AP42 Section:	9.2.1
Background Ch	2
Reference:	22
Title:	H. L. Bohn et al., *Soil Chemistry*, John Wiley & Sons, New York, 1985.

Sect 2
#22

SOIL CHEMISTRY

Second Edition

HINRICH L. BOHN
University of Arizona
BRIAN L. McNEAL
University of Florida
GEORGE A. O'CONNOR
New Mexico State University

A WILEY-INTERSCIENCE
PUBLICATION

JOHN WILEY & SONS

New York Chichester
Brisbane Toronto Singapore

the atmosphere to a limited extent when lightning provides sufficient activation energy.

Nitrogen reactions are generally highly irreversible, and enzymatic catalysis is necessary for nitrogen conversions in soils. Redox irreversibility is unfortunate from the standpoint of studying redox reactions, but is absolutely necessary for life. Reversibility would bring with it equilibrium, and all orga- nisms would be transformed into CO_2, N_2, NO_3^-, and H_2O.

Irreversibility means that more energy is required to carry out, and less energy is derived from, reactions. While natural reactions are remarkably conservative of chemical energy, energy optimization is not the only criterion that determines which reactions occur. Unstable compounds, such as nitrite and nitrous oxide (N_2O), for example, would not be produced if soil microor- ganisms were only concerned with optimal utilization of available chemical energy. Spring thaw can bring about temporary nitrite accumulation in soils, apparently because microbial nitrite reducers respond less quickly to in- creased temperature than do the microbes that reduce nitrate to nitrite. In addition, nitrate fertilization or wetting of dry soil initially stimulates N_2O production, so that up to 25 to 50% of the nitrogen lost by denitrification can be lost as N_2O. Both N_2O and nitrite production appear to be temporary maladjustments during the flurry of microbial activity after a sudden environ- mental change.

A.10.2.2 Sulfur

Figures 10.4 and 10.5 show the equilibrium relations of the sulfur oxidation states—sulfate, elemental sulfur, and sulfide—which are stable within the stability limits of water. Note the similarity to the stable oxidation states of nitrogen. Elemental sulfur, however, is much less stable than is elemental nitrogen. Elemental sulfur is stable only under acid conditions.

Figure 10.4 shows the sulfur stability regions for unit activity of sulfate and sulfide. The sulfur region diminishes with decreasing sulfate and sulfide ac- tivities. The sulfur in the amino acid cysteine (HS—CH_2—$CHNH_2$—COOH) is more stable against oxidation than is the nitrogen in alanine. The cysteine- sulfate boundary is shown as a dashed line because it is unstable at $Eh° =$ 0.31 V with respect to CO_2, S, and N_2. Like alanine, its stability is a steady state dependent upon continuing production of organic compounds. The sta- bility region of cysteine increases with increasing concentrations of sulfate compounds.

Figure 10.5 is a pe + pH diagram of sulfur at pH 7 and 10^{-3} *M* soluble sulfur species. Only SO_4^- and HS^- are stable, with the HS^- stable only under strongly reducing conditions. The soluble sulfur concentration is too low and

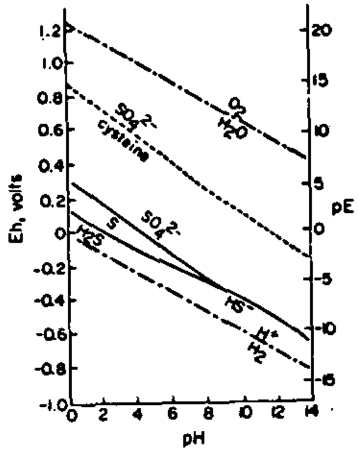

Fig. 10.4 *Eh*-pH diagram of the S-H_2O-O_2-amino acid system.

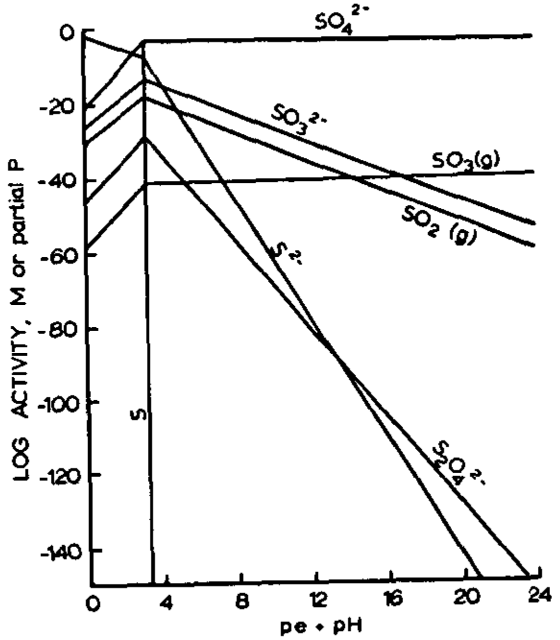

Fig. 10.5 Distribution of solid, gaseous, and aqueous sulfur species at pH 7 and 10^{-3} *M* total soluble sulfur. (Adapted from Lindsay, 1979.)

the pH too high to permit elemental sulfur stability. Figure 10.5 also ignores organic sulfur compounds.

The redox reactions of sulfur seem to be more reversible than those of nitrogen. Intermediate compounds in the reaction series from sulfate to sulfur or sulfide, and vice versa, do not appear in soils. Sulfur also differs from nitrogen in that little sulfur volatilizes from soils. Although H_2S is a gas, apparently any H_2S formed in soils reacts subsequently with iron and other transition metals to form sulfides. Some organic gases containing —SH groups are occasionally liberated during decomposition of fresh organic matter, but the amounts are small.

A.10.2.3 Carbon

The redox reactions of carbon should perhaps have been discussed before those of nitrogen and sulfur, for the energies and electrons that drive nitrogen and sulfur redox reactions come almost exclusively from the oxidation of carbon compounds. Redox reactions of soil carbon have been largely ignored in soils, however, because (1) carbon lacks immediate economic importance, and (2) soil carbon, except for CO_2, exists as unknown polymers (Chapter 5) rather than as well-defined simple molecules.

The ΔG of formation and the *Eh*° of SOM are unknown, so its stability to oxidation cannot be plotted on an *Eh*-pH diagram. At present, only the energies of formation of simple organic compounds are available. The electrode potentials of the redox couples of CO_2 with phenol, acetic acid, ethanol, and glucose are shown in Table 10.4. The half-reactions are written as if CO_2 were being reduced in order to assign the proper sign to *Eh*°. Table 10.4 also includes the potential of the H^+-H_2 couple as a reference. Glucose is unstable at equilibrium in the presence of water. The other organic compounds are stable in water, but only under strongly reducing conditions. Their stability increases slightly with increasing carbon oxidation state, from glucose to ethanol to acetic acid. Phenol may be slightly more stable than the other compounds because of electron resonance in its benzene ring.

TABLE 10.4
Electrode Potentials of Phenol, Acetic Acid, Ethanol, and Glucose Compared to the Lower Stability Limit of Water

REDOX COUPLE	Eh° (V)
Phenol-CO_2 $6CO_2 + 28H^+ + 28e^- = C_6H_5OH + 11H_2O$	+0.102
Acetic Acid-CO_2 $2CO_2 + 8H^+ + 8e = CH_3COOH + 2H_2O$	0.097
Ethanol-CO_2 $2CO_2 + 11H^+ + 11\,e^- = CH_2CH_2OH + 3H_2O$	0.079
H^+-H_2 $H^+ + e^- = \frac{1}{2}H_2$	0.0
Glucose-CO_2 $6CO_2 + 24H^+ + 24e^- = C_6H_{12}O_6 + 6H_2O$	−0.014

These simple organic molecules are among the many components that polymerize into SOM. Because of its predominance, SOM is presumably more stable than the simple molecules. Polymerization probably increases the equilibrium stability somewhat, but may have an even greater effect by slowing the oxidation rate of SOM.

A.10.2.4 Iron

Electron exchange between the various oxidation states of iron tends to be more reversible than is electron exchange between the oxidation states of nitrogen, sulfur, or carbon. Iron redox reactions occur at appreciable rates in soils without enzymatic catalysis. The Fe(II) minerals in parent material oxidize spontaneously, though slowly, in aerobic soils. The electron availability for subsequent iron redox reactions in soils is determined by microbial oxidation of carbon compounds. The reduction of Fe(III) in acid solutions is given by

$$Fe^{3+} + e^- = Fe^{2+} \tag{10.33}$$

At the pH of typical soils, Fe^{3+} is hydrolyzed to $Fe(OH)_2^+$, so the reduction of dissolved Fe(III) is more realistically

$$Fe(OH)_2^+ + e^- + 2H^+ = Fe^{2+} + 2H_2O \tag{10.34}$$

The concentrations of Fe(III) at normal pH levels are very low. As a result, Equation 10.34 consumes a negligible number of electrons. The major reaction by which Fe(III) accepts electrons in soils is the reduction of solid-phase Fe(III) hydroxyoxide:

$$FeOOH + e^- + 3H^+ = Fe^{2+} + 2H_2O \tag{10.35}$$

Substituting Equation 10.35 into the Nernst equation (10.20) yields

$$Eh = Eh° - 0.059(\log(Fe^{2+}) + 3\text{ pH}) \tag{10.36}$$

denitrification, although ammonia readily volatilizes from the surface of alkaline soils. Nitrification ($NH_4^+ \rightarrow NO_3^-$) inhibitors are commercially available. They are being actively investigated as a means of maintaining fertilizer nitrogen in the NH_4^+ form, thus retarding denitrification and leaching losses.

11.6.2 Sulfur

Although sulfur is less volatile than carbon or nitrogen, organic decay at the soil surface sometimes releases a little sulfur as methyl mercaptan (CH_3SH), dimethyl sulfide ($CH_3—S—CH_3$), dimethyl disulfide ($CH_3—S—S—CH_3$), and perhaps hydrogen sulfide (H_2S). Hydrogen sulfide generally reacts with metal ions and precipitates in soils as FeS_2, MnS, and other transition metal sulfides rather than escaping to the atmosphere. If soil emissions of H_2S and the organic sulfide gases were substantial, their pungent odors would be readily noticeable. Although those odors are rare naturally, sulfur emission worldwide from anaerobic soils and swamps has been estimated as 30 Tg yr^{-1}.

Figure 10.3 showed common sulfur equilibria with respect to oxidation-reduction conditions. Sulfate predominates, with elemental sulfur being stable only at acid pH and under moderate reducing conditions. Sulfide is the stable form under more strongly reducing conditions. In organic compounds, the sulfhydryl (—SH) state is stable up to moderately oxidizing conditions.

Oxidation states other than sulfate, elemental sulfur, sulfide, and sulfhydryl are absent in soils. Elemental sulfur is rare naturally in soils but is sometimes added to soils as an amendment, and sulfides are common in many mining wastes. When elemental sulfur and sulfides are exposed to oxygen in well-aerated soils, they oxidize to H_2SO_4. Soil acidities as high as pH 2 may persist until the sulfide or sulfur has all been oxidized and leached away.

Major sulfur inputs to soils include atmospheric SO_2 and its various oxidation products from coal combustion (100 Tg yr^{-1} sulfur in 1971), petroleum processing (30 Tg yr^{-1}), ore smelting (15 Tg yr^{-1}), and sulfate from sea spray (20 Tg yr^{-1}). Most of the atmosphere's anthropogenic sulfur falls near the industrial areas where it is produced. The sulfur fallout over West Germany, for example, is about 50 kg ha^{-1} yr^{-1} in nonforested areas and 80 kg ha^{-1} yr^{-1} in forests. The fallout occurs both as acid rain and as direct plant absorption; direct soil absorption of atmospheric sulfur apparently is minor in humid and temperate regions. Sulfur dioxide and its oxidation products are absorbed directly and rapidly by the basic soils in arid regions.

Small amounts of atmospheric sulfur can be carried long distances. In regions of sulfur-deficient soils, atmospheric sulfur at low concentrations is a beneficial supplement to plant nutrition. Benefits from the low concentrations, however, must be weighed against the associated acidification of freshwater, phytotoxicity, health hazards, smog, and building deterioration.

Sulfate anions are retained only weakly by soils, but the retention increases with soil acidity (Section 11.2). Sulfate anions are absorbed readily by plants and incorporated into biomass. Hence, biomass and SOM constitute large sulfur reservoirs at the earth's surface. The carbon/sulfur mass ratio in SOM is typically about 100/1. The sulfate content of soils increases with aridity and with salt accumulation.

Widespread sulfur deficiencies in many agricultural soils became more obvious in recent decades as "treble superphosphate" began to supplant "superphosphate" as a phosphate fertilizer. Superphosphate is made with H_2SO_4 and contains about 50 mole percent sulfate. This inadvertent sulfur fertilization ended when higher purity treble superphosphate, made with H_3PO_4, was substituted. The "improved" treble superphosphate sometimes produced lower crop yields than did ordinary superphosphate, until the sulfur deficiency was recognized and corrected.

11.6.3 Iron and Manganese

Flooding restricts O_2 diffusion into soils. After soil microorganisms exhaust their dissolved supply of O_2, NO_3^-, and SO_4^{2-}, they must make do with Fe(III) and Mn(III-IV) compounds as electron acceptors (Chapter 10). The amounts of solid-phase Fe(III) in soils are large, and the soil solution concentration of Fe(II-III) can increase from less than 10^{-5} *M*, typical of aerobic soils (Table 11.3), to as high as 10^{-3} *M*. The Mn^{2+} concentration also can increase to 10^{-3} *M*, but this is less common and due as much to soil acidity as to anaerobiosis. High Fe^{2+} and Mn^{2+} concentrations are phytotoxic, but problems due to oxygen insufficiency usually appear first in waterlogged plants. Manganese toxicity is more evident for rice and for animals grazing on acid, marshy pastures. It can be overcome in rice paddies by liming.

Soils subjected to periodic flooding or to seasons of water saturation develop "mottles," a variegation of reddish soil containing Fe(III) mixed with blue or gray soil containing Fe(II). Permanently wet mineral (Gley) soils are characteristically blue or gray because of the predominance of Fe(II).

Aerated soils contain local areas of reduced O_2 availability that probably contain more Fe^{2+} and Mn^{2+} than does the bulk solution of the soil as a whole. Inasmuch as Fe(III) and Mn(III-IV) are very insoluble, small volumes of reduced soil may supply much of the iron and manganese that is used by plants and extracted by various soil-testing solutions. Iron and manganese are nonetheless in short supply for irrigated crops grown on alkaline soils.