainties.

Acid humic drainage waters from Finnemarka, Southern Norway

Finnemarka is an acidified area (see Grøterud 1987). Some data from acid humic drainage water are presented below (Grøterud unpublished data):

Date	pH	Colour,mgPt/L	Conductivity, $\mu\text{S}/\text{cm}$
22.July 1993	4.00	225	43.4
9.Sept. 1995	3.91	175	41.7
16.Sept. 1995	3.92	185	37.7

Table 4. Some data from acid humic drainage waters from Finnemarka

Calculated conductivity = Σ cond. BC + cond. AN + cond. $[\text{H}^+]$ + cond. [OA]

BC = base cations = $[\text{Ca}] + [\text{Mg}] + [\text{Na}] + [\text{K}]$;

AN = acid anions = $[\text{SO}_4] + [\text{Cl}] + [\text{NO}_3]$

[OA] = organic anions > 0 and subsequently cond. > 0 , but unknown.

The symbol ($>$) means the same as pointed out above.

The calculated conductivity values according to the equation above are given in the table below:

	Cond. meas.	Cond.BC	Cond.AN	Cond. $[\text{H}^+]$	Σ cond.calc	Difference	
Date	$\mu\text{S}/\text{cm}$	$\mu\text{S}/\text{cm}$	$\mu\text{S}/\text{cm}$	$\mu\text{S}/\text{cm}$	$\mu\text{S}/\text{cm}$	$\mu\text{S}/\text{cm}$	%
22.July 93	43.4	3.2	9.7	32.4	>45.3	>1.9	>4.4
9.Sept.95	41.7	1.9	9.0	39.9	>50.8	>9.1	>21.7
16.Sept.95	37.7	2.0	8.7	38.9	>49.6	>11.9	>31.6

Table 5. Calculated conductivity values for drainage waters from Finnemarka.

The discrepancies are somewhat different for the three water samples. According to our experiences the stability of the conductivity meter is

much higher than that of the pH meter. Consequently most of these discrepancies seem to be connected to the pH measurements.

	Cond. meas.	Cond.BC	Cond.AN	Cond.[H ⁺]	Σcond.calc	Difference	
Date	μS/cm	μS/cm	μS/cm	μS/cm	μS/cm	μS/cm	%
19.Oct.81	28.0	>0	>0	40.8	>40.8	>12.8	>57.0

Table 6. Rough estimate of the calculated conductivities for drainage waters from Birkenes.

Acid humic drainage waters from Birkenes, Southern Norway

The data are taken from Rosenqvist (1981). Some of them are somewhat doubtful, and there are especially one measurement of pH and conductivity which are worth special mentioning. The values were used in comparing the water acidity with another field where there had been a forest fire some years ago. Other measurements were unfortunately not reported. pH was determined to 3.9 and the conductivity to 28.0 μS/cm. A rough estimate of the calculated conductivities were given in the table below.

BC, AN and [OA] > 0 and subsequently conductivity > 0, but not known. So, the pH determination was probably the most questionable and that this should weaken the conclusion in the paper referred to.

Acid humic water from Rio Negro, Brazil

In connection with the World Congress for limnologists in Sao Paulo 1995, an excursion to Rio Negro in Amazonian was organized. At this event it was given possibilities to borrow equipments of the same types as used in Norway for measuring both pH and conductivity. Two parallell measurements were carried out in situ and the mean values of these were pH = 4.40 and conductivity = 11.5 μS/cm (Grøterud unpublished data). A water sample from the same locality was taken to Norway for further analyses of BC and AN ions and TOC. The calculated values are presented in the table below.

In addition TOC = 13.3 mg/L ([OA] > 0 and subsequently conductivity >

	Cond. meas.	Cond.BC	Cond.AN	Cond.[H ⁺]	Σcond.calc	Difference	
Date	μS/cm	μS/cm	μS/cm	μS/cm	μS/cm	μS/cm	%
2.Aug.95	11.5	1.5	3.7	12.9	>18.1	>6.6	>57.4

Table 7. Calculated values for acid humic water from Rio Negro.

	Cond. meas.	Cond.BC	Cond.AN	Cond.[H ⁺]	Σcond.calc	Difference	
Date	μS/cm	μS/cm	μS/cm	μS/cm	μS/cm	μS/cm	%
Black streams	30.6	> 0	> 0	43.7	>43.7	>13.1	>42.9
Clear streams	10.5	> 0	> 0	17.4	>17.4	>6.9	>65.7

Table 8. Calculated values for black and clear streams in the Amazonian basin.

0, but not known). The conductivity difference is high and in accordance with some of the other examples given above. The discrepancy may partly be due to the time difference between the in situ measurements and the laboratory measurements in Norway. Ions could have been released from particles and colloids during the storage and analytical procedure. But the pH value alone indicates that something is wrong with the data. pH is considered to be the most questionable parameter.

Black and clear streams in the Amazonian basin

These data are taken from Walker (1995) and consist of average values for pH, conductivity and humic substance in 15 black and 12 clear streams. Other chemical analyses are not given. The calculated values are given in the table below.

Measured average pH = 3.87, conductivity = 30.6 μS/cm and humic substance = 51.5 mg/L for the 15 black streams and measured average pH = 4.27, conductivity = 10.5 μS/cm and humic substance = 13.1 mg/L for 12 clear streams (Walker 1990). [OA]

> 0 and consequently the conductivity > 0 for both group of streams, but not known. The conductivity differences are very high, particularly because the conductivities of neither the BC nor the AN are calculated.

Bog lakes in Latvia

pH and conductivity measurements of bog lakes in Latvia (Klavins et al. 2003) have shown discrepancies which have the same problem as pointed out above.

Concluding remarks

- 1) There exist obviously published water analyses which have a questionable tenability, as in this case the pH values of acid humic soft water.
- 2) Conductivity is of special importance with regard to controlling low pH values (< 5.0).
- 3) Both pH and conductivity measurements involve using electrodes which need a regular cleaning, maintenance and calibration procedure, especially used in dirty or humic water. This applies especially to the pH electrodes.
- 4) Discrepancies between

conductivity and pH values can be explained by difference in time between the two measurements. It is therefore important to make both measurements at the same time.

5) Some ions, particularly the base cations, may be released during the analytic procedure (e.g. by atomic absorption photometry.) which can explain some of the discrepancies.

6) pH measurements are generally much more doubtful than conductivity measurements.

7) No experiences so far indicate that the discrepancies are greater in humic than in clear waters. Consequently, there is not clear whether the humic substances are able to disturb the pH and perhaps the conductivity determinations.

8) The scientific works which make their conclusions based on these questionable data should be partly valueless and handled with care.

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