

Effects of redox processes on soil acidity

N. van Breemen

Department of Soil Science and Geology, Wageningen Agricultural University,
P.O. Box 37, NL 6700 AA Wageningen, Netherlands

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Summary

Redox processes due to alternating aerobic and anaerobic conditions may give rise to strongly acidic or alkaline soils and waters. First, oxidized chemical components tend to be more acidic or less alkaline than their reduced counterparts. Second, and more important, redox processes often lead to the simultaneous formation of acidic (or potentially acidic) and alkaline substances with different mobility (dissolved or gaseous versus adsorbed or solid), so that one of the two substances can be exported, leaving a more acidic or more alkaline residue. Examples of acidification or alkalinization processes in wetlands based on these principles are: (1) formation of acid sulfate soils (transformation of seawater sulfate and sedimentary iron to immobile potential acidity (FeS_2) and mobile alkalinity (HCO_3^-), followed by oxidation of FeS_2 after the alkalinity has disappeared), (2) alkalinization of periodically flooded acid sulfate soils (formation of dissolved ferrous sulfate during reduction, and oxidation of the ferrous sulfate to ferric oxide and sulfuric acid at the soil surface, followed by drainage of the acid floodwater), (3) ferrollysis (immobilization of seasonally reduced ferric iron as exchangeable Fe^{2+} , and removal of replaced bases by drainage, followed by oxidation of Fe^{2+} -clay to H^+ -clay), and (4) soil alkalinization in closed depressions (reduction of sodium sulfate to sodium (hydrogen) carbonate and volatile H_2S).

Introduction

Oxidation and reduction processes in periodically drained wetlands and at boundaries of oxidized and reduced zones in sediments and waters may have important effects on pH, alkalinity and acidity (Ponnamperuma, 1972). Dramatic cases of soil acidification or alkalinization due to redox processes in wetlands include acid sulfate soils (van Breemen, 1976), formation of sodium carbonate in submerged saline soils (Janitsky & Whittig, 1964), and the process of ferrollysis (Brinkman, 1979). The aim of this paper is to outline the principles involved in soil acidification or al-

kalinization under the influence of redox processes, applying a recently developed general approach to describe soil acidification/alkalinization (van Breemen et al., 1983; van Breemen, 1987b).

Acidification and alkalinization of soils can be characterized by capacity and intensity factors. A titration curve combines these two factors: the horizontal axis usually refers to the capacity factor and may show the amount of strong acid added, while the vertical axis shows the intensity factor, e.g. the pH or the degree of base saturation of the exchange complex. Hypothetical titration curves of a calcareous clay soil to which strong acid is added slowly or quickly are shown in Fig. 1. The curves illustrate that the value of the intensity factor does not change in a simple manner with the amount of H^+ added, due to stronger buffering in certain pH ranges: buffering by $CaCO_3$ around pH 7, and by exchangeable bases between pH 5 and 4. Furthermore, Fig. 1 shows that quick addition of strong acid depresses the pH more strongly than slow addition. This kinetic effect is due to the fact that relatively slow buffer reactions, e.g. the dissolution (weathering) of silicate minerals, can consume more H^+ upon slow than upon quick addition of strong acid. Because pH cannot be predicted in a simple manner from the amount of acid (or base) added, it is not a convenient parameter for defining soil acidification. Here we will express soil acidification or alkalinization in terms of capacity factors: the amounts of strong acid or strong base added, or the changes in the acid- or base-neutralizing capacity (ANC or BNC) of a soil system. This choice is not only a matter of convenience: changes in the components making up the ANC of the soil often directly reflect the processes responsible for changing ANC. To translate ΔANC into changes in the ecologically more relevant intensive parameters such as soil pH and base saturation, one needs realistic, kinetically relevant titration curves.

The ANC of mineral soil material, $ANC_{(s)}$, is made up of contributions by the solid phase, $ANC_{(s)}$, and the aqueous phase, $ANC_{(aq)}$:

$$ANC_{(s)} = ANC_{(s)} + ANC_{(aq)} \tag{1}$$

Although, due to the very wide mass ratio of solid to dissolved components in soils, $ANC_{(aq)}$ is quantitatively negligible compared to $ANC_{(s)}$, the distinction between the two is useful when describing soil acidification or alkalinization. $ANC_{(s)}$ is equal

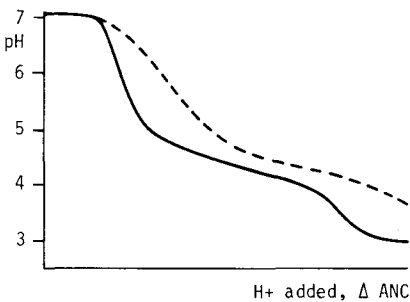


Fig. 1. Hypothetical titration curve of a calcareous clay soil upon slow (broken line) or quick (solid line) acidification.

to the quantities of basic solid components minus those of acidic components. What is 'acidic' or 'basic' depends on the reference pH chosen. When titrating a soil down to pH 5, CaO, MgO, K₂O, Na₂O, FeO and NH₃ are basic components: they may accept protons, for example, according to the reaction:



SO₃, P₂O₅ and HCl, on the other hand, are acidic:



At a reference pH of 3, Al₂O₃ must be included as a basic component, because of the appreciable solubility of aluminium at low pH:



Most other components in soils are either too weakly acidic (SiO₂, CO₂, H₂O, H₂S) or too weakly alkaline (Fe₂O₃) to release or accept protons at the reference pH values of 3 or 5. So,

$$\text{ANC}_{(s,pH5)} = 2[\text{CaO}] + 2[\text{MgO}] + 2[\text{K}_2\text{O}] + 2[\text{Na}_2\text{O}] + 2[\text{FeO}] + [\text{NH}_3] - 2[\text{SO}_3] - 2[\text{P}_2\text{O}_5] - [\text{HCl}] - 2[\text{N}_2\text{O}_5] \quad (5)$$

with brackets denoting molar quantities. The components in Eq. 5 may be present in crystalline, amorphous or sorbed form. Disregarding trace elements, all quantitatively important mineral substances in soils can be considered to consist of the components listed so far, added in various molar proportions. Nitrate-N (N₂O₅) is highly soluble and can be neglected as a solid component in all but the most arid soils.

Aqueous acid neutralizing capacity, ANC_(aq,pH5) could be written in terms of the components of Eq. 5 but is usually ascribed to alkalinity due to carbonate plus organic (A⁻) anions, minus free mineral acidity:

$$\text{ANC}_{(aq,pH5)} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] + [\text{A}^-] - [\text{H}^+] \quad (6)$$

In summary, soil acidification and soil alkalization can be defined in terms of addition or removal of the components of Eq. 5, as follows:

$$\text{soil acidification} = -(\text{soil alkalization}) = -\Delta\text{ANC}_{(s,pH5)}$$

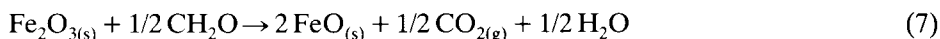
Changes in ANC_(s) resulting from transfer of solid matter, for instance by erosion and sedimentation, will not be considered here, and I will deal only with changes in ANC_(s) resulting from processes (including addition or removal of dissolved substances) in a given bulk of solids and solutes that makes up a soil. Practically all such acidification and alkalization processes can be seen as consequences of (1) addi-

tion of dissolved strong acids and bases, (2) soil internal production of various acids, (3) the effects of assimilation by biota, and (4) reduction-oxidation processes. Here, attention will be paid only to the effect of redox processes. Examples of the effects of other processes on $ANC_{(s)}$ have been described elsewhere (van Breemen et al., 1983; van Breemen, 1987b).

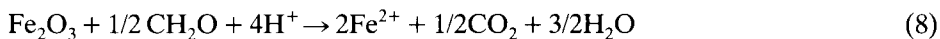
Effect of redox on $ANC_{(s)}$ and pH in soil systems closed for exchange of solutes and gases

A well-known effect of waterlogging of soils is that the pH of acidic soils increases, and that the pH of alkaline soils decreases, while the pH generally stabilizes at values between approximately 6 and 7 after several weeks or months of flooding (Ponnamperuma, 1972). The increase in pH of initially acidic soils is a consequence of chemical reduction of acidic (N_2O_5 , SO_3) or 'inert' (Fe_2O_3) components to their reduced basic (NH_3 , FeO) or weakly acidic (H_2S) counterparts under the influence of organic matter. Inspection of Eq. 5 shows that chemical reduction of each of the three oxidized components causes $ANC_{(s)}$ to increase.

In most reduced soils the transformation of iron is quantitatively most important, and this process will be described in some detail. If an aerobic soil containing metabolizable organic matter is submerged, the rate of oxygen consumption by microorganisms normally exceeds the rate of supply of O_2 from the atmosphere. Generally, O_2 concentrations drop to very low levels within a few days, and ferric oxide (e.g. goethite (α $FeOOH$) or ferrihydrite ($Fe_2O_3 \cdot H_2O$)) takes over the role of O_2 as electron acceptor in the oxidation of organic matter (CH_2O):



The bulk of the reduced iron is solid or adsorbed, but up to a few percent of it appears in solution as Fe^{2+} , normally accompanied by hydrogen carbonate or organic anions. Formation of ionic Fe^{2+} involves consumption of H^+ :



which directly explains the increase in pH. Proton donors may be adsorbed aluminium (causing a forced exchange of Fe^{2+} for Al^{3+} , which is precipitated as aluminium hydroxyde; cf. Cate & Sukhai, 1964) or CO_2 or organic acids (causing the appearance of hydrogen carbonate and organic anions along with Fe^{2+} ; cf. van Breemen, 1987a). The pH normally stabilizes at between 6 and 7, at a value which can be explained by equilibria involving ferrous hydroxide (or ferrous carbonate), ferric oxide, dissolved ferrous iron and CO_2 . If the initial (aerobic) soil pH exceeds 7, the solubility of FeO -containing phases is too low to produce appreciable ionic Fe^{2+} , and the pH-depressing effect of CO_2 produced generally exceeds the pH-increasing effect of the reduction of iron. The result is a decrease in pH (in spite of an increase in $ANC_{(s)}$!).

When a waterlogged soil dries out so that air can penetrate, FeO is oxidized

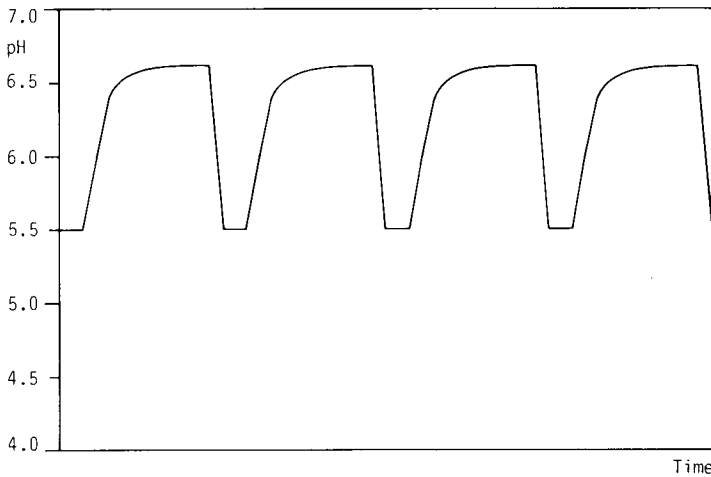


Fig. 2. Temporal variation in pH in seasonally flooded soils; each cycle refers to one year (hypothetical).

quickly to Fe_2O_3 , causing the pH to revert to the previous (aerobic) value. Seasonal cycling of oxidized and reduced conditions thus causes a fluctuation of $\text{ANC}_{(s)}$ and pH as shown in Fig. 2. So $\text{ANC}_{(s)}$ and pH switch back and forth seasonally, with the oxidation of organic matter as the only net change taking place. Clearly, to keep the cycle going, fresh organic matter must be supplied regularly.

Effect of redox on $\text{ANC}_{(s)}$ and pH in soil systems open for exchange of solutes and gases

As will be shown below, redox processes often lead to the formation of pairs of acidic (or potentially acid) and basic components of widely different mobility. If the soil system is open for removal of the most mobile components by leaching or volatilization, at least part of the change in $\text{ANC}_{(s)}$ due to the redox reaction will be permanent. Examples of such permanent changes in ANC are (1) the formation of acid sulfate soils, (2) alkalization of periodically flooded surface horizons of acid sulfate soils, (3) the process of ferrollysis, and (4) alkalization by volatilization of H_2S or gaseous N from reduced soils. Each of these will be described in some detail below.

Acid sulfate soils

Formation of acid sulfate soils (Kittrick et al., 1982) is preceded by a reduced stage (generally in tidal marshes). In this stage ferrous sulfide (or pyrite) is formed by reduction of sulfate from seawater and sedimentary iron, while dissolved hydrogen carbonate (plus the cation that was associated with the sulfate, M in Fig. 3) are removed by diffusion or by convection due to tidal action. $\text{ANC}_{(s)}$ increases due to the $\text{Fe}_2\text{O}_3 \rightarrow \text{FeO}$ transformations, as was described previously. More important,

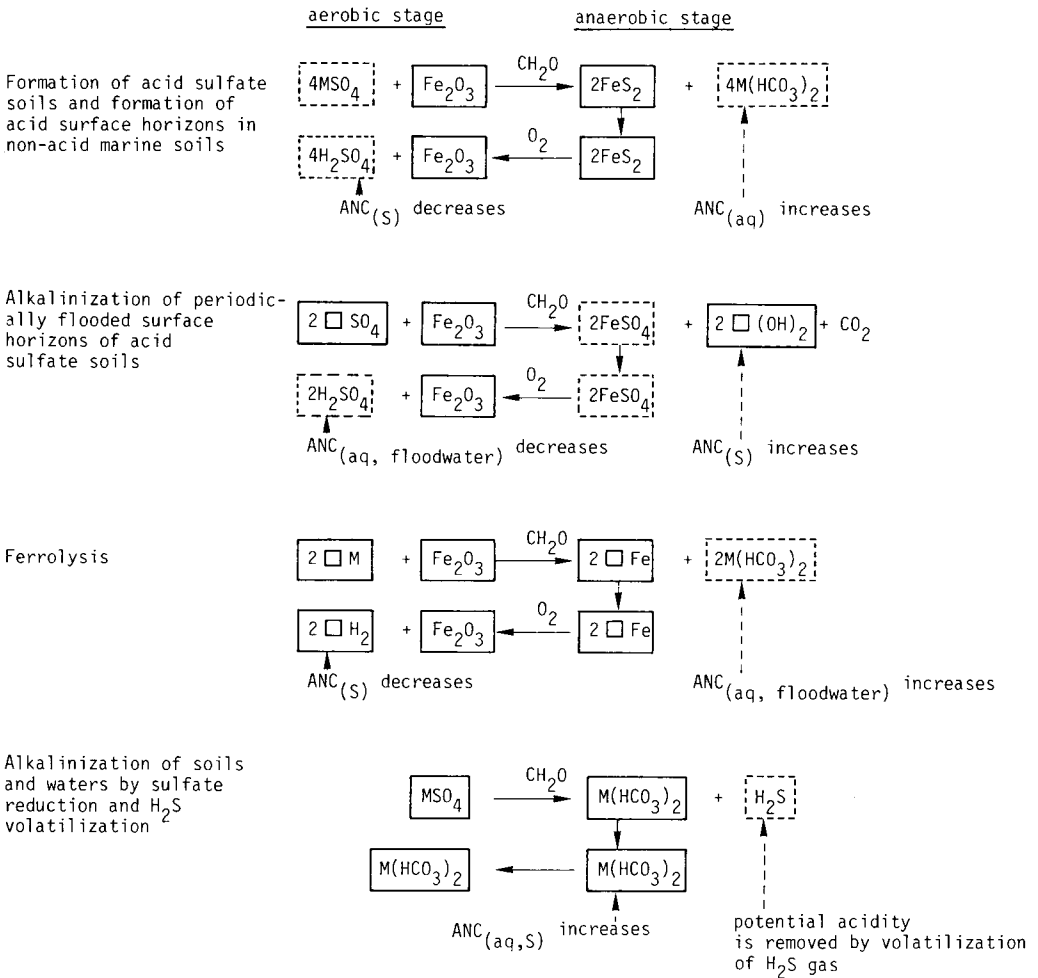


Fig. 3. Diagram illustrating the chemical changes in alternating aerobic (left) and anaerobic (right) soils. Components in solid rectangles are immobile, components in broken-line rectangles are mobile. Small squares denote exchange sites. M stands for a divalent cation (Ca²⁺ or Mg²⁺), and CH₂O refers to oxidizable organic matter.

however, is that sulfate (MSO₄) from seawater is 'split' into mobile alkalinity (M(HCO₃)₂) and immobile potential acidity (FeS₂) that stays behind in the sediment. Over several years to decades, appreciable amounts of sulfide can be accumulated in tidal sediments.

Upon drainage of such marshes, oxidation of iron sulfide leads to strong acidification by formation of H₂SO₄. As a result, ANC_(S) decreases by a combination of base cation leaching by sulfuric acid, and by an increase in the SO₃ content of the soil. If, during the reduced stage, M(HCO₃)₂ were retained in the system, e.g. as precip-

itated carbonate, the acidity formed in sulfide oxidation would have been neutralized exactly by the carbonate formed, without permanent change in ANC.

A similar process involving formation of FeS, not FeS₂, in young non-acid marine clay soils (which still contain appreciable dissolved sulfate of seawater origin) may lead to a rapid acidification of seasonally flooded surface soils (van Breemen, 1975).

Alkalinization of periodically flooded surface horizons of acid sulfate soils

When acid sulfate soils are flooded and undergo reduction, ferrous sulfate, not ferrous hydrogen carbonate, appears in the soil solution (Fig. 3). This is because sulfate adsorbed on positive colloids or basic iron sulfates or aluminum sulfates (e.g. jarosite and jurbanite) serve as proton donors in the reduction of ferric iron (cf. Eq. 8). Part of the ferrous sulfate is oxidized at the interface between the soil and the surface water, producing a ferric oxide coating on the soils surface and releasing sulfuric acid in the floodwater. The ferrous sulfate concentration gradient caused by these processes promotes further transport of ferrous sulfate to the soil surface. Lateral drainage of the acid floodwater will lead to a permanent increase in ANC_(S) by removal of SO₃. This process (van Breemen, 1975) can be of practical importance, both in the amelioration of acid sulfate soils, and in (unwanted) surface water acidification (e.g. in fishponds in acid sulfate soil areas).

Ferrollysis

The soil acidification taking place in the process of ferrollysis (Brinkman, 1979) resembles that involved in the formation of acid sulfate soils. In ferrollysis, however, exchangeable ferrous iron takes the place of ferrous sulfide as the immobile, poten-

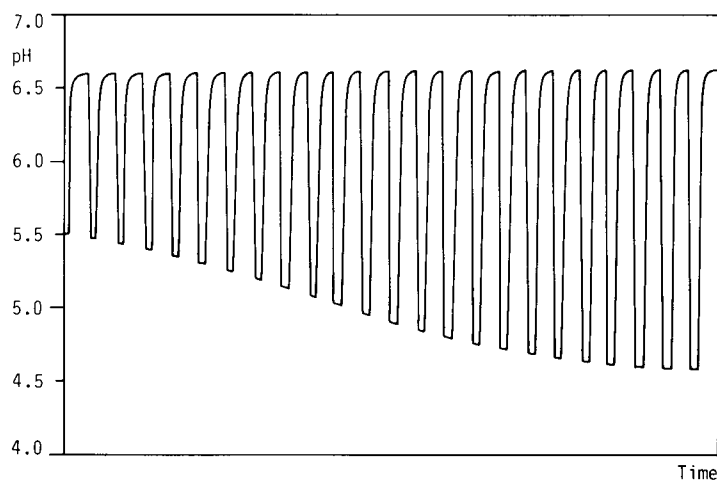


Fig. 4. Temporal variation in pH in a seasonally flooded soil undergoing ferrollysis; each cycle refers to one year (hypothetical).

tially acid substance formed during reduction, while exchangeable H^+ is the acidic product formed after oxidation of exchangeable ferrous iron (Fig. 3). Ferrolysis is typical for soils of older river- or marine terraces in monsoon climates which have a seasonal perched water-table, caused by submergence with rain water. In those conditions, hydrology favours either lateral or vertical drainage, and, hence, removal of bases liberated from the exchange complex by ferrous iron. Over a number of years, the permanent decrease in $ANC_{(S)}$ is reflected by a decrease in the pH of the aerobic, non-flooded soil (Fig. 4). Every year, however, upon flooding the pH will return to a value between 6 and 7, the equilibrium pH of the ferrous hydroxide (or ferrous carbonate)-ferric oxide- CO_2 system.

Alkalinization by volatilization of H_2S or gaseous N-species from reduced soils

Closed depressions which accumulate sulfate-containing runoff in arid to semi-arid areas may become highly alkaline after volatilization of H_2S from sulfate reduction, and retention of $M(HCO_3)_2$ in a saline-alkaline lake or marsh (Fig. 3). The difference with acid sulfate soil formation is that here the system is losing more H_2S (potential acidity) to the atmosphere, than $M(HCO_3)_2$ (actual alkalinity) by drainage. So, the effect is the reverse of that in acid sulfate soil formation, and the system undergoes a permanent alkalinization. If the system would reoxidize, it would only reacidify partly, viz to the extent that reduced sulfur has been retained in the system (e.g. as FeS) and is available for the formation of sulfuric acid. As described by Janitzky & Whittig (1964), sodium rather than a divalent cation is usually involved in this process. Eventually Na_2CO_3 may accumulate, leading to pH values well above 9.

A similar process has been described recently by Kelly et al. (1982) and Kilham (1982) in lakes receiving runoff from areas affected by acid atmospheric deposition. By sulfate reduction, denitrification and assimilation of nitrate by aquatic plants, such lakes could become more alkaline. Seen in a broader perspective, soils in the watersheds acidify by neutralizing acidic deposition (sulfuric and nitric acid), resulting in export of base cations as sulfates and nitrates into streams and lakes. After reduction of the strongly acid components sulfate and nitrate to weakly acidic (H_2S) and inert (N_2) components in the stream or lake bottom, the cations betray their basic origin by balancing the hydrogen carbonate formed during sulfate reduction and denitrification, e.g.:



The alkalinization due to denitrification is permanent, but alkalinization due to sulfate reduction would be temporary if H_2S were fixed as iron sulfide and became oxidized later.

Conclusions

Redox processes can cause strong acidification or alkalinization in soils and aquatic environments for two main reasons. Oxidized components happen to be more acid-

ic (SO_3 , N_2O_5) or less basic (Fe_2O_3) than their reduced counterparts (H_2S , N_2 , NH_3 , FeO). As a result, alkalinity and pH of soil and water tend to increase upon chemical reduction, and to decrease upon oxidation. With the exception of denitrification to N_2 , these processes are fully reversible on a seasonal timescale.

On the other hand, however, changes in ANC may become permanent, because redox reactions often cause the formation of pairs of components that differ both in acid-base strength, and in mobility. Depending on whether the acidic or the basic component is the more mobile one, removal of one of the pair of components leads to a 'residue' system that has become permanently acidified or alkalized. A number of examples, all variations on the same theme, have been illustrated in this paper.

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