Chapter 2

Effects of Redox Processes on Acid-Producing Potential and Metal Mobility in Sediments

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INTRODUCTION

Both pH and redox potential in sediment/water systems are significant parameters for mobilization and transformation of metals.[1,2] Many investigations have shown that pH decreases during oxidation of sediments.[3–7] Recently, considerable attention has been paid to the environmental impact on acid-sensitive waters and soils caused by redox processes.[8–14]

The concepts of acid-producing potential (APP) and potential acidity have been used in the prediction and calculation of acid mine drainage and waste tailing management.[15–17] Ferguson and Erickson[18] have summarized studies on acid mine drainage in North America. Recently, this concept has been applied to the oxidation research of anoxic sediments and other solid earth materials.[10,19]

Acidification in sediment/water systems occurs when hydrogen ions are generated during oxidation.[5,10,20] The acidification sensitivity depends on the acid neutralizing capacity (ANC) of the system.[20,21] When APP is addressed, ANC also should be considered, especially relative to its role in regulating the acid-base equilibrium of the system.[22–24]

There is increasing interest in the effects of periodical redox changes on APP and subsequent mobility of metals,[10,25,26] which has led to the development of several new concepts.[3,19] This paper will review the following processes related to metal availability:

1. Sources of acids in redox processes and APP in natural sediment/water systems;
2. Acid buffering capacity in the systems;
3. Periodical redox processes and their effects on APP;
4. Effects of redox processes on the mobilization of metals in sediment.

THE SOURCES OF ACIDS IN REDOX PROCESSES AND THE ACID-PRODUCING POTENTIAL (APP) IN SEDIMENT/WATER SYSTEMS

Main Oxidation Reactions of Acid Producers

In the presence of molecular oxygen, SO_4^{2-} and NO^{3-} are the thermodynamically stable forms of S and N. Compounds containing Fe, N, and S in lower oxidation states are ultimately oxidized to Fe^{3+}, $FeOOH$, NO^{3-}, and SO_4^{2-}, thereby releasing equivalent amounts of H^+ into the environment. Most of these oxidation reactions are microbially mediated.[24] Proton transfer processes which are important in the oxidation of sediment/water systems are summarized in Table 1.

S, Fe, and N are the most important elements in redox processes of a sediment/water system. This is not only due to their chemical reactivity, but also to their abundance in natural waters and sediments. For example, in tidal marsh sediments, pyrite contents (FeS_2) are often on the order of 1 to 5% on a mass basis, or higher.[28,30]

If chemical components in the sediment are known, APP can be calculated. The molar ratio of the reducing species to the produced hydrogen ions is listed in Table 1. We call this ratio the

Table 1.   Main Oxidation Reactions in Sediment/Water Systems

Elements oxidized	Reaction equations	f [a]	Ref.
Inorganic			
S	$H_2S + 2 O_2 = SO_4^{2-} + 2 H^+$	2	27
S	$S° + 3/2 O_2 + H_2O = SO_4^{2-} + 2 H^+$	2	28
S, Fe	$FeS + 9/4 O_2 + 3/2 H_2O = FeOOH + SO_4^{2-} + 2 H^+$	2	27[b]
S, Fe	$FeS_2 + 15/4 O_2 + 5/2 H_2O = FeOOH + 2 SO_4^{2-} + 4 H^+$	4	29
Fe	$Fe^{2+} + 1/4 O_2 + 5/2 H_2O = Fe(OH)_3 + 2 H^+$	2	27
N	$NH_4^+ + 2 O_2 = NO_3^- + H_2O + 2 H^+$	2	27
N	$NO_x + 1/4(5-2x) O_2 + 1/2 H_2O = NO_3^- + H^+$	1	27
Organic			
N	$R-NH_2 + 2 O_2 = R-OH + NO_3^- + H^+$	1	27
S	$R-SH + H_2O + 2 O_2 = R-OH + SO_4^{2-} + 2 H^+$	2	27[b]

[a] f = Acid-producing coefficient.
[b] The coefficients have been revised by the authors of this paper.

acid-producing coefficient f. For example, 1 mol of FeS_2 can produce 4 mol of hydrogen ions. Because of its high f and its abundance in anoxic sediments, this reaction has been extensively discussed.[29-34]

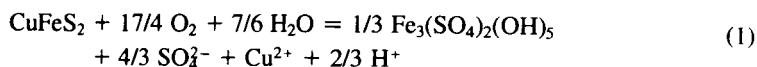## Acid Production from the Oxidation of Inorganic Species

Oxidation of Sulfides

The oxidation of sulfides is a typical example of an acid source from inorganic species. A number of iron sulfide minerals are present in sedimentary environments: amorphous FeS, mack-inawite (tetragonal FeS), greigite (cubic Fe_3S_4), and pyrite (cubic FeS_2).[32] In most cases, pyrite is the most important because of its relative abundance; hence, the oxidation of pyrite plays a significant role in acidification of sediments, soils, and other solid materials.[10,29,31]

Pyrite is stable only under strongly reduced conditions and changes into iron(II) sulfate at low pH and medium Eh, into iron-(hydr)oxides under near-neutral oxidizing and moderately reducing conditions (Table 1), and into jarosite ($KFe_3(SO_4)_2(OH)_6$) at low pH and high Eh.[29] The processes involved in oxidation of pyrite have been extensively studied in relation to acid mine drainage and were summarized by Nordstrom[31] and Ferguson and Erickson.[18] Numerous investigations[33,34] have shown that pyrite oxidation proceeds much faster in the presence of the chemoautotrophic micorbial genus, *Thiobacillus*.

Oxidation of Chalcopyrite

Oxidation of waste sulfidic ores in some special sites, particularly in the aquatic environment of mine tailing drainage areas, is one of the acid-producing sources. S^{2-} is completely oxidized to SO_4^{2-} and Fe^{2+} to Fe^{3+}, which tends to hydrolyze and precipitate as jarosite, thus releasing acid. The overall reaction is a net acid production:[35]

$$CuFeS_2 + 17/4 O_2 + 7/6 H_2O = 1/3 Fe_3(SO_4)_2(OH)_5 + 4/3 SO_4^{2-} + Cu^{2+} + 2/3 H^+ \tag{1}$$

The relationship between acid production and ore oxidation in the environment has been summarized by Ferguson and Erickson.[18]

Oxidation of Ammonium

Inorganic N is formed by the decomposition of organic matter and industrial sources in waters. When the pH value of a system is below about 9, NH_3 consumes H^+ from solution to

form the weak acid ammonium (NH_4^+). The alkalinity associated with NH_4^+, in turn, is transferred to the solution or perhaps to the exchange complex.[36] When ammonium is oxidized (nitrification) by autotrophic microbes which obtain energy from the reaction, the acidity associated with ammonium is released and the Lewis acidity of the oxygen is transferred to nitric acid:[36]
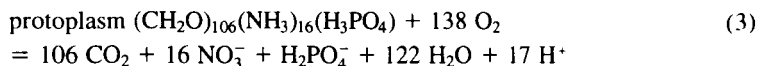
$$NH_4^+ + 2\,O_2 = NO_3^- + H_2O + 2\,H^+ \tag{2a}$$

or

$$NH_3 + 2\,O_2 = NO_3^- + H_2O + H^+ \tag{2b}$$
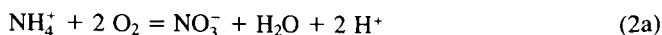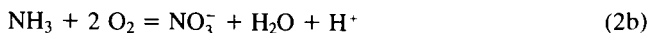
Acid Production from the Oxidation of Organic Matter

Oxidation of Organic Nitrogen

The sediments in oceans, estuaries, and rivers can contain significant amounts of organic matter resulting from the decomposition of organisms.[37] Besides C and O, the elements most involved in redox cycles are those that are abundant in living matter: N and S. A stoichiometric description of the oxidation of protoplasm (as represented by the average proportions of the major elements in algal biomass) in natural waters is provided by the following reactions:[24,28]

$$\text{protoplasm } (CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138\,O_2 \tag{3}$$
$$= 106\,CO_2 + 16\,NO_3^- + H_2PO_4^- + 122\,H_2O + 17\,H^+$$

When NO_3^- is the product of the oxidation, the alkalinity decreases by 0.16 ($= 17/106$) equivalent per mole of C fixed. When there is not enough oxygen for oxidizing all reducing compounds to their oxidized states, NH_4^+ will be produced; which consumes H^+. However, subsequent oxidation of NH_4^+ produces more H^+; summarized by Equation 3.

Oxidation of Organic Sulfur

Organic matter in sediments and soils contains many sulfur groups. For example, the amino acids cysteine[37] and methionine, and derivatives such as methionine sulfoxide,[39] methionine sulfone,[40] and cysteic acid[41] have been obtained from soil hydrolyzates. Clearly, the decomposition products of amino acids will include SO_4^{2-} and H^+ resulting from the oxidation of organic S:[27]

$$R\text{-}SH + H_2O + 2\,O_2 = R\text{-}OH + SO_4^{2-} + 2\,H^+ \tag{4}$$
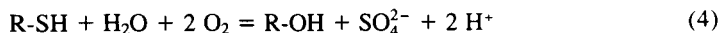
Some other organic compounds such as oxalic acid, acetic acid, and hydroquinone can also produce hydrogen ions when they are oxidized.[42]

Calculations of Acid-Producing Potential (APP)

Acid-Producing Potential

APP can be defined as the largest amount of H^+ produced by the oxidation of the components per unit weight of sediments (or other solid materials), per unit volume of water (or other liquid substances), or in the whole sediment/water system. After the components of a sample are identified, APP can be easily calculated by using the following equations:

$$APP(s) = f \cdot \frac{C(s)}{M} \tag{5}$$

$$APP(aq) = f \cdot \frac{C(aq)}{M} \tag{6}$$

Table 2. Average Acid-Producing Potential (APP) of Some Samples

Parameter	Average content (mg/g)	C/M (mmol/g)	f	In suspension (1:10) APP (mmol/g)	[H⁺]ᵃ (mmol/l)	pHᵃ
Suspension I						
Organic carbonᵇ	36					
Org-Nᵇ	2.7	0.19	1	0.19	19	1.72
Org-Sᵇ	0.49	0.015	2	0.030	3.0	2.52
Whole system				0.22	22	1.66
Suspension II						
FeS₂ᶜ	1–5	0.083–0.417	4	0.332–1.668	33.2–166.8	1.48–0.78

ᵃValues calculated theoretically from Equations 5 and 7.
ᵇFrom Reference 44, average values of 14 samples.
ᶜFrom Reference 28, no other reducing species data are available for the calculation.

where $C(s)$ and $C(aq)$ are the contents (in grams per kilogram or grams per liter) of the reducing species (oxidized compounds) in 1 g of solid material and in 1 l of liquid, respectively. M is the molecular weight of the oxidized compound in grams per mole. The units of $APP(s)$ and $APP(aq)$ are moles per gram and moles per liter, respectively.

Total $APP(s)$ is the sum of the $APP(s)$ of each oxidized species (i):

$$T\text{-}APP(s) = \Sigma\ APP(s)(i) \tag{7}$$

and analogous for T-APP(aq):

$$T\text{-}APP(aq) = \Sigma\ APP(aq)(i) \tag{8}$$

So we have

$$T\text{-}APP = \Sigma\ APP(i) \tag{9}$$

Some Examples of APP

Experimental approaches for calculating APP for sulfidic mining residues have been summarized.[18] A test described by Sobek et al.[43] involves the analysis of total pyritic sulfur, whereas Bruynesteyn and Hackl[15] calculated APP from total sulfur analysis. However, the APP of sediments is more complex than that in sulfidic ores because the APP from organic matter also must be considered.

The N/C ratio in protoplasm is basically stable (16:106). If no directly measured org-N data are available, the $APP(s)$ of org-N originating from the oxidation of N in protoplasm can approximately be calculated from a known carbon content in the sediment:

$$APP(s)\ (\text{org-N}) = 16/106 \times f \times C/12 \tag{10}$$

where C is the carbon content in the sediment.

The $APP(s)$ of 14 samples were calculated by Swift,[44] according to the average content of each reducing species. We calculated the concentration of H^+ in a corresponding solid/liquid suspension of 1:10, disregarding the buffering and the oxidation kinetics. The results indicate that oxidation of either org-N or org-S can lead to a high concentration of H^+ and a low pH value in such systems (Table 2).

Apparent Acid-Producing Potential

In practice, actual APP is more important than the theoretically calculated values: how many hydrogen ions actually will be produced after overcoming buffering of the systems, and how
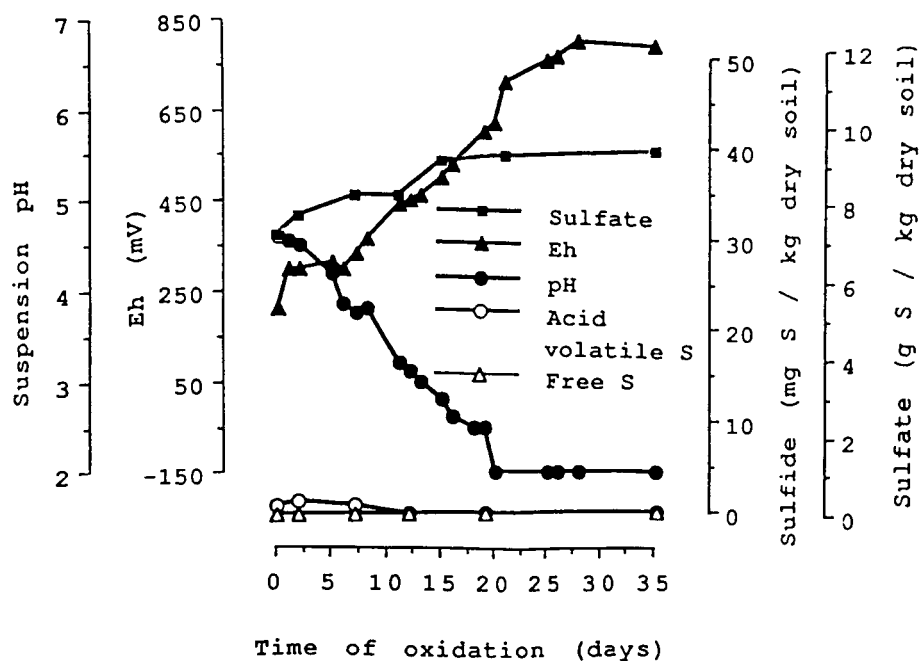
Figure 1. Changes in Eh, pH, sulfide, and sulfate concentrations in soil suspensions following continuous incubation for 35 days under aerobic conditions. (From Charoenchamratcheep, C., Smith, C.J., Stawathananont, S., and Patrick, W.H., Jr., *Soil Sci. Soc. Am. J.*, 51, 630, 1987. With permission.)

much is the pH value actually decreased during the oxidation under certain conditions? This leads to the development of the concept of "apparent APP." An acidification efficiency (β) related to the apparent APP has been developed:

$$\beta = H(a)/H(c) \tag{11}$$

with $\beta \leq 1$

where H(a) and H(c) are the amount or concentration of H^+ produced at given (a) and calculated (c) conditions, according to the reactions and the components of the sample, respectively.

Decreases in pH during oxidation have been found by many researchers.[4-7] Calmano et al.[6] observed the continuous decrease after pumping air in a poorly buffered sediment/water system. Charoenchamratcheep et al.[4] studied the changes in pH during oxidation and reduction in a soil/water suspension system. The decrease in pH was accompanied by an increase of SO_4^{2-} concentration in the solution. The pH values of all suspensions studied decreased below 4 (Figure 1). We have observed pH values of about 3 in a sediment/water experimental device after undergoing periodical redox processes.

BUFFERING PROCESSES DURING OXIDATION IN SEDIMENT/WATER SYSTEMS

When reducing species are oxidized, strong acidity may be produced (Table 2). However, buffering substances (or alkalinity)[21,24] also exist in most solid/water systems. In the buffering process the system restrains the pH change while H^+ is produced (input) or consumed. Many reactions participate in the buffering process (Figure 2 and Table 3).
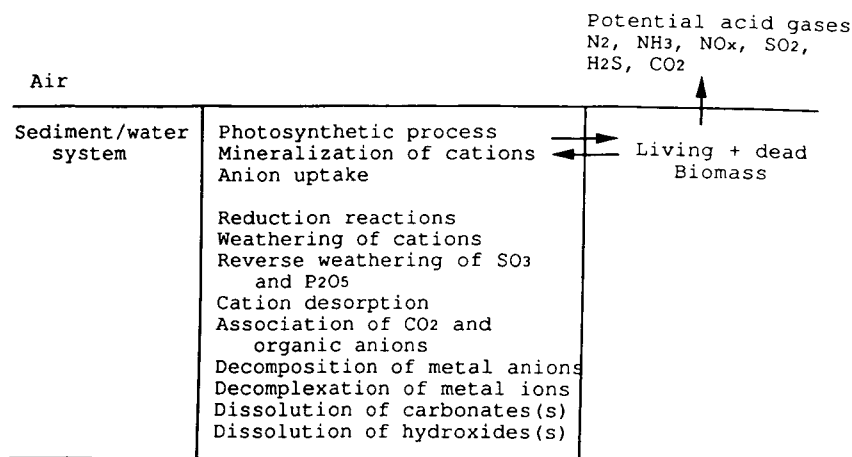
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                                                    Potential acid gases
                                                    N2, NH3, NOx, SO2,
                                                    H2S, CO2
               Air                                          ↑
          ─────────────────────────────────────────────────┼──────────
          Sediment/water │ Photosynthetic process ──────┐
             system      │ Mineralization of cations ◄───┤── Living + dead
                         │ Anion uptake                  └──   Biomass
                         │
                         │ Reduction reactions
                         │ Weathering of cations
                         │ Reverse weathering of SO3
                         │     and P2O5
                         │ Cation desorption
                         │ Association of CO2 and
                         │     organic anions
                         │ Decomposition of metal anions
                         │ Decomplexation of metal ions
                         │ Dissolution of carbonates(s)
                         │ Dissolution of hydroxides(s)
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Figure 2. Conceptual model of H^+ consumption. (Modified from Driscoll, C.T. and Likens, G.E., *Tellus*, 34, 283, 1982.)

Table 3. Proton Consuming Processes in Terrestrial and Aquatic Ecosystems

Mineralization of cations: (EQ. #)

$$(R\text{—}O)_n M(org) + n \ H^+(aq) \rightarrow M^{n+}(aq) + n \ R\text{—}OH(org) \qquad (12)$$

Assimilation of anions:

$$n \ R\text{—}OH + A^{n-}(aq) + n \ H^+(aq) \rightarrow n \ H_2O + R_n\text{—}A(org) \qquad (13)$$

Protonation of anions:

$$A^{n-}(aq) + n \ H^+(aq) \rightarrow H_n A(aq) \qquad (14)$$

Reductions:

$$OX^{n-}(aq, s, g) + r \ H^+(aq) \rightarrow Red(aq, s, g) + m \ O_2 + n \ H_2O \qquad (15)$$

Weathering of metal oxide components:

$$1/2 \ n \ M_{2/n}O(s) + n \ H^+(aq) \rightarrow M^{n+}(aq) + 1/2 \ n \ H_2O \qquad (16)$$

Reverse weathering of anions:

$$NO_{(2m+n)}^{2m-}(aq) + 2 \ m \ H^+(aq) \rightarrow NO_{(m+n)} \ (s) + m \ H_2O \qquad (17\text{–}1)$$

Dissolution of carbonate minerals:

$$M_n CO_3 + 2 \ H^+ \rightarrow CO_2 + H_2O + n \ M^{2/n} \qquad (17\text{–}2)$$

Note: Quantitatively important cations (M^{n+}) include Ca^{2+}, Mg^{2+}, Na^+, K^+ (eq. 12, 16), NH_4^+ (eq. 12) and Al^{3+} (eq. 16). Important anions (A^{n-}) are $H_2PO_4^-$ (eq. 13, 17–1), NO_3^- (eq. 13) and SO_4^{2-} (eq. 13, 17–1). Mineralization and assimilation of SO_4^{2-} and NO_3^- involves oxidation and reduction processes but the net reactions are equivalent to eq. 13. Important reduction (red)-oxidation (OX)couples in gas/water/sediment (soil) systems include NH_4^+/ NO_3^-, N_2/NO_3^-, H_2S/SO_4^{2-}, and Fe^{2+}/Fe_2O_3. Reduction/oxidation reactions (15) have been coupled to the O_2-H_2O system. In fact, organic matter (CH_2O) is usually the electron donor in reduction reactions (14); CH_2O oxidation is implicitly expressed in this reaction because organic matter is oxidized during aerobic respiration ($O_2 + CH_2O \leftrightarrow H_2O + CO_2$). Cation and anion exchange reactions can be represented by reactions (16) and (17–1).
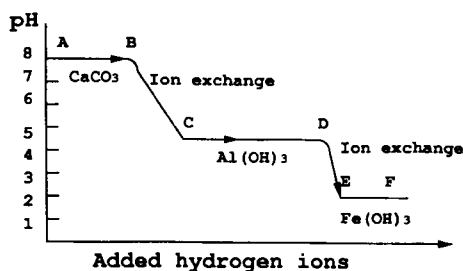
Figure 3. Acid buffering processes in sediments. (From Prenzel, J., *Z. D. Geol. Ges.*, 136, 293, 1985. With permission.)

Acidification/buffering interactions often have been investigated by adding strong acid into a sediment (or soil)/water system. A typical curve is given in Figure 3.[46] The curve combines two factors: the horizontal axis usually refers to the "capacity" factor, which shows the amount of strong acid added, whereas the vertical axis indicates the "intensity" factor (e.g., the pH or the degree of base saturation of the exchange complex).

Figure 3 summarizes many important aspects of acidification in a sediment/water system. Protons initially added to the system will associate with $CaCO_3$, resulting in mineral dissolution. As long as $CaCO_3$ is present, added protons will be consumed by the dissolution reaction and the pH of the system will remain constant (A → B in Figure 3). When the $CaCO_3$ is depleted by addition of protons, the system pH will decrease until the added protons associate with the next available proton energy level (B → C).

Between B and C the exchangeable bases on the exchange sites of clay are displaced by hydrogen ions. In this stage, sorbed metal ions will be released into the water phase. Ultimately, this process leads to the dissolution of clay minerals, which also results in buffering (C → D). Due to the abundance of Al in clay minerals, the buffering capacity in this process is high. When the reservoir of clay minerals is exhausted, further addition of protons results in an increase in dissolved [H^+] and decrease in solution pH, respectively (D → E). The dissolution of ferric oxide or hydroxide will consume hydrogen ions and resist the pH decrease (E → F).[47] More acidic phenomena are rarely observed in natural environments.

Buffering Factors

For long-term effects, Binkley et al.[36] indicated that there are only four major processes consuming H^+ in ecosystems. They include:

1. Release of basic cations by decomposition of organic matter;
2. Specific anion adsorption;
3. Mineral weathering; and
4. Unbalanced reduction of oxidized compounds.

The release of basic cations from oxidized organic matter produces alkalinity in sediments, thus neutralizing the production of acidity. In sediments, SO_4^{2-} and PO_4^{3-} may be specifically adsorbed (enter into the hydration sphere) by aluminum and iron sesquioxides.[48] This adsorption transfers alkalinity associated with SO_4^{2-} to the water solution by consumption of 2 H^+. Of course, the acidity is actually retained in the sediment or soil at the sesquioxide surface, and subsequent desorption would restore the alkalinity to the SO_4^{2-} and the acidity to the solution. Because the oxidation of pyrite in sediments can produce SO_4^{2-}, this species becomes an important component in the sediment/water system. This problem will be discussed in greater detail later in this paper relative to its effects on the change in APP.

The weathering of minerals can consume or release H^+, but in most situations H^+ consumption predominates. For example, the weathering of aluminosilicate minerals consumes 1 mol of

H^+ per mole of charge of cation released. The aluminum released is considered to be an acidic cation because it behaves as an acid by H^+ donoring. As pH decreases, aluminum consumes H^- and acts as a base. However, as the pH increases aluminum hydrolyzes, releasing H^+ to the solution and behaving as an acid. Similarly, Fe^{3+} will form different complex compounds consuming or releasing H^+.[49]

To date, the consumption of H^+ by photosynthetic processes has usually been neglected.[10,24] However, photosynthetic processes can consume significant amounts of hydrogen ions[24] (the reverse of Equation 3). The same net effect of acidity consumption occurs if nitrate is used as terminal electron acceptor (denitrification or dissimilatory nitrate reduction).[38]

Acid Neutralizing Capacity (ANC) of Sediment/Water Systems

The amount of H^+ required to reduce the pH in a system to a reference pH value is denoted ANC.[27] For example, a sediment with high carbonate content has higher ANC than one with low carbonate content. The ANC of a sediment/water or soil/water system consists of contributions by the solid phase ANC(s) and the aqueous phase ANC(aq):[10]

$$ANC = ANC(s) + ANC(aq) \tag{18}$$

In aqueous solutions, ANC(aq) is defined as the base equivalence less the strong acid equivalence of the system, and is determined by strong acid titration to a reference pH. In most natural environments, ANC(aq) is mainly attributed to the bicarbonate concentration. However, at extreme pH or in the presence of additional weak bases such as natural organic anions (A^-), other species may contribute to ANC(aq):[27]

$$ANC(aq) = [HCO_3^-] + 2\,[CO_3^{2-}] + [OH^-] + [A^-] - [H^+] \tag{19}$$

Other researchers[22] have indicated that most common species contributing to ANC in freshwater are

$$ANC(aq) = [HCO_3^-] + 2\,[CO_3^{2-}] + 2\,[S^{2-}] + [HS^-] + [NH_3] - [H^+] \tag{20}$$

Silicates, borates, phosphates, and organic bases may also contribute to ANC, but usually only to a very small degree. Breemen[10] indicated that in natural waters ANC(aq) is quantitatively negligible compared to ANC(s).

The ANC of most sediments or soils is associated with silicate minerals, which have very slow dissolution kinetics. In practice, the best way to estimate the ANC(s) is by determination of component composition:[10]

$$\begin{aligned} ANC(s) = {}& 6\,[Al_2O_3] + 2\,[CaO] + 2\,[MgO] + 2\,[Na_2O] + 2\,[K_2O] \\ & + 4\,[MnO_2] + 2\,[MnO] + 6\,[Fe_2O_3] \\ & + 2\,[FeO] - 2\,[SO_4^{2-}] - 2\,[P_2O_5] - [HCl] \end{aligned} \tag{21}$$

Above pH 5, the dissolution of Fe_2O_3, Al_2O_3 and MnO_2 is negligible. At a reference pH of 3, Al_2O_3 must be included as a basic component because of the appreciable solubility of aluminum at low pH.[10] Under extremely low pH conditions, e.g., in acid leaching procedures for contaminated sediments, significant dissolution of ferric iron and manganese(IV) will occur.

Acidification sensitivity is strongly associated with ANC. In fact, it is an index to overcome the acid buffering of the sediment/water system. Acidification sensitivity expresses the degree of pH change after H^+ are produced in the system or put into the system.

Four parameters have been defined as important in estimating soil or sediment sensitivity to acid water:

1. The total buffer capacity or cation exchange capacity (CEC), provided primarily by the clay minerals and organic matter;
2. The base saturation of that exchange capacity, which can be estimated by the pH of the sediment;
3. Anthropogenic influence; and
4. The presence or absence of carbonates in the sample.[50]

Experimental Determination of Buffer Capacity

Sobek et al.[43] studied the neutralization potential of mine tailings. Neutralization potential was obtained by adding a known amount of HCl, heating the sample, and titrating with standardized NaOH to pH 7. The method of Bruynesteyn and Hackl,[15] the so-called "determination of acid-consuming ability", is obtained by titration with standardized sulfuric acid to pH 3.5.

Calmano[51] has suggested a simple procedure to test the buffer intensity of a sludge: 10% sludge suspensions in distilled water (pH_o) and in 0.1 N acid (pH_x) are shaken for 1 h and the difference for the obtained pH values is calculated:

$$pH_{diff} = pH_o - pH_x \qquad (22)$$

Three categories of values can be established, ranging from $pH_{diff} < 2$ (strongly buffered), $pH_{diff} = 2$ to 4 (intermediate), to $pH_{diff} > 4$ (poorly buffered). These criteria should be used to decide if a dredged mud has to be stabilized for deposition, e.g., by addition of lime or limestone. It is also helpful to use this method for the judgement of the acidification or acidification sensitivity analysis of a sediment/water system.

EFFECTS OF PERIODIC REDOX PROCESSES ON ACID-PRODUCING POTENTIALS

Periodic redox processes can cause an increase or decrease in APP or pH in a sediment/water system. In a *closed* system, periodical redox processes can lead to the change or transfer between APP(s) and APP(aq), but the total APP of the system does not change. Conversely, in an *open* system, the total APP of the system will change, depending on the properties of the system and the reaction processes. Some processes are irreversible, e.g., when the components producing or consuming H^+ leave the system and cause the change in APP(s), APP(aq), and permanent ANC or BNC (base neutralizing capacity).

Change in APP By "Ferrolysis" in Periodical Redox Processes

Ferrolysis ("dissolution by iron") in redox processes was proposed by Brinkman.[52] When a system becomes reduced, part of the Fe^{2+} formed becomes exchangeable and displaces other cations, such as Ca^{2+} and Mg^{2+}. The displaced cations, together with the anions that appear simultaneously with dissolved Fe^{2+} (mainly HCO_3^- and organic anions), can be removed by percolation or by diffusion into the surface water followed by lateral flow. If the supply of cations by flood water, ground water, or mineral weathering is negligible, the surface complex may eventually become depleted of bases. The depletion is not immediately apparent in the reduced stage when the pH is high. During aeration of the system, however, exchangeable Fe^{2+} is oxidized to essentially insoluble Fe^{3+} oxide, and H^+ takes the place of adsorbed Fe^{2+} to such an extent that formerly adsorbed base cations are leached.[53]

In ferrolysis, exchangeable ferrous iron takes the place of ferrous sulfide as the immobile potentially acid substance formed during reduction, while exchangeable H^+ is the acidic product formed after oxidation of exchangeable ferrous iron. Breemen[10] suggested that ferrolysis is typical for the sediments or soils of older river or marine terraces in monsoon climates, which have a
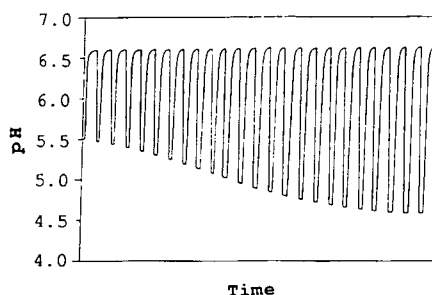
Figure 4. Temporal variation in pH by ferrolysis in periodical redox processes. (From Breemen, van, N., *Neth. J. Agric. Sci.*, 35, 271, 1987. With permission.)

seasonally alternate water table caused by submergence with rain water. In those conditions, hydrology favors either lateral or vertical drainage and, hence, removal of bases liberated from the exchange sites by ferrous iron. Over a number of redox cycles, the permanent decrease in ANC(s) is reflected by a decline in the pH of the aerobic system (Figure 4).[10]

Change in APP By the "Split" of Sulfate

Permanent acidification in alternating aerobic and anaerobic systems can occur in two stages.[27] The first stage is characterized by the reduction of SO_4^{2-}, particularly in tidal flats or sea bottom sediments. Most of the sulfide formed is fixed in the sediment as FeS or FeS_2. It leads to the increase in APP(s), while ANC(aq) (HCO_3^-) formed during sulfate reduction is removed by tidal turbulence or by diffusion into the overlying water. As a result, mobile ANC(aq) (HCO_3^-) and immobile potential acidity (FeS_2) are separated or "split". The increase in APP(s) leads to a permanent decrease in the ANC(aq) after the next aeration and oxidation cycle, and results in extreme acidification of the system.

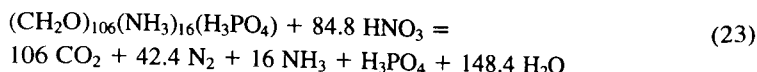### Change in APP By Fe³⁺ Reduction and Some Displacement Reactions

The alkalinization by Fe^{3+} reduction and the desorption or displacement of SO_4^{2-} from solid surfaces has been reported.[27] The $FeSO_4$ concentration gradient caused by these processes promotes further transport of $FeSO_4$ to the sediment or soil surface. These processes will lead to a decrease in ANC(aq) and a permanent increase in ANC(s) by the adsorption of OH^- displacing SO_4^{2-}.

Change in APP By Volatilization of H₂S

A sediment/water system containing sulfate becomes alkaline after volatilization of H_2S from periodic sulfate reduction and retention of $M(HCO_3)_2$ in a saline alkaline lake or marsh. If the system reoxidizes, it will only reacidify partly, i.e., to the extent that reducing sulfur has been retained in the system (e.g., as FeS) and is available for the formation of H_2SO_4. A similar process has been described by Kelly et al.[22] and Kilham[23] in lakes receiving runoff from areas affected by acid atmospheric deposition. Thus, by sulfate reduction and volatilization of H_2S, such waters (lakes) could become more alkaline.

Change in APP By Denitrification

In periodical redox processes, APP(s)(org-N) will decrease due to the decomposition of solid organic matter. If denitrification does not occur, the total APP will not change but the APP(s)(org-N) transfers into APP(aq)(NH_3). On the other hand, if denitrification takes place, both the APP(s) and total APP in the system will decrease.[10,24]

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 84.8\ HNO_3 = \qquad (23)$$
$$106\ CO_2 + 42.4\ N_2 + 16\ NH_3 + H_3PO_4 + 148.4\ H_2O$$

Because of the escape of N_2, the acidity from nitric acid before denitrification can not be reproduced by the next oxidation cycle, thus leading to a decline of APP in the system. Under certain conditions, including low pH and high NO_3^- concentrations, denitrification sometimes results in the formation of N_2O rather than N_2.[54]

EFFECTS OF REDOX AND pH VARIATIONS ON THE MOBILITY OF METALS

Typically, for systems involving solution/solid interactions, "mobility" reflects the flux of metal species in a certain medium, which contains both accelerating and inhibiting factors and processes.[55] The former influences comprise effects of pH lowering, redox changes, inorganic and organic complexation, and microbially mediated species transformations such as biomethylation. Among the spectrum of "barriers",[56] physical processes include adsorption, sedimentation, and filtration; chemical barriers comprise mechanisms such as complexation and precipitation; biological barriers are often associated with membrane processes which can limit translocation of metals (e.g., from plant roots to the shoots and fruits). "Complexation" in its various forms can both inhibit and accelerate metal flux,[55] particularly in biological systems consisting of different types of membranes.

Pore Water Chemistry Reflecting Metal/Solid Interactions

The composition of interstitial water is the most sensitive indicator of the types and the extent of reactions that take place between chemicals on sediment particles and the aqueous phase which contacts them. Particularly for fine-grained material, the large surface area related to the small volume of its entrapped interstitial water ensures that minor reactions with the solid phase will be indicated by major changes in the composition of the aqueous phase. Salomons[57] emphasized that it is important to know whether the concentrations of different components in pore waters are determined by adsorption/desorption processes or by precipitation/dissolution processes. If the latter is the case, pollutant concentrations in pore waters are somewhat independent from their respective concentrations in the solid phase.

In sediment, precipitation of sulfides is considered the dominant mechanism limiting the solubility of many trace elements.[58] Sulfide coordination is particularly strong for metals exhibiting so-called "B-character", such as Cu(I), Ag, Hg, Cd, Pb, and Zn; it also is an important mechanism for transition elements in decreasing order of the Irving-Williams series Cu(II) > Ni(II) > Co(II) > Fe(II) > Mn(II). There is strong direct[59,60] and indirect[61] evidence that the concentrations of Cu, Zn, and Cd in sulfidic pore waters are determined by precipitation/dissolution processes, whereas the concentrations of As and Cr in anoxic pore waters are probably controlled by adsorption/desorption processes.[57]

According to Davies-Colley et al.,[62] two situations can be distinguished in natural systems: the existence of a certain sulfide precipitation capacity (SPC), or (when exceeding the SPC) the accumulation of free sulfide (as H_2S or HS^-) in the aqueous phase. Concentrations of SO_4^{2-} and reducible Fe seem to be the principle factors influencing different evolutionary sequences in anoxic fresh and marine waters.[63] At excess S^{2-} concentrations (e.g., in Fe-poor environments), solubility of some metals can be increased by the formation of thio complexes. However, the stability of thio complexes is still questionable, possibly resulting in underestimates in most equilibrium models.[64]

There is some agreement that complexation by natural organic ligands is not important for most metals except Cu and Pb, due mainly to the competition by ions such as Ca^{2+}, Mg^{2+}, Fe^{2+},

Table 4.   Relative Mobilities of Elements in Solids and Sediments as a
            Function of Eh and pH

Relative mobility	Electron activity		Proton activity	
	Reducing	Oxidizing	Neutral-alkal.	Acid
Very low mobility	Al,Cr,Mo,V, U,Se,S,B,Hg, Cu,Cd,Pb	AL,Cr,Fe,Mn	Al,Cr,Hg,Cu, Ni,Co	Si
Low mobility	Si,K,P,Ni	Si,K,P,Pb	Si,K,P,Pb,Fe, Zn,Cd	K,Fe(III)
Medium mobility	Mn	Co,Ni,Hg,Cu, Zn,Cd	Mn	Al,Pb,Cu, Cr,V
High mobility	Ca,Na, Mg,Sr	Ca,Na,Mg,Sr, Mo,V,U,Se	Ca,Na,Mg,Cr	Ca,Na,Mg, Zn,Cd,Hg, Co,(Mn)
Very high mobility	Cl,I,Br	Cl,I,Br,B	Cl,I,Br,S,B Mo,V,U,Se	Cl,I,Br,B

From Plant, J.A. and Raiswell, R., *Applied Environmental Geochemistry*, Thornton, I., Ed., Academic Press, London, 1983. With permission.

and Mn^{2+}.[63-65] Even at high concentrations of organic substances (and high complexing capacity) from digested sewage sludge, only Cu and Pb seem to be slightly competitive with Ca and Mg ions.[66]

Typical curves for the adsorption of metals onto inorganic substrates, such as iron oxyhydrate, increase from almost nothing to near 100% as pH increases through a critical range of 1 to 2 units wide.[67] It is important to note that the location of the pH adsorption "edge" depends on adsorbent concentration. In the few cases where kinetics of sorption have been investigated, surface reactions were not found to be a single-step reaction.[68] Experiments performed by Benjamin and Leckie[69] showed an initial, rapid and almost complete metal uptake process perhaps lasting no more than a few minutes to hours, followed by a second, slower uptake process requiring from a few days to a few months. The first effect was thought to be true adsorption, and the second to be slow adsorbate diffusion into the solid substrate or coagulation of colloidal to filterable particles.[70]

For systems rich in organic matter, metal adsorption curves cover a wider pH range than is observed for inorganic substrates. Typically, a reduced reversibility of metal sorption has been observed in these organic systems.[71] Such effects may be important restrictions to using distribution coefficients in the assessment of metal mobility in rapidly changing environments, such as rivers, where equilibria between the solution and the solid phase often can not be achieved completely due to short residence times. In practice, applicability of distribution coefficients may find further limitations due to methodological problems. Sample pretreatment (e.g., dry or wet condition), solid/liquid separation technique (filtration or centrifugation), and grain size distribution of solid material all strongly affect K_D factors of metals.[72,73]

Redox Reactions Influencing Metal Mobility in Sediments

Regarding the potential release of metals from sediments, changes in the pH and redox conditions are of prime importance (Table 4). It can be expected that changes from reducing to oxidizing conditions, which involve transformations of sulfides and a shift to more acid conditions, increase the mobility of typical "B" or "chalcophilic" elements, such as Hg, Zn, Pb, Cu, and Cd. On the other hand, the mobility is characteristically lowered for Mn and Fe under oxidizing conditions. Elements exhibiting anionic species, such as S, As, Se, Cr, and Mo are solubilized, for example, from fly ash sluicing/ponding systems at neutral to alkaline pH conditions.[75,76]

Processes affecting metal mobilization from sulfide oxidation are highly complex. Factors involved are not only the extent of protonation, but also exchange processes involving interactions with Fe^{3+} and alkaline earths as well as the buffering effect of organic substances. Organic matter
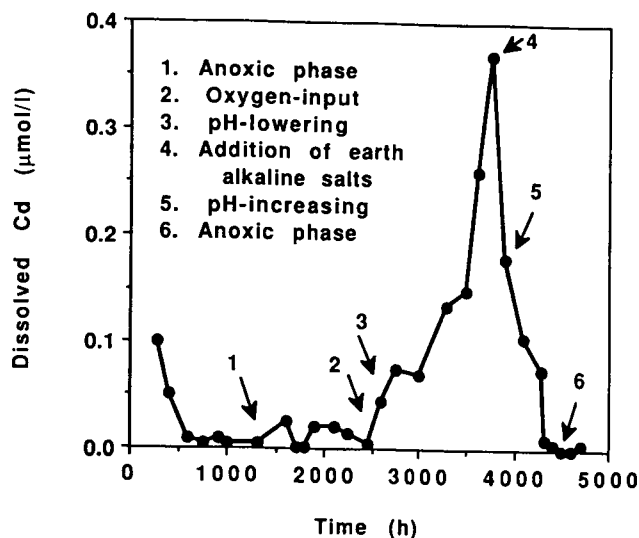
Figure 5. Experiments on cadmium release from solid waste material. (From Peiffer, S., Dissertation, Universitat Bayreuth, München, 1989. With permission.)

plays a major role as a buffer for acidity. Either acid-producing Fe^{3+} is directly taken up, or there is a permanent titration of the organic matter with H^+ from the hydroxide precipitation of $Fe(OH)_3$. This titration leads to the release of metals, and the increase in concentration of released metals should equal to the increase in SO_4^{2-} concentration. During resuspension/oxidation of harbor sediments, Eh of the system increased and concentrations of trace metals were highly correlated (r = 0.98, 0.98, 0.93, and 0.92 for Cu, Zn, Cd, and Pb, respectively).[77] These results demonstrate that metal sulfide oxidation provides an important source of metal release.

The solubility of sulfide minerals is quite low. In an estuarine environment before the sediment is suspended, sulfide ions in the anoxic environment will "titrate" heavy metal ions,[78] resulting in their removal from pore waters and precipitation as solid phase. Moreover, pyrite formed during the "titration" can adsorb or coprecipitate heavy metal ions.[79] The results from the sequential extraction for chemical forms of heavy metals indicated that the metals in sulfidic/organic fraction can reach a high percentage of the total. The percentage of this fraction for heavy metals is typically between 30 to 90%.[6,80]

Using scanning electron microscopy with energy dispersive X-ray analysis on sediments of Newark Bay, New Jersey, Luther et al.[59] detected zinc sulfide minerals. This was the first report of sulfide minerals which contain a cation, other than Fe^{2+}, as the major constituent in recent estuarine sediments. Similarly, using an electron beam microprobe, Lee and Kittrick[60] found that 89% of the Cd and 83% of the Zn were associated with S in an anoxic harbor sediment heavily contaminated with trace metals.

Iron is one of the major components of most sediments. Under an anoxic diagenetic environment, it will probably be precipitated as pyrite. Kornicker and Morse[79] reported pyrite adsorption for divalent cations of heavy metals increased in the order: $Co^{2+} < Cd^{2+} < Mn^{2+} < Ni^{2+} < Zn^{2+}$. This adsorption or coprecipitation is often observed in pyrite samples.[81] If the pyrite is subsequently oxidized, heavy metals adsorbed on the pyrite can be released to solution.

Experimental investigations by Peiffer[64] on the long-term development of organic-rich solid matter provide detailed insight into the sequence of processes taking place in the postmethanogenic stage of such deposits (Figure 5). During an initial phase, anoxic cadmium is bound to sulfides, resulting in very low metal concentrations in solution (phase 1). Aeration by addition of dissolved oxygen initiates release of cadmium from the solid substrate (phase 2); this process is enhanced

by the production of acidity, which lowers the pH from 6.7 to approximately 6.4 (phase 3). An even stronger effect is observed from the addition of alkaline earth ions (phase 4); such competitive desorption of trace metals has been widely overlooked so far, but seems to be a characteristic factor in these complex interactions. The pH increase, which may be induced from buffering components within the system, leads to a decrease in the dissolved cadmium concentration (phase 5). Formation of new sulfide ions from the degradation of organic matter brings the concentrations of dissolved cadmium back to its original, extreme low level (phase 6). The observed pH decrease seems to indicate that zinc and cadmium are being exchanged for protons, whereas lead and copper, because of their much stronger bonding to the solid substrate, are not.

Metal Mobilization from Aquatic Sediments

Release of potentially toxic metals from contaminated sediments poses problems both in aquatic systems and in subsequent land deposition of dredged materials. Effects of resuspension/oxidation on metal release have been intensively investigated.[5,6,8,77,82,83] Khalid et al.[8] and Wallmann[7] found an increase in dissolved Cu, Cd, and Pb with time during the oxidation of an anoxic estuarine sediment in seawater and freshwater. In these experiments, the pH was not controlled and it progressively decreased. Förstner et al.[84] reported 1.3% of total Cu was released from the dredged mud of Hamburg harbor when treated with seawater in a 3-week suspension experiment. Calmano et al.[85] observed that 9.1% of the total Zn in dredged mud was released during a suspension experiment when treated with seawater.

Some other examples illustrating the major factors, processes, and rates of metal mobilization in aquatic sediments follow:

- Field evidence for changing cadmium mobilities was reported by Holmes et al.[86] from Corpus Christi Bay harbor. During the summer when the harbor water was stagnant, Cd precipitated as CdS at the sediment/water interface; in the winter months, however, the increased flow of O_2-rich water into the bay resulted in a release of the precipitated metal.
- In the St. Lawrence estuary, Gendron et al.[87] found evidence for different release mechanisms near the sediment/water interface. The profiles for Co resemble those for Mn and Fe with increased concentration with depth, suggesting a mobilization of these elements in the reducing zone and a reprecipitation at the surface of the sediment profile. On the other hand, Cd appeared to be released at the surface, probably as a result of the aerobic remobilization of organically bound Cd.
- Biological activities are typically involved in these processes. Remobilization of trace metals has been explained by the removal of S^{2-} from pore waters via ventilation of the upper sediment layer with oxic overlying water by the biota, allowing the enrichment of dissolved Cd that would otherwise exhibit very low concentrations due to the formation of insoluble sulfides in reduced, H_2S-containing sediments. Emerson et al.[88] suggest a significant enhancement of metal fluxes to the bottom waters may occur by these mechanisms. As evidenced by Hines et al.,[89] biological activity in surface sediments greatly enhances remobilization of metals by the input of oxidized water; these processes are more effective during spring and summer than during the winter months.
- Prause et al.[83] studied the release of Pb and Cd from contaminated dredged material after dumping in a harbor environment. During an observation period of up to 24 h, no significant Cd or Pb release could be found from the dredged sludge used in the experiments. But during long-term experiments, extensive Cd remobilization of 1 to 2 mg/kg solids occurred.
- Cores were taken from tidal Elbe River sediments, where diurnal inundation of the fine-grained fluvial deposits takes place.[90] In the upper part of the sediment column, total particulate Cd content was approximately 10 mg/kg, whereas in the deeper anoxic zone 60 to 80% of the Cd was associated with the sulfidic/organic fraction. In the upper zone (oxic and transition) the association of Cd in the carbonatic and exchangeable fractions simultaneously increased up to 40% of total Cd. This distribution suggests that the release of metals from particulate phases into the pore water, and further transfer into biota, is controlled by the frequent downward flux of oxygenated surface water.[90]

Typical early diagenetic geochemical changes and subsequent element mobilization via pore water result from dredging activities. A study performed by Darby et al.[91] in a man-made estuarine

Table 5.   Metal Mobilization from Dredged Material after Land Deposition

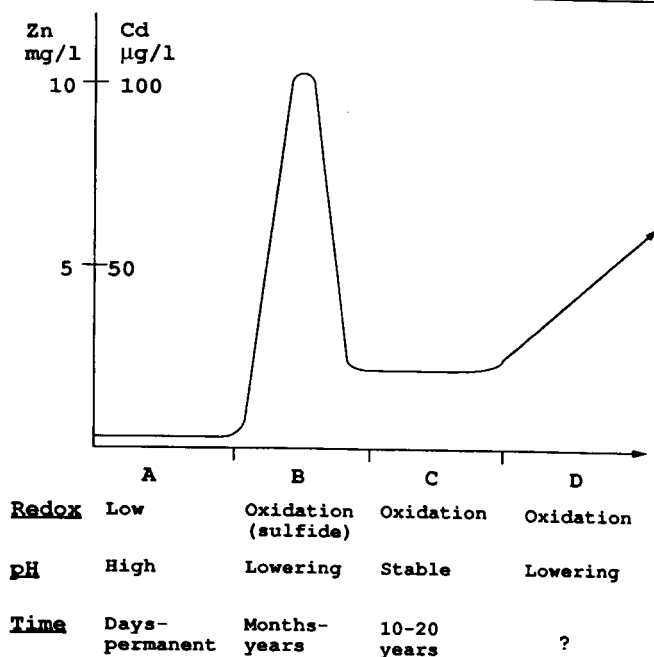|	Reducing water	Oxidizing water
NH_4^+	125 mg/l	< 3 mg/l
Fe	80 mg/L	<3 mg/L
NO_3^-	<3 mg/L	120 mg/L
Zn	<10 mg/L	5000 µg/L
Cd	<0.5 µg/L	80 µg/l

Figure 6. Schematic diagram illustrating different phases of metal release from land-disposed dredged material. (From Maass, B. and Miehlich, G., *Mitt. Dtsch. Bodenkunde Ges.*, 56, 289, 1988. With permission.)

marsh demonstrates the characteristic effects of oxidation. Compared to the river water concentration, the channel sediment pore water was enriched by a factor of 200 for Fe and Mn, 30 to 50-fold for Ni and Pb, approximately 10-fold for Cd and Hg, and 2 to 3-fold for Cu and Zn. Following hydraulic dredging, the expected concentration of metals which had been calculated based on a ratio of pore water to river water of about 1:4, were compared with the actual measurements at the pipe exiting the dredging device. Negative deviations were found for Fe and Mn, suggesting reprecipitation of Fe/Mn oxide minerals; the positive deviations of Zn (factor of 80), Cu, Pb, and Cd (factors of 7 to 8) indicate that during dumping of the sludge-water mixture significant proportions of these elements were mobilized and transferred into the effluent water.

Pore water data from dredged material from Hamburg harbor indicate typical differences in the kinetics of proton release from organic and sulfidic sources (Table 5). Recent deposits are characterized by low concentrations of NO_3^-, Cd, and Zn; when these low-buffered sediments are oxidized during a time period of a few months to years, the concentrations of NH_4^+ and Fe in the pore water typically decrease, whereas those of Cd and Zn increase. The different steps are schematically shown in Figure 6. Oxidation of sulfides during stage B strongly increases the concentrations of Cd and Zn relatively fast. When acidity is consumed by buffer reactions (phase C), Cd and Zn concentrations decrease, but are still higher than in the original sulfidic system. In phase D, oxidation of organic matter again lowers pH values and can induce a long-term mobilization of Zn and Cd.

Metal Transfer Between Inorganic and Organic Substrates

With respect to modeling metal partitioning between dissolved and particulate phases in a natural system, e.g., for estuarine sediments, the following requirements have been listed by Luoma and Davis:[94]

- Binding intensities and capacities for important sediment components,
- Relative abundance of these components,
- Assessment of the effect of particle coatings and of multicomponent aggregation on binding capacity of each substrate,
- Consideration of the effect of major competitors (Ca^{2+}, Mg^{2+}, Na^+, Cl^-),
- Evaluation of the kinetics of metal redistribution among sediment components.

It seems that thermodynamic models are still restricted because:

1. Adsorption characteristics are related not only to the system conditions (e.g., solid types, concentrations, and adsorbing species), but also to changes in the net system surface properties resulting from particle/particle interactions such as coagulation;
2. Influences of organic ligands in the aqueous phase can rarely be predicted as yet;
3. Effects of competition differ between various sorption sites; and
4. Reaction kinetics of the individual constituents cannot be evaluated in a mixture of sedimentary components.
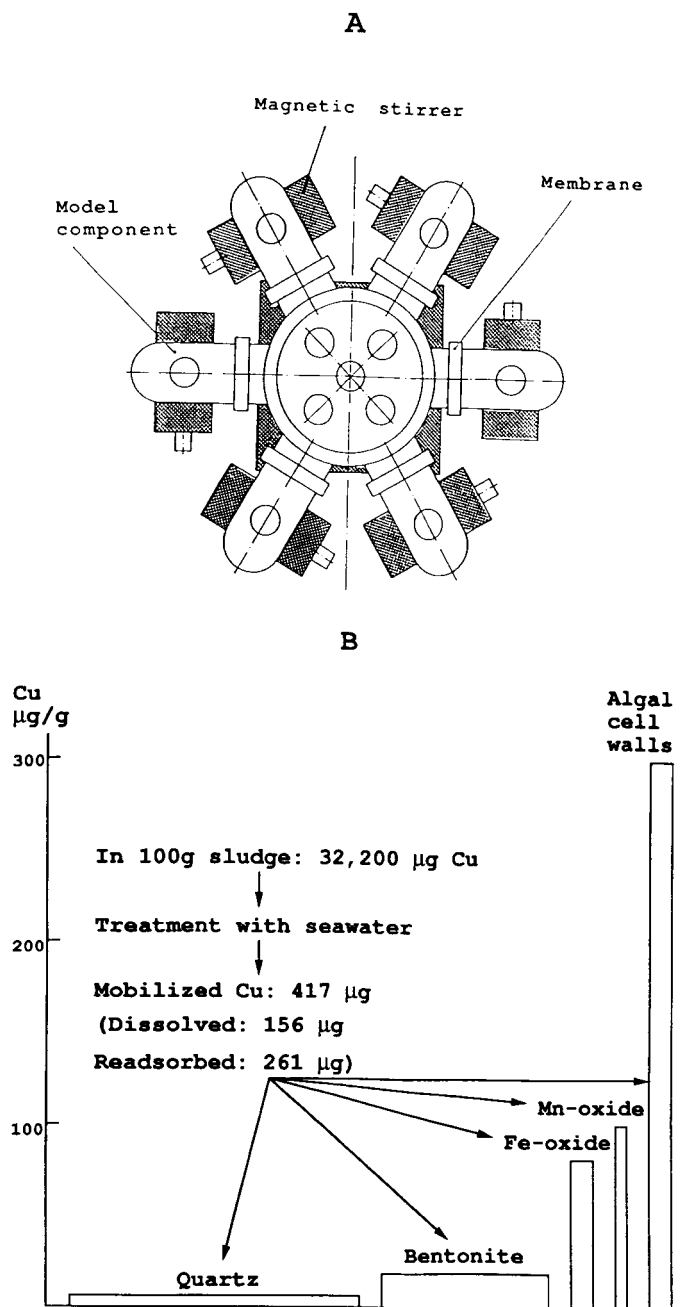
At present, experimental studies on the dissolved/solid interactions in such complex systems seem to be more useful. One approach employs a six-chamber device, where the individual components are separated by membranes which still permit phase interactions via solute transport of the elements.[85] In this way, exchange reactions and biological uptake rates can be studied for individual phases under the influence of pH, redox, ionic strength, solid and/or solute concentration, and other parameters.

This system is made of a central chamber connected with six external chambers and separated by membranes of 0.45-μm pore diameter (Figure 7). The volume of the central chamber is 6 l and each of the external chambers contains 250 ml. Either a solution or a suspension can be inserted into the central chamber; in each external chamber the individual solid components are kept in suspension by magnetic stirring. Redox, pH, and other parameters may be controlled and adjusted in each chamber. In an experimental series on the effect on salinity by disposal of anoxic dredged mud into sea water, quantities of model components were chosen in analogy to an average sediment composition; i.e., 0.5 g algal cell wall (5%), 3 g bentonite (30%), 0.2 g manganese oxide (2%), 0.5 g goethite (5%), and 5 g quartz powder (50%). In the central chamber, 100 g of anoxic mud from Hamburg harbor was inserted; salts were added corresponding to the composition of sea water. After 3 weeks, solid samples and filtered water samples were collected from each chamber and analyzed.

The effect of salinity on metal remobilization from contaminated sediments is different for the individual elements. While approximately 16 and 9% of Cd and Zn, respectively, in the dredged mud from Hamburg harbor is released; for metals such as Cu, a salinity increase seems to be less important in the transfer, both among sediment substrates and to aquatic biota. This is, however, not true, as can be demonstrated from a mass balance for the Cu in Figure 7B: only 1.3% of the inventory of Cu of the sludge sample was released when treated with seawater. Only one third stays in solution, equivalent to approximately 40 μg l^{-1}, and there is no significant difference from conditions before salt addition; two thirds of the released Cu is reabsorbed at different affinities to the model substrates. Slight enrichment of Cu is observed in the iron hydroxide (approximately 80 mg/kg) and manganese oxide (100 mg/kg), whereas the cell walls—a minor component in the model sediment—accumulated nearly 300 mg/kg of Cu.

The dominant role of organic substrates in the binding of metals such as Cd and Cu is of particular relevance for the transfer of these elements into biological systems. It can be expected

A

Magnetic stirrer

Membrane

Model
component

B

Cu
μg/g

Algal
cell
walls

300

In 100g sludge: 32,200 μg Cu

Treatment with seawater

200

Mobilized Cu: 417 μg

(Dissolved: 156 μg

Readsorbed: 261 μg)

Mn-oxide

Fe-oxide

100

Bentonite

Quartz

Figure 7. Metal transfer between sedimentary components. 7A: Schematic view of the multichamber device. 7B: Transfer of copper from anoxic harbor mud into different model substrates after treatment with artificial seawater. (From Calmano, W., Ahlf, W., and Förstner, U., *Environ. Geol. Water Sci.*, 11, 77, 1988. With permission.)

Table 6.   Some Examples from *In Situ* Studies for Prediction of Trace Metal Availability to Benthic Organisms from Sediment Characteristics

Organism	Metal	Best predictor in the sediment	Ref.
Scrobicularia plana	Pb	[Pb]/[Fe] extracted with 1 *N* HCl	98
Scrobicularia plana	As	[As]/[Fe] extracted with 1 *N* HCl	99
Scrobicularia plana and *Macoma balthica*	Hg	[Hg] extracted with HNO_3/organic content (%)	100
Anadonta grandis and *Elliptio complanata*	Cu	[Cu]/[Fe] extracted with $NH_2OH \cdot HCl$	101 102

From Tessier, A. and Campbell, P.G.C., *Hydrobiologia*, 149, 43, 1987. With permission.

that even at relatively small percentages of organic substrates, these materials are primarily involved in metabolic processes, and thus may constitute the major carriers by which metals are transferred within the food chain.

Bioavailability of Sediment-Bound Metal Species

Estimation of the remobilization of metals under changing environmental conditions and of the potential uptake by biota are two major objectives of species differentiation on particle-bound trace metals.[95] However, many authors have shown that with respect to bioavailability, as distinct from geochemical mobility, the present state of knowledge on solid matter speciation of metals is still unsatisfactory. For example, the leachable fraction does not necessarily correspond to the amount available to biota.[96] This handicap is primarily due to a lack of information about the specific mechanism by which organisms actively translocate trace-element species. In the case of plant root activities, interactions with soil and sediment components include redox changes, pH alterations, and organic complexing processes.

Studies on the prediction of the trace-metal levels in benthic organisms have shown that the prognostic value of extraction data is improved when the trace-metal concentrations are normalized with respect to the Fe (hydrous oxide) and/or organic content of the sediments[97] (Table 6).

It has been inferred by Tessier and Campbell[97] that a strong dependence of trace metal accumulation upon sediment characteristics does not imply that the main route of entry of trace metals is necessarily via ingestion of particulate metals. It can be explained by a control through adsorption reactions of the dissolved trace metal concentrations in the solution to which the organisms are exposed, such as in the case of filter-feeders, where high levels of trace metals were found associated with the gills and mantle.[102] For the latter pathway, study of the intermediate water phase (e.g., pore water) and the different forms and availabilities of metals in this medium seems to be particularly promising.[103]

Recently, there have been a number of studies focused on evaluating the bioavailability to benthos of heavy metals in anoxic sediments relative to the ratio of acid volatile sulfide (AVS) to those metals.[103–106] Metal ions in pore water can displace iron from iron monosulfide to form metal sulfide:

$$Me^{2+} + FeS(s) \leftrightarrow Fe^{2+} + MeS(s). \tag{24}$$
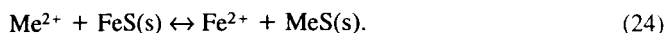
In this process, Me^{2+} forms essentially insoluble precipitates and is scavenged from the pore water of the sediment. If no other strong complexing ligand is present, the metal activity will approximate the metal in excess of the AVS. Hence, the concentration of AVS determines the boundary between low metal activity and potentially high metal activity. In the experiment carried out by Di Toro et al.,[107] if [SEM (simultaneously extracted metal concentration)]/[AVS] < 1, no acute toxicity (mortality > 50%) has been found in any sediment for any benthic test organism. The mortality of sensitive species increases in the ratio range of 1.5 to 2.5.[107]

SUMMARY

Redox processes can significantly affect the acid-producing potential and metal bioavailability in sediments. Many oxidation reactions producing acid can occur in natural aquatic sediment systems and human-affected environments. S, Fe, and N are the most important elements involved in redox processes of sediment/water systems. A calculation method developed in this paper can be used to assess APP in such systems. The actual extent of acidification in a sediment/water system depends not only on APP, but also on the acid neutralizing capacity (ANC) of the system.

Periodic redox processes leading to "ferrolysis", "split" of sulfate, and the volatilization of H_2S can cause changes in APP, and then affect metal transformation and bioavailability. The effects of redox and pH variations on the mobility of metals has been successfully assessed by pore water chemistry, which reflects the interactions of metals in aqueous and solid systems under changing redox environments with depth of sediments. Redox reactions, especially reoxidation of anoxic sediments, can lead to metal release from contaminated sediments. The bioavailability of metals in sediments depends on metal species, especially metal sulfide species.

A lack of understanding of the kinetic processes controlling acid production and about the accurate determination of ANC quantitatively limits our ability to predict apparent APP. Heavy metal mobility following oxidation of anoxic sediments has been observed. Although acid volatile sulfide (AVS) may control the toxicity of heavy metals in anoxic sediments, under changing redox conditions AVS is oxidized and dissolved metal sulfates are released. Furthermore, the acidity which follows sulfide oxidation may accelerate metal release. Thus, assessment of the relationship between metal sulfides and their bioavailability in periodic redox environments needs much more research.

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