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SHORT COMMUNICATIONS

Acid–Base Equilibrium in the Surface Waters of the Humid Zone

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EVALUATION OF THE CONTRIBUTION OF DIFFERENT SYSTEMS TO THE ACIDITY AND ALKALINITY OF NATURAL WATERS

The acidity and alkalinity of natural waters can be affected by various systems: carbonate (CO_2–HCO_3^-–CO_3^{2-}), humic (HA_{org}–A^-_{org}), silicate (H_4SiO_4–$H_3SiO_4^-$), phosphate (H_3PO_4–$H_2PO_4^-$). In some situations, the hydrolysis of Al, Fe(II), and Fe(III) salts may be important in this respect.

In the general form, the alkalinity of water can be described with the following components:

$$\mathrm{Alk} = [HCO_3^-] + 2[CO_3^{2-}] + x[A^-_{opr}]$$
$$+ y[H_3SiO_4^-] + z[H_2PO_4^-] + [OH^-] - [H^+],$$

and the acidity of the solutions is controlled by the concentrations of weak acids and Al and Fe salts:

$$\mathrm{Acid} = [HA_{org}] + [CO_2] + x[Al^{3+}, Fe^{3+}, Fe^{2+}]$$
$$+ y[H_4SiO_4] + [H^+] - [OH^-].$$

In order to assay the contribution of each of these systems to the acid–base equilibrium, it is pertinent to consider data on the Karelian hydrographic district, whose surface waters provide a good example of waters in the humid zone (Table 1).

The greatest variability is characteristic for the alkalinity of water and for concentration of hydrocarbonates and anions of organic acids. The acidity of the waters vary less significantly than these parameters. Because the Al concentrations are very low, it does not appreciably affect the acidity of waters, and this also pertains to Fe. The latter element occurs in waters as particulate matter and dissolved humic complex compounds [4]. Considering the maximum Fe concentration in these waters (4.6 mg/l or 0.08 mmol/l) with regard for the particulate mode of Fe in Karelian surface waters (50%) and its dissolved complex compounds (70% of all of its dissolved species), the Fe contribution to the acidity of the water at the complete first hydrolysis reaction of the cation ionic Fe compounds does not exceed 0.01 mmol/l.

The acidity of the solutions can also be affected by Si, because it occurs mostly as undissociated H_4SiO_4 within the pH range typical of surface waters (4.0–8.0) [5]. The contribution of silicic acid to the acidity of waters can be assayed with regard for the observed concentrations of silicon in surface waters in Karelia. Taking into account the pH of the waters, we will consider only the first dissociation reaction of silicic acid ($pH \ll pK_1 = 9.6$). At the maximum Si concentration (0.34 mmol/l) and minimum pH (4.0), silicic acid was determined to be able to slightly contribute to the acidity of water. Considering that acidity is determined by titrating a sample by Na hydrocarbonate to pH 8.3, we can calculate the $[H_3SiO_4^-]$ concentration corresponding to this pH value:

$$\frac{[H_3SiO_4^-]\cdot 10^{-8.3}}{[H_4SiO_4]} = 10^{-9.6},$$

$$\frac{[H_3SiO_4^-]\cdot 10^{-8.3}}{0.34 - [H_3SiO_4^-]} = 10^{-1.3} = 0.05,$$

$$[H_3SiO_4^-] = 0.016 \text{ mmol/l}.$$

We obtained a small value for the maximum possible contribution of H_4SiO_4 to the acidity of water (as little as 5% of the initial H_4SiO_4 concentration). With regard for the Si distribution in most waters in Karelia (third quartile—0.09 mmol/l), this contribution is still smaller (≤0.004 mmol/l). It can be concluded that silicic acid does not significantly contribute to the acidity of humic acids, and, based on the facts and considerations presented above, the actual acidity of natural waters is controlled by the presence of the free H^+ ion, CO_2, and weak organic acids, first of all, humic ones

$$\mathrm{Acid} = [H^+] + [CO_2] + [HA_{org}]. \quad (1)$$

The acidity of surface waters is the most significantly affected by carbon dioxide, as also follows from experimental data on pH measurements in humic waters after carbon dioxide was removed from them.

Table 1. Alkalinity, acidity, pH, and the concentrations of Fe, Si, Al, and anions of organic acids (mmol/l) in surface waters of Karelia, mmol/l

Statistical parameter	Alk	Acid	A^-_{org}	Fe	Si	Al	pH
min	<0	0.005	0.01	<0.0002	<0.002	<0.0001	4.07
max	4.44	0.64	1.24	0.082	0.34	0.005	8.00
Av. arithm.	0.23	0.16	0.09	0.010	0.06	0.001	6.58
Av. geom.	0.13	0.10	0.09	0.006	0.05	0.0002	6.55
Median	0.12	0.09	0.08	0.008	0.06	0.0008	6.64
Stand. deviation	0.38	0.16	0.10	0.0048	0.05	0.001	0.60
1st quartile	0.06	0.05	0.04	0.0007	0.03	0.0001	6.25
3nd quartile	0.26	0.25	0.13	0.015	0.09	0.001	6.99
n	801	329	440	801	794	85	797

The alkalinity of humic waters is controlled mostly by hydrocarbonates, carbonates, and anions of organic acids. The effect of the anions of silicic acid is absent because all of its salts are completely hydrolyzed within the pH range in question, and the alkalinity created by them is neutralized by carbon dioxide. This can be illustrated by the evaluation of the effect of $H_3SiO_4^-$ on water alkalinity at the maximum SiO_2 concentrations and the highest pH values (8.0): $0.34 - [H_3SiO_4^-] = 10^{-1.6} = 0.025$, $[H_3SiO_4^-] = 0.008$ mmol/l. This value is very low and lies within the error in the measured values of water alkalinity. Because of this, the effect of salts of silicic acid on the alkalinity of waters can be neglected. Phosphates are contained in the waters in amounts of the order of a few micrograms, and their contribution to the alkalinity of the waters is negligible. Hydrosulfides and sulfites can hardly be contained in surface waters because the latter pervasively contain oxygen. The estimation of the contribution of anions of organic acids demonstrates that they provide approximately 8% of their concentration [6].

DEPENDENCE OF THE pH OF HUMIC WATERS ON THE ALKALINITY AND ACIDITY OF SOLUTIONS

For alkaline waters with pH ≤ 8.0, which bear very low H^+ and OH^- concentrations and practically no carbonates, the concentrations of the aforementioned components can be ignored, and the alkalinity of the waters can be determined by the formula

$$\mathrm{Alk} = [HCO_3^-] + 0.08[A^-_{org}]. \qquad (2)$$

Let us express $[HCO_3^-]$ and $[A^-_{org}]$ through their acidic constituents with regard for the dissociation constants of carbonic (K_1) and humic (K_{hum}) acids:

$$[HCO_3^-] = \frac{K_1[CO_2]}{[H^+]}, \quad [A^-_{org}] = \frac{K_{hum}[HA_{org}]}{[H^+]}.$$

We get

$$\mathrm{Alk} = \frac{K_1[CO_2]}{[H^+]} + 0.08\frac{K_{hum}[HA_{org}]}{[H^+]},$$

$$\mathrm{pH} = \log\frac{\mathrm{Alk}}{K_1[CO_2] + 0.08K_{hum}[HA_{org}]} \qquad (3)$$

$$= \mathrm{p}K_1 + \log\frac{\mathrm{Alk}}{[CO_2] + 0.08\dfrac{K_{hum}}{K_1}[HA_{org}]}.$$

Substituting the values of the dissociation constants for carbonic ($\mathrm{p}K_1 = 6.4$) and humic ($\mathrm{p}K_{hum} = 4.0$), the pH value can be expressed as

$$\mathrm{pH} = \mathrm{p}K_1 + \log\frac{\mathrm{Alk}}{[CO_2] + 20[HA_{org}]}. \qquad (4)$$

Equation (4) contains, along with alkalinity, concentrations of CO_2 and HA_{org}, which cannot be determined individually. Moreover, water alkalinity for acidic humic waters is either very low or even negative. Because of this, formula (4) cannot be utilized to calculate pH for all water types. At the same time, for alkaline waters, whose $[HA_{org}]$ concentrations are extremely low, $20\,[HA_{org}] \ll [CO_2]$ and, in fact, the sum $[CO_2] + 20\,[HA_{org}]$ is equal to the acidity of the water, which depends mostly on the CO_2 concentration. Hence, for these waters,

$$\mathrm{pH} = \mathrm{p}K_1 + \log\frac{\mathrm{Alk}}{\mathrm{Acid}}. \qquad (5)$$

Testing this formula for our natural surface water samples, which had positive alkalinity values, has shown good consistency of the calculated and measured pH values (within ±0.1 pH units) (Table 2, pH_1). For most of our samples, this difference corresponded the determination error of ≤0.05 pH units. Model solutions 2 and 3, which contained $NaHCO_3$, Na benzoate, and benzoic acid, showed significant discrepancies between the cal-

Table 2. Parameters of acid–base equilibria in some water bodies and model solutions. Calculated and measured pH values

Water body	Sample no.	Alk	HCO_3^-	A_{org}^-	Acid	pH_1 (5)	pH_2 (7)	pH_{meas}	$p\tilde{K}$
		mmol-equiv./l							
L. Konchezero	1	0.712	0.710	0.026	0.045	7.60	7.60	7.50	6.3
L. Ukshezero	2	0.422	0.436	0.065	0.055	7.28	7.30	7.30	6.3
L. Pryazhinskoe	3	0.303	0.294	0.115	0.058	7.12	7.11	7.08	6.2
L. Lizhmenskoe	4	0.038	0.034	0.051	0.050	6.28	6.24	6.36	6.1
Shuya R.	5	0.059	0.051	0.096	0.080	6.27	6.21	6.30	5.9
Lamba Vekshelitskaya	6	0.033	0.032	0.012	0.055	6.18	6.17	6.19	6.2
Saarijarvenjoki R.	7	–0.020	–	0.151	0.305	–	–	4.85	5.0
L. Salonjarvi	8	0.014	0.005	0.111	0.130	5.43	5.02	5.45	5.4
L. Vuontelenjarvi	9	–0.027	–	0.127	0.225	–	–	4.73	4.7
L. Suojarvi	10	0.047	0.040	0.082	0.065	6.21	6.20	6.20	5.9
L. Iso-Puhajarvi	11	0.108	0.103	0.098	0.055	6.69	6.67	6.63	6.2
L. Imatozero	12	0.336	0.333	0.032	0.062	7.13	7.13	7.20	6.3
L. Sjamozero	13	0.152	0.151	0.008	0.042	6.96	6.96	6.86	6.2
Model solution 1	14	–0.036	–	0.261	0.136	–	–	4.71	4.3
Model solution 2	15	0.072	0.038	0.303	0.038	6.68	6.42	6.39	5.4
Model solution 3	16	0.174	0.138	0.310	0.028	7.19	7.10	7.02	5.8

culated and measured pH values, particularly for the solution with a low HCO_3^- concentration. This can be explained by the greater contribution of benzoates to the alkalinity of the solution than the contribution of organic anions in natural waters.

The analysis of data on the territory indicates that pH is strongly correlated with the $\log\frac{\mathrm{Alk}}{\mathrm{Acid}}$ for waters with Alk > 0 (Fig. 1):

$$\mathrm{pH} = 6.57 + 0.81\log\frac{\mathrm{Alk}}{\mathrm{Acid}}, \quad r = 0.94, (n = 300). \quad (6)$$

The obtained dependence is slightly different from formula (5). If the pH value calculated by formulas (5) and (6) for the same Alk/ Acid ratios are compared, it can be noted that the greatest discrepancies (up to 0.55) occur at low pH values (<5.0). This is explained by the fact that carbon dioxide contributes less significantly to the pH of the solution in the presence of humic acids than could be expected in their absence, and consequently, the acidity of the environment affects less significantly the pH of the water. This results in a strong correlation between pH and $\log \mathrm{Alk}$ ($r = 0.87$) for all data sets ($n = 745$): $\mathrm{pH} = 7.48 + 0.96\ \log\mathrm{Alk}$.

Water acidity can also be used to determine the pH dependence on the components of the acid–base equilibrium. As was demonstrated previously for humic acids,

$$\mathrm{Acid} = [CO_2] + [HA_{org}] + [H^+],$$

$$[CO_2] = \frac{[H^+][HCO_3^-]}{K_1}, \quad [HA_{org}] = \frac{[H^+][A_{org}^-]}{K_{hum}}.$$

$$[\mathrm{Acid}] = [H^+]\left(\frac{[HCO_3^-]}{K_1} + \frac{[A_{org}^-]}{K_{hum}} + 1\right),$$

$$\frac{1}{[H^+]} = \frac{[HCO_3^-]K_{hum} + K_1[A_{org}^-] + K_1K_{hum}}{K_1K_{hum}[\mathrm{Acid}]}$$

$$= \frac{[HCO_3^-]\frac{K_{hum}}{K_1} + [A_{org}^-] + K_{hum}}{K_{hum}[\mathrm{Acid}]},$$

$$\mathrm{pH} = \mathrm{p}K_{hum} + \log\frac{K[HCO_3^-] + [A_{org}^-] + K_{hum}}{[\mathrm{Acid}]}, \text{ or}$$

$$\mathrm{pH} = \mathrm{p}K_1 + \log\frac{[HCO_3^-] + \frac{[A_{org}^-]}{K} + K_1}{[\mathrm{Acid}]},$$

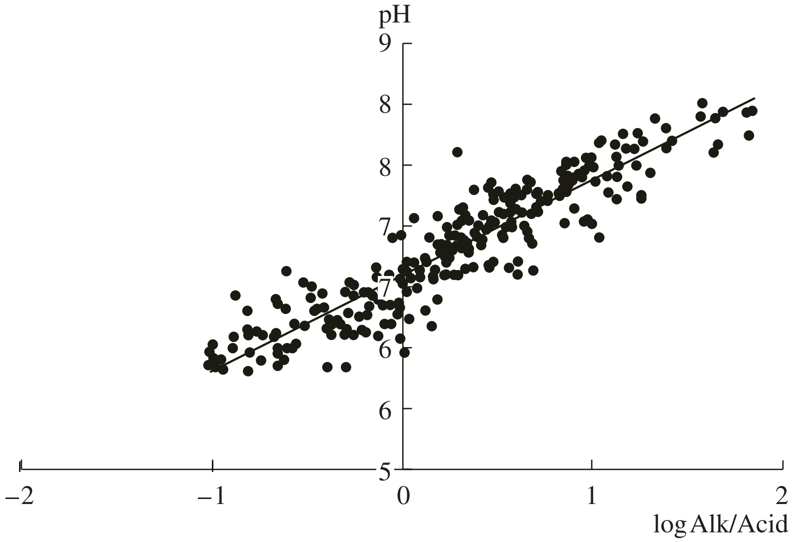

Fig. 1. Dependence of pH on the log (Alk/Acid) ratio for various water bodies in Karelia.

where $K = \frac{K_{hum}}{K_1}$. In as much as K_1 is very small (0.0004 mmol/l), it can be neglected, and pH can be determined by the formula

$$pH = pK_1 + \log \frac{[HCO_3^-] + \frac{[A_{org}^-]}{K}}{[Acid]}. \qquad (7)$$

Equation (7) is analogous to Eq. (4), but the pH dependence in it is deduced from the salt components of the acid–base equilibrium. Calculations by this formula are possible, like calculations by Eq. (5), only for samples in which hydrocarbonates and $[A_{org}^-]$ can be reliably determined from the alkalinity and ionic balance of the water. The pH calculations conducted by formula (7) for natural water samples yielded results analogous to those obtained by formula (5), except Salonjarvi Lake (Table 3). The water of this lake is weakly acidic (pH 5.45), and its HCO_3^- and A_{org}^- concentrations can hardly be exactly determined by the method [6]. At the same time, the model solutions (nos. 2 and 3) display the opposite dependences. Their pH values calculated by formula (7) were closer to the measured values than those calculated by formula (5). In this case, we managed to exclude the effect of benzoates observed in the pH calculations by formula (5).

DEPENDENCES OF THE pH OF HUMIC WATERS ON THE CONCENTRATIONS OF THE COMPONENTS OF ACID–BASE EQUILIBRIUM

One of the disadvantages of derived formulas (4), (5), and (7) is that they cannot be used to calculate the concentrations of components of acid–base equilibrium for the whole pH range observed in natural waters. We can try to attack this problem in a general form, considering that acid–base equilibrium in humic waters is controlled by two systems: $HA_{org}–A_{org}^-$ and $CO_2–HCO_3^-$. Inasmuch as humic acids are stronger than carbonic acid, equilibria like

$$HCO_3^- + HA_{org} \rightleftharpoons A_{org}^- + H_2O + CO_2.$$

Table 3. Concentrations (mmol-equiv./l) of the components of acid–base equilibrium in acidic humic waters and model solution

Water body	pH_{meas}	Alk	Acid	a	m	HA_{org}	CO_2	A_{org}^-	HCO_3^-	$p\tilde{K}$
	Measured values					Calculated values				
L. Salonjarvi	5.45	0.014	0.130	0.115	0.126	0.004	0.122	0.101	0.014	5.5
Saarijarvenjoki R.	4.85	–0.020	0.305	0.151	0.291	0.022	0.269	0.143	0.008	5.1
L. Vuontelenjarvi	4.73	–0.027	0.225	0.127	0.206	0.024	0.182	0.123	0.004	4.9
Model solution 1	4.71	–0.036	0.136	0.264	0.117	0.073	0.044	0.263	0.001	4.4

take place in their presence. The equilibrium constant is defined by the equilibrium concentrations of all components: $K = \dfrac{[CO_2][A^-_{org}]}{[HA_{org}][HCO_3^-]}$. Its numerical value is equal to the ratio of the dissociation constants of humic acids to that of the first dissociation reaction of carbonic acid (K_{hum}/K_1).

Assume that we know the proportions of weak acids in the solution ($b = [CO_2]/[HA_{org}]$) and their total concentration ($[CO_2] + [HA_{org}] = m$); then $[HA_{org}] = m/(1 + b)$. With regard for the equilibrium constant and ionic balance of water ($[HCO_3^-] + [A^-_{org}] = a$), we obtain $HCO_3^- = b[A^-_{org}]/K$, $b[A^-_{org}]/K + A^-_{org} = a$, and $[A^-_{org}] = aK/(b + K)$. The pH value of water can be expressed by the formula $pH = pK_{hum} + \log\dfrac{[A^-_{org}]}{HA_{org}}$. Upon the substitution of corresponding $[HA_{org}]$ and $[A^-_{org}]$ values into this formula, we obtain

$$pH = pK_{hum} + \log\frac{aK(1+b)}{(b+K)m} = pK_{hum} + \log\frac{K(1+b)}{b+K} + \log\frac{a}{m} = pK_1 + \log\frac{1+b}{b+K} + \log\frac{a}{m}. \tag{8}$$

Eventually we derive a general form for the dependence of the pH of natural waters on the concentrations of the components of the acid–base equilibria: the bulk concentrations of weak acids (m) and their anions (a) in the solution and the proportions of weak acids (b). If the $[CO_2]/[HA_{org}]$ ratio is substituted into formula (8) in place of b, then

$$pH = pK_1 + \log\frac{a}{[CO_2] + K[HA_{org}]}. \tag{9}$$

Assuming that the concentrations of hydrocarbonates and anions of organic acids in the solution are known, we can analogously determine that

$$pH = pK_{hum} + \log\frac{K+b'}{b'+1} + \log\frac{a}{m} = pK_{hum} + \log\frac{K[HCO_3^-] + [A^-_{org}]}{m} = pK_1 + \log\frac{[HCO_3^-] + [A^-_{org}]/K}{m}, \tag{10}$$

where $b' = \dfrac{[A^-_{org}]}{[HCO_3^-]}$. Formulas (4), (5), and (7) presented above are a special case of dependences (9) and (10) for alkaline waters. Formulas (8), (9), and (10) are convenient because they make it possible to calculate the concentrations of all components of acid–base equilibrium in natural humic waters, if the alkalinity, acidity, and pH of the these waters are known and its ionic balance is taken into account. The application of these formulas can be complicated only if the exact value of the average dissociation constant of humic acids is unknown.

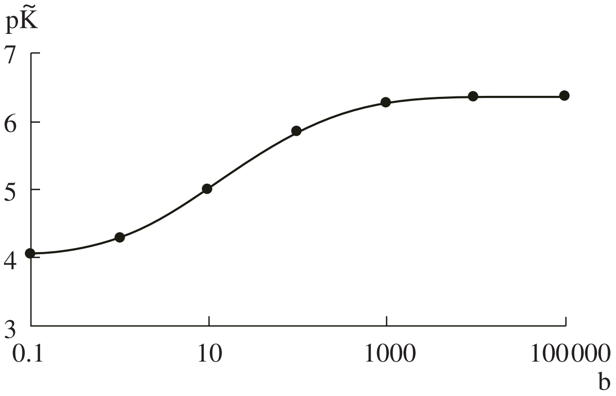

Fig. 2. Dependence of pK on the concentration proportion (b) of carbon dioxide and humic acids.

It was mentioned in the literature that the pK varies from 3 to 6 [7]. In any event, humic acids are stronger than carbonic acid. It was demonstrated in [6], which was devoted to the analysis of the dependence of the alkalinity of natural waters at its zero values, that pK_{hum} is close to 4.0, and this was confirmed by conductometric and potentiometric techniques for determining dissociation constants. Even admitting some inaccuracy of the determined pK_{hum} value, Eqs. (8) and (10) can be used to identify the general relations of acid–base equilibria in natural humic waters.

Now we can consider the dependence $pK_1 + \log\dfrac{1+b}{b+K} = p\tilde{K}$ on the proportion of the concentrations of carbonic and humic acids (Fig. 2). With regard for the average dissociation constant of humic acids ($pK_{hum} = 4.0$) and carbonic acid ($pK_1 = 6.4$), we calculated K = 250. The derived graphical dependence (Fig. 2) can be subdivided into two segments: carbonate–humic ($b \geq 15.4$, $p\tilde{K} \geq 5.2$) and humic–carbonate ($b \leq 15.4$, $p\tilde{K} \leq 5.2$). Note that $p\tilde{K}$ varies from 4.0 to 6.4 depending on the contributions of each of the systems to the acid–base equilibrium, and the pH of water can be expressed by the formula

$$pH = p\tilde{K} + \log\frac{a}{m}. \tag{11}$$

The form of this formula corresponds to simple buffer systems with a salt and acid with the only difference of variable $p\tilde{K}$. Formula (11) is convenient because this formula makes it possible to readily calculate $p\tilde{K}$ and immediately determine which system controls the acid–base equilibrium. If $p\tilde{K} \geq 5.8$, the predominant system is carbonate, and if $p\tilde{K} \leq 4.6$, the equilibrium is controlled by the humic system. In the transitional region at $4.6 < p\tilde{K} < 5.2$, the equilibrium is controlled by the humic–carbonate system; at $5.2 \leq p\tilde{K} < 5.8$, the equilibrium is predominantly controlled by the carbonate–humic system. The results of pK calculations are summarized in Tables 2 and 3. For example, for alkaline waters with pH > 6.0, $p\tilde{K} > 5.9$, and the $p\tilde{K}$ of the acidic humic waters of lakes Salonjarvi and Vuontelenjarvi and the Saarijarvenjoki are 5.5, 4.9, and 5.1, respectively. The acid–base equilibrium in their waters is significantly contributed by the humic system (particularly, for Lake Vuontelenjarvi, whose water is the most acidic). Using Eqs. (9) and (10), we calculated the concentrations of all components of the acid–base equilibrium of these waters (Table 3). The highest concentrations of humic acids and the lowest concentrations of carbonates were determined in the water of Lake Vuontelenjarvi, whose water is the most acidic. All samples of acidic humic waters show the highest CO_2 concentrations compared to those in humic alkaline waters. For the model solution containing Na benzoate and benzoic acid, the calculated concentrations of the components correspond to the initial values taken for this research. It should be emphasized that it is not principally important in this situation whether the exact value of the dissociation constant of humic acids is known. For example, at pK_{hum} greater than 4.0, we would have narrower $p\tilde{K}$ ranges for the corresponding regions of the acid–base equilibrium, but the general situation would correspond to that considered above.

Acid–base equilibrium in the surface waters of the humid zone is thus controlled by two buffer systems: carbonate and humic. This equilibrium is controlled by the carbonate system in alkaline waters (pH ≥ 6.0), by both systems in the weakly acidic range pH 5.0–6.0, and predominantly by the humic system in the acidic region (pH < 5.0).

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