

APPENDIX

Acids, Bases and pH

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Each of the proteolytic species in an aquatic system has an equilibrium constant. If we consider the acid HA and the dissociation process:



we have

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad (\text{A2})$$

where K_a = the equilibrium constant.

It is possible, when the composition of the aquatic system is known, to calculate both the alkalinity and the buffering capacity, using the expression for the equilibrium constants. However, these expressions are more conveniently used in logarithmic form. If we consider the expression for K_a for a weak acid, the general expression (A2), may be used in a logarithmic form:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]} = \text{p}K_a + \log [\text{A}^-] - \log [\text{HA}] \quad (\text{A3})$$

multiplying both sides of the equation with -1 and using the symbol p for “-log” and pH for “-log H^+ ”.

It is often convenient to plot concentrations of HA and A^- versus pH in a

logarithmic diagram. If C denotes the total concentrations $C=[HA]+[A^-]$, we have at low pH:

$$[HA] \approx C$$

$$\log[A^-] = \text{pH} - \text{pK}_a + \log C \quad (\text{A4})$$

This means that $\log[A^-]$ increases linearly with increasing pH, the slope being +1. The line goes through $(\log C, \text{pK}_a)$ as $\text{pH}=\text{pK}_a$ gives $\log[A^-] = \log C$, see equation (A4).

Correspondingly, at high pH, $[A^-] = C$ and

$$\log [HA] = \text{pK}_a - \text{pH} + \log C \quad (\text{A5})$$

which implies that $\log[HA]$ decreases with increasing pH, the slope being -1. This line also goes through $(\log C, \text{pK}_a)$.

$$\text{At } \text{pH} = \text{pK}_a, [A^-] = [HA] = C/2 \text{ or } \log [A^-] = \log [HA] = \log C - 0.3$$

Fig. A1 and Fig. A2 show the result of these considerations for a single acid-base system.

Note that for H_2A the slope will be -2 at $\text{pH} > \text{pK}_2$, corresponding to the dissociation of $2H^+$:

$H_2A \rightarrow 2H^+ + A^{2-}$ and for A^{2-} the slope will be +2 at $\text{pH} < \text{pK}$. This is demonstrated in Fig. 5.12.

β , the buffer capacity, is defined as $\beta = dC / d\text{pH}$.

It can now be shown that

$$\log \left(\frac{\beta}{2.3} \right) = \log \left([H_3O^+] + [OH^-] + \sum \frac{[A^-][HA]}{c} \right) \quad (\text{A6})$$

At $\log \text{pH}$ $[HA] = C$, and only $[H_3O^+]$ plays a role.

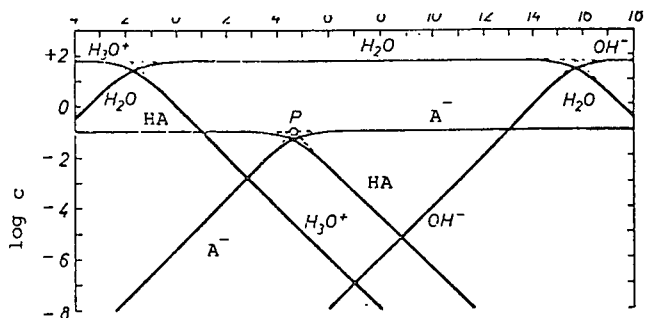


Fig. A1 H_3O^+ , OH^- and water + HA/A^- . $pK_a = 4.64$ and $C = 0.1$ M.

At higher pH, $\frac{[A^-][HA]}{c} = [A^-]$ also contributes to $\frac{\beta}{2.3}$

where $[H_3O^+] = [A^-]$, $\log\left(\frac{\beta}{2.3}\right) = \log(2[H_3O^+]) = -pH + 0.3 = \log(2[A^-])$.

At still higher pH, but with values of $pH < pK_a$, $\log [A^-]$ dominates.

At $pH = pK_a$ $\log \frac{\beta}{2.3} = \log \frac{C/2 * C/2}{C} = \log \frac{C}{4} = \log C - 0.6$

At $pH > pK_a$, $[A^-] = C$ and $\log [HA]$ contributes the most to $\frac{\beta}{2.3}$

At very high pH, $\log [OH^-]$ will dominate. These considerations are used in the construction of Fig. A2.

Fig. A3 is a double logarithmic diagram for seawater. The proteolytic species mentioned above are represented in their appropriate concentrations. The important species are hydrogen and hydroxide ions, boric acid (HB) and carbonate ions (C_2^-). The arrow in the diagram indicates the pH value of seawater - about 8.1.

Based on such a diagram it is possible to set up another diagram, representing the buffering capacity as a function of pH, see Fig. A4. For those who are interested in the relationship between the two diagrams, see Hägg (1979).

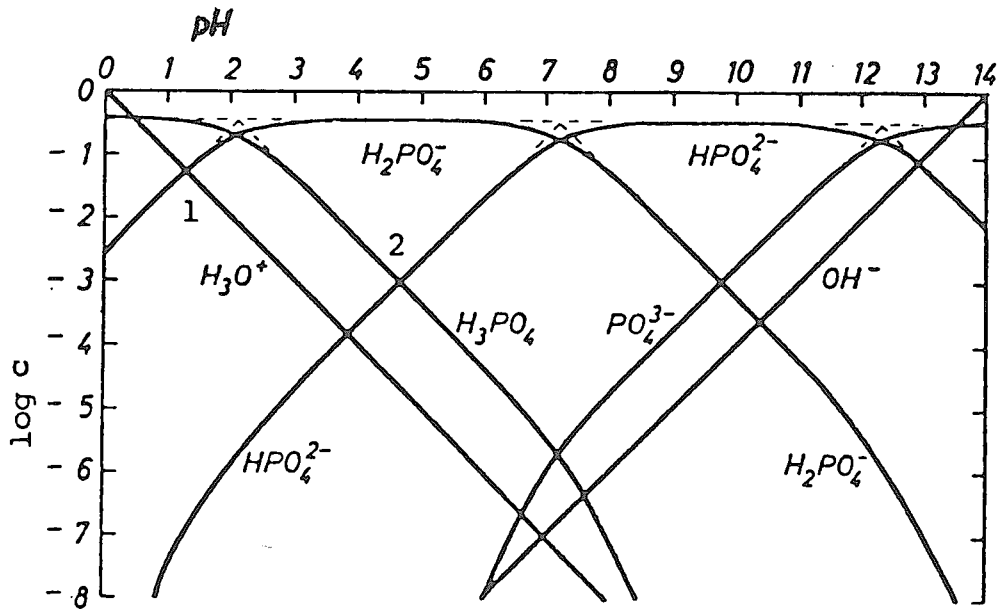


Fig. A2 pH-log c diagram for phosphoric acid.

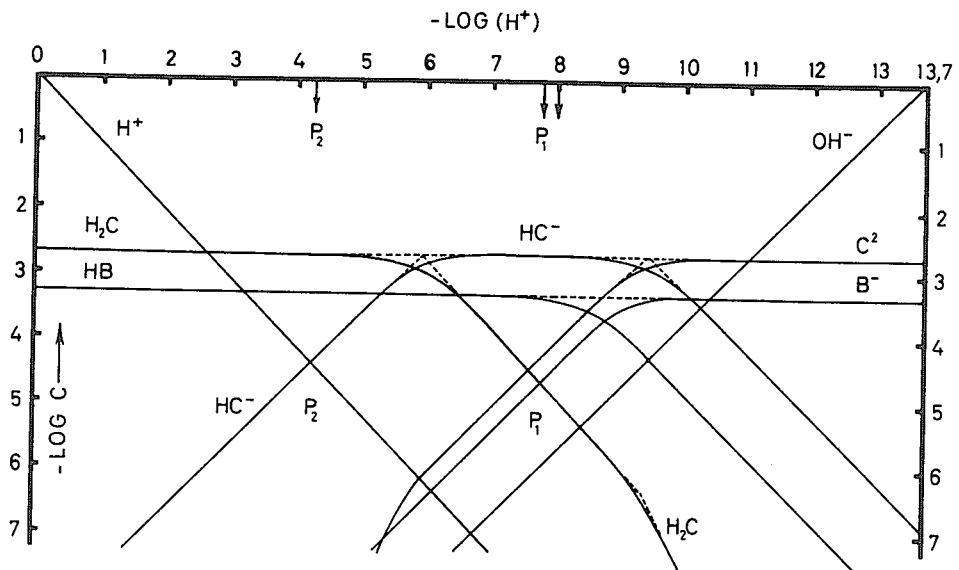


Fig. A3: pH-diagram. $H_2C = H_2CO_3$, $HC^- = HCO_3^-$, $C^2 = CO_3^{2-}$, $B^- = \text{borate}$. pH of the sea is indicated by an arrow.

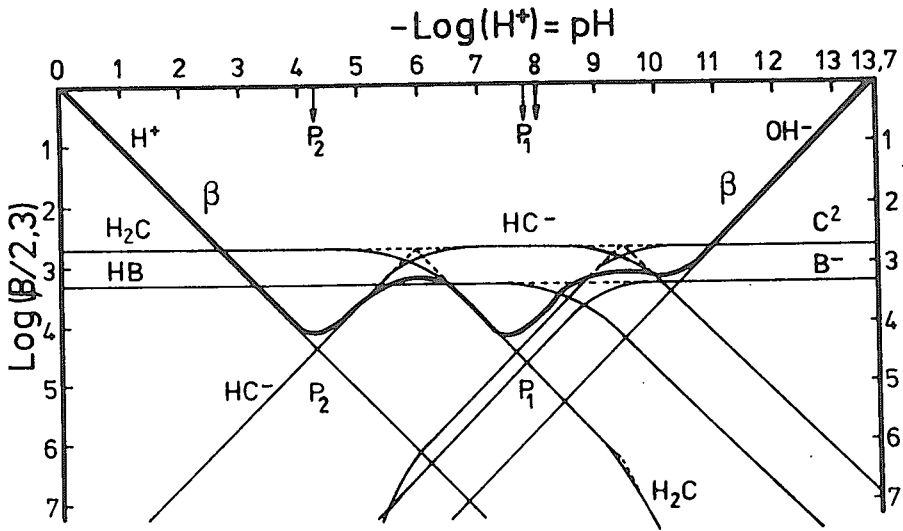


Fig. A4 Buffering capacity of the sea as a function of pH (β).

APPENDIX 2

Global Acidic Atmospheric Deposition

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Acidification of surface ecosystems results from the combination of sensitive soils and lakes and acidic atmospheric deposition. The main chemical constituent of acid deposition are oxides of sulfur and nitrogen, with chloride and some organic acids contributing to a lesser degree.

Figure A5 shows schematically regions of the world where soils are sensitive to acid deposition and regions where high emissions of acidifying pollutants occur. Locations that combine sensitive soils and high emissions - parts of eastern North America, northern and central Europe, and southern China - represent today's problem areas. Potential problem areas, identified by soil sensitivity and expected future emission rates are also shown in Fig. A5.

Both wet and dry atmospheric deposition contribute to acidification. Wet deposition is measured in many parts of the world, and extensive data are available in North America, Europe, and parts of Asia. However, yet, a reliable global wet deposition data base does not exist. Dry deposition estimates, derived from ambient concentration measurements, are even more limited.

An alternative approach to estimate global wet deposition is to use large-scale chemical transport models. Figure A6 shows calculated annual wet deposition of non-sea-salt sulfur (Langner and Rohde, 1991). Since sulfur is the main contributor to precipitation acidity, the areas of high sulfur deposition are identical with the problem areas that appear in Fig. A5.

Agreement between model predictions and observations is generally rather good. For example, the predicted wet deposition rates over eastern North America

and Europe up to $> 1 \text{ g S / m}^2 / \text{y}$ compare favorably with the observed maxima of about 1 and $2 \text{ g S / m}^2 / \text{y}$ in North America (Vet et al., 1992) and Europe (Hanssen et al., 1990) respectively. In remote areas, modelled sulfur deposition is in the range of $50 - 250 \text{ mg S / m}^2 / \text{y}$, while observations are in the range of $30 - 400 \text{ mg S / m}^2 / \text{y}$ (Galloway, 1985).

An intensive effort is now underway through the World Meteorological Organization and the United Nations Environment Program to augment global monitoring of precipitation composition and deposition within the Global Atmosphere Watch, and to prepare a comprehensive global assessment of acid deposition.

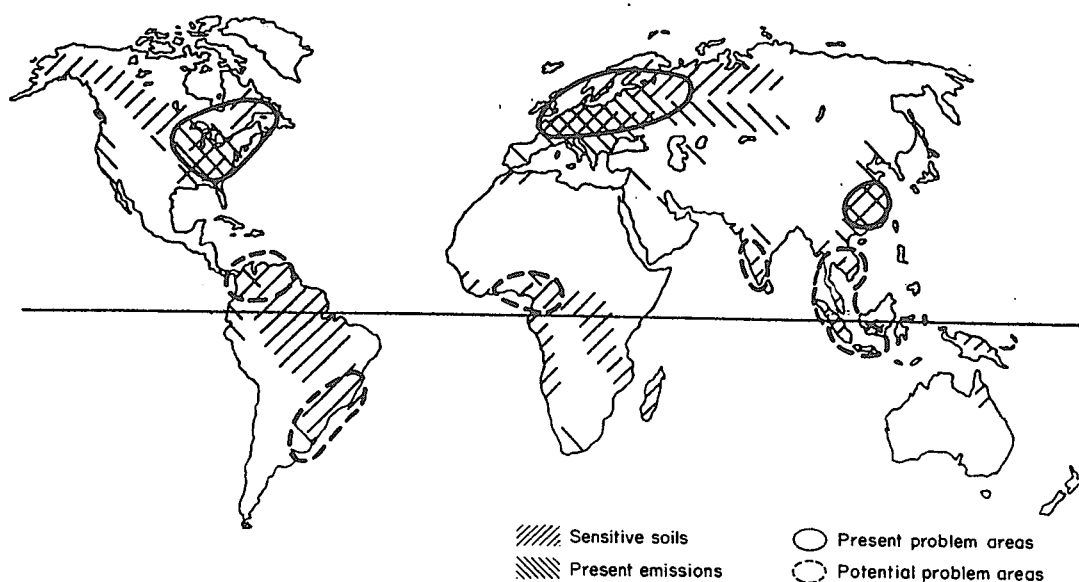
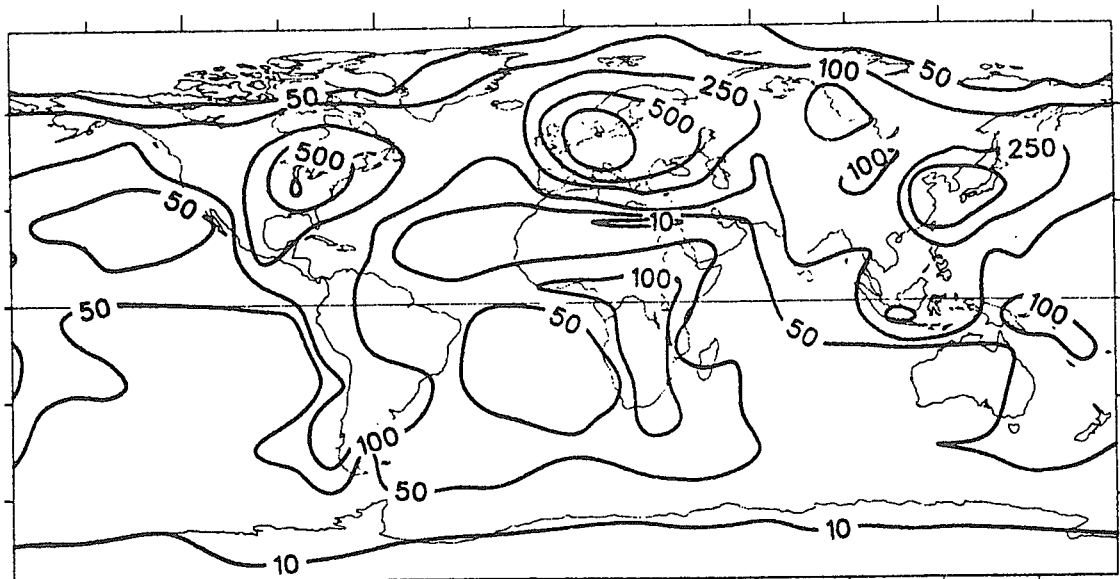


Fig. A5 Schematic map showing regions that currently have acidification problems, and regions where, based on soil sensitivity, expected further emission and population density, acidification might become severe in the future. Reproduced from Rohde and Herrera (editors), 1988.



Isolines are: 10, 50, 100, 250, 500, 1000

Fig. A6 Calculated annual wet deposition of non-sea-salt. Reproduced from Langner and Rohde, 1991.

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Table 2.2 Characteristics of the most important greenhouse gases (Rounded figures). The global warming potentials (GWP) and relative contributions are calculated for a time horizon of 100 years. Emissions are only anthropogenic. For the hydrocarbons (NMHC) and chlorofluorocarbons (FC) total and average values are given.

Compound	Lifetime years	Global emission mio ton/year	GWP rel. CO ₂	Contribution %
CO ₂	120	26.000	1	61
CH ₄	10	300	21	15
N ₂ O	150	6	290	4
CO		200	3	1
NO _x		66	40	6
NMHC		20	11	1
CFC	100	1	5000	12

Table 2.3 The most important characteristics of ozone depleting compounds (Rounded figures).

Compound	Lifetime years	Global emission mio ton/year	GWP rel. CO ₂	Contribution %
CFCl ₃ (CFC 11)	140	340	1	30
CF ₂ Cl (CFC 12)	120	440	1	40
CCl ₄	150	100	1	10
C ₂ F ₃ Cl ₃ (CFC 113)	90	160	0.8	12
CHF ₂ Cl (CFC 22)	90	200	0.07	1
C ₂ H ₃ Cl ₃	130	550	0.1	5
CBrF ₃ (Halon 1301)	150	2	10	2

Table 2.1 Emission factors for use of fossil and a few other fuels in Denmark. Unit kg/GJ.

Fuel % sulphur	Application	SO ₂	NO _x	CO ₂	N ₂ O	CH ₄	NMVOG
<i>Coal</i>							
1,0	Power plants	0,714	0,440	95,0	0,003	0,0003	
0,9	District heating	0,584	0,200	95,0	0,003	0,0002	
0,9	Process (industry)	0,584	0,200	95,0	0,003	0,0003	
<i>Fuel oil</i>							
1,0	Power plants	0,495	0,280	78,0	0,003	0,0001	
1,0	District heating	0,495	0,150	78,0	0,003	0,0001	
1,0	Process (industry)	0,495	0,150	78,0	0,003	0,0001	
1,0	Ships	0,495	1,733	78,0	0,051	0,0083	0,1987
<i>Diesel oil</i>							
0,2	Cars <3,5 t	0,094	0,303	74,0	0,009	0,0050	0,1190
0,2	Cars >3,5 t	0,094	1,509	74,0	0,051	0,0072	0,1738
0,2	Ships	0,094	1,733	74,0	0,051	0,0083	0,1987
<i>Gas oil</i>							
0,2	District heating	0,094	0,100	74,0	0,003	0,0001	
0,2	Domestic heating	0,094	0,050	74,0	0,003	0,0030	
0,2	Process (industry)	0,094	0,100	74,0	0,003	0,0001	
<i>Petrol</i>							
0,05	Cars	0,022	0,723	73,0	0,022	0,0974	1,1676
<i>Natural gas</i>							
~0	Power plants	~0	0,240	56,9	0,002	0,0003	
~0	Gas turbine	~0	0,200	56,9	0,0002	0,0003	
~0	Gas engine	~0	0,200	56,9	0,0002	0,0003	
~0	Process (industry)	~0	0,100	56,9	0,002	0,0003	
~0	District heating	~0	0,150	56,9	0,002	0,0003	
~0	Domestic heating	~0	0,050	56,9	0,002	0,0010	
<i>Waste</i>							
0,3	District heating	0,675	0,150	117,0	0,003	0,0003	
<i>Straw</i>							
0,1	District heating	0,130	0,130	102,0	0,003	0,0002	
0,1	Domestic heating	0,130	0,050	102,0	0,003	0,1500	
<i>Biogas</i>							
~0		~0	0,05-0,15	56,9	0,002	0,0003	