REDOX, SOILS, AND CARBON SEQUESTRATION

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Abstract. One of the ecological functions of soil is to act as a short term carbon reservoir through which CO_2 passes from gas to solid as a result of the process of photosynthesis, then back to gas by oxidation of the solid forms. How long the carbon resides in the soil as solid organic matter is a function, amongst other factors, of redox potential. The issue is examined here in the context of a series of Eh-pH diagrams. This leads to the overall conclusion that controlling the level of atmospheric CO_2 by soil-management practices compares unfavourably with other techniques, and cannot be considered as other than a stop-gap measure.

Resumen. Una de las funciones ecológicas del suelo es actuar, a corto plazo, como un reservorio de carbono a través del cual el CO_2 pasa de gas a sólido como resultado del proceso de fotosíntesis, devolviéndose a la forma gaseosa por oxidación de las formas sólidas. La duración del tiempo de residencia de la materia orgánica en el suelo es una función, entre otras variables, del potencial redox. A partir de una serie de diagramas Eh-pH se concluye que controlar el nivel de CO_2. a través de prácticas de manejo del suelo es desfavorable respecto a otras técnicas.

INTRODUCTION

The world's major carbon reservoirs are shown in Table 1, which incorporates data from the IPCC. Clearly, the major reservoir is marine, followed by fossil fuel, with soil at number three.

TABLE 1. World's carbon reservoirs.

Reservoir	Size (Gt C)
Atmosphere	750
Forests	610
Soils	1580
Surface ocean	1020
Deep ocean	38100
Fossil fuels	
Coal	4000
Oil	500
Natural gas	500
Total fossil fuels	5000

Carbon dioxide is the principle component of the carbon cycle that enables the transfer of C between air, land, and sea, and evidence from gas trapped in ice cores indicates a closely controlled atmospheric composition during the Quaternary. For example, the Vostock core, shows a remarkably consistent periodicity between high approaching 300 ppm (by volume) during interglacials and lows of 180 ppm during glacial events. The fact that current values of 370 ppm clearly fall outside the prehistoric range has become a matter of concern.

The concern arises because CO_2 in the present day atmosphere bears an unmistakable fossil fuel signature, so that anthropogenic activities are responsible, at least in part, for this perturbation. The range of human perturbations is shown in Tabla 2.

In other words, there has been a significant and unprecedented transfer of carbon from long term geological reservoirs to the short term sinks at the earth's surface. A consensus has developed over the last decade that this transfer may be responsible for an episode of global warming that the planet is currently experiencing. Hence the search for ways of extracting carbon from the

atmosphere and. sequestering it into the land
and ocean pools

TABLE 2. Human perturbations.

	Flux (Gt C yr^{-1})
CO_2 sources	
Fossil fuel combustion and cement production	5.5±0.5
Tropical deforestation	1.6±1.0
Total anthropogenic emissions	7.1±1.1
CO_2 sinks	
Storage in the atmosphere	3.3±0.2
Uptake by the ocean	2.0±0.8
Northern hemisphere forest regrowth	0.5±0.5
Other terrestrial sinks (CO_2 fertilization, N fertilization, climatic effects)	1.3±1.5

Source: Houghton et al. (1995).

The CO_2 cycle in soil

Sequestration of carbon in soil, and specifically redox constraints on the process, are the focus of this paper. Soil accomplishes the sequestration of carbon in two ways. It serves (i) as a growth medium for the CO_2 consuming standing biomass, and (ii) as a repository for the organic matter detritus (OM) produced by dead and decaying biomass. As a complementary and opposite function, the soil also serves as a CO_2 generator when biomass and OM burns or decays. In other words, the soil can be considered as a flow through reaction vessel or reservoir, in which the transient uptake of atmospheric CO_2 results in the storage of carbon in soil for residence time that depends, amongst other factors, on the nature of the chemical environment in the soil. The carbon cycle in the soil is shown in Figura. 1.
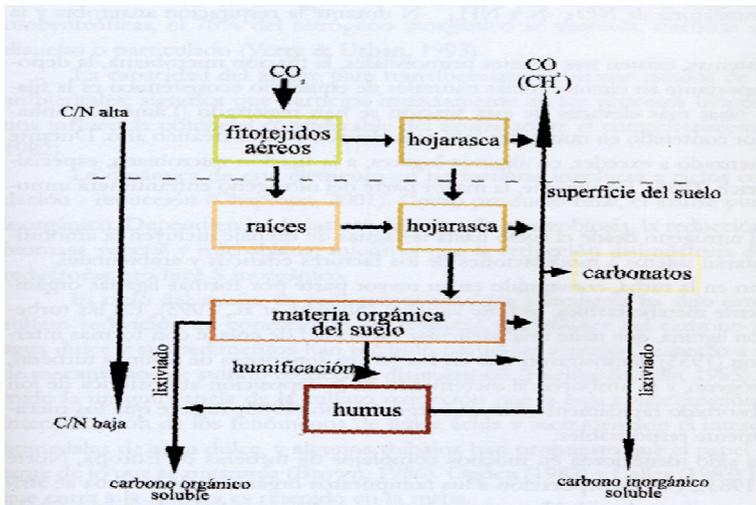

FIGURE 1. Ciclo de C en sistemas edáficos (Pontevedra, 2002).

A small fraction of soil-carbon avoids direct recycling by being incorporated into longer lived organic deposits (for example fossil fuels), or by being taken up as mineral carbonate (with calcite predominating), in the inorganic exogeochemical cycle. Two parameters useful in defining the chemical nature of the soil-environment are pH and pE (or Eh):

pH = - log (thermodynamic activity of protons)
pE = - log (thermodynamic activity of electrons)
Eh = pE (in millivolts)/59.2

These parameters are important in determining the residence time of carbon in the soil, which of course bears directly on the effectiveness of using soil to sequester C. Here, I will examine the question by means of a series of Eh-pH diagrams.

THE DIAGRAMS

Eh-pH diagrams were first developed by Pourbaix for use in metallurgy. The first application to the earth sciences was by Krumbein and Garrels. Figure 2 shows the range of Eh and pH to be expected in soils and peats on the earth's land surface. The diagram is based on work by Chesworth and Macías (1984), Macías et al. (1987), Chesworth (1996), and Martínez Cortizas et al. (2001).
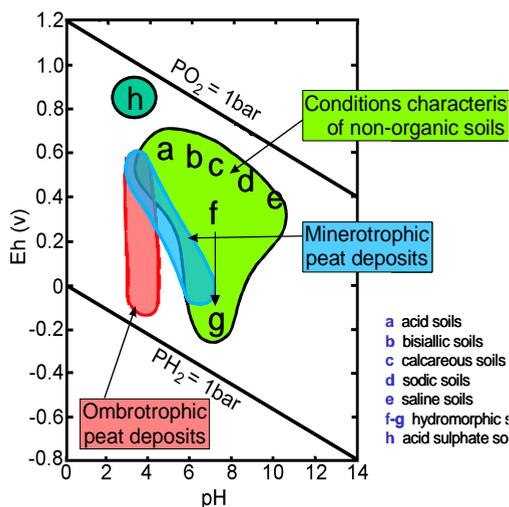

FIGURE 2. Eh-pH range in soils and peats. Modified from Martínez Cortízas et al. (2001).
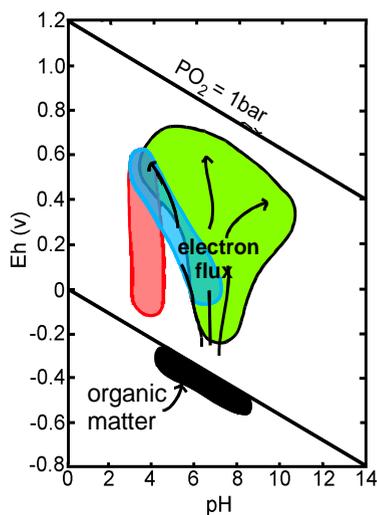

FIGURE 3. Organic matter as electron pump.

Figure 3 shows that organic matter is the most reduced part of the soil ecosystem. It is also the most prolific source of electrons in soil, and during decay may be looked upon as an electron-pump supplying electrons to more oxidized species in the soil. Ferrous iron is the second most important source with sulphides and native metals of lesser importance in the system.

Figure 4 shows electron-flow in soils in more detail, with a number of notable electron acceptors as sinks. This represents the overall "big picture". Sub-systems within the total system will be characterised by reactions involving localised cells in which a sink is coupled with a source lower in the redox scale at a given pH. A large number of local and microscopic equilibria are possible, and measured Eh in soil represents a redox value resulting from the total mosaic of all such local reactions.

Within the upper, organic-rich part of the solum, microbially mediated breakdown of OM will give a range of possible Eh values up to the lower limit of O_2 oxidation in soil. Generally speaking, exponential growth of the microbial biomass will tend to keep redox conditions at this limit, which acts as a Malthusian demostat on the microbial population. It thereby constitutes the "organic fence" in soils postulated by Chesworth and Macías (1987), following the basic ideas of Krumbein and Garrels already cited.

Figure 4 is based on the dominant redox-reaction possibilities in the soil. In the absence of free oxygen (or in the localised sub-systems already mentioned), other electron acceptors allow the CO_2-generating breakdown of OM. The sequence shown in Table 3 follows the sequence of diminishing energy production (at pH 7) utilised by the microbial population. Table 4 gives two reducing reactions, which take place below the sulphate-sulphide barrier.
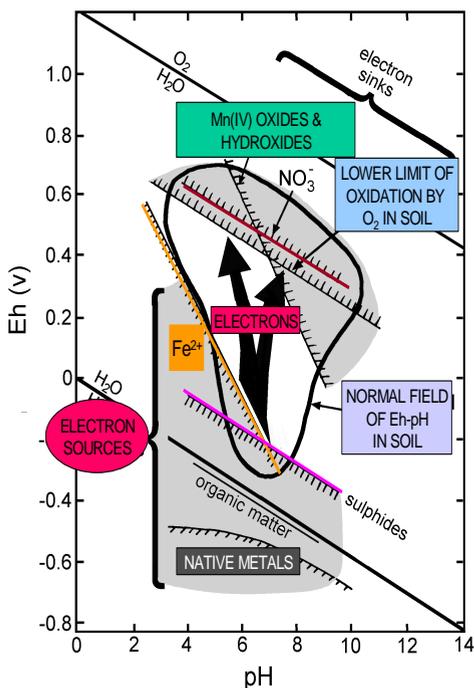
FIGURE 4. Fluxes between electron sources and sinks in soil.

TABLE 3. Typical redox reactions.

Aerobic oxidation
$CH_2O + O_2 = CO_2 + H_2O$
Denitrification
$CH_2O + 0.8NO_3^- = CO_2 + 0.4N_2 + 1.4H_2O$
Manganese reduction
$CH_2O + 2MnO_2 + 4H^+ = CO_2 + 2Mn^{2+} + 3H_2O$
Iron reduction
$CH_2O + 2FeOOH + H^+ = CO_2 + 2Fe^{2+} + H_2O$
Sulphate reduction
$CH_2O + 0.5SO_4^{2-} + 0.5H^+ = CO_2 + 0.5HS^- + H_2O$
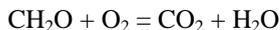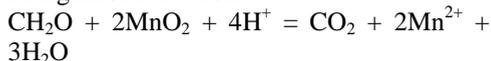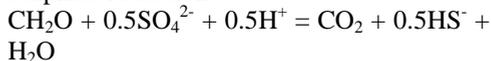
TABLE 4. Other redox reactions.

Methane formation

$CH_2O + 0.5CO_2 = CO_2 + 0.5CH_4$

Proton reduction

$CH_2O + H_2O = CO_2 + 2H_2$
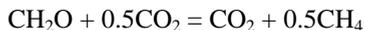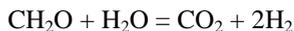
The reactions of Table 3 account for the fact that CO_2 only has a transient stop-over in the soil reservoir. How long that stop-over may be is largely a function of which of the tabulated reactions is the dominant one in the system as a whole. Generally speaking, the residence time of C in the soil will increase the lower down the Eh series the terminal acceptor lies. Figure 5 shows semi-quantitative estimates.
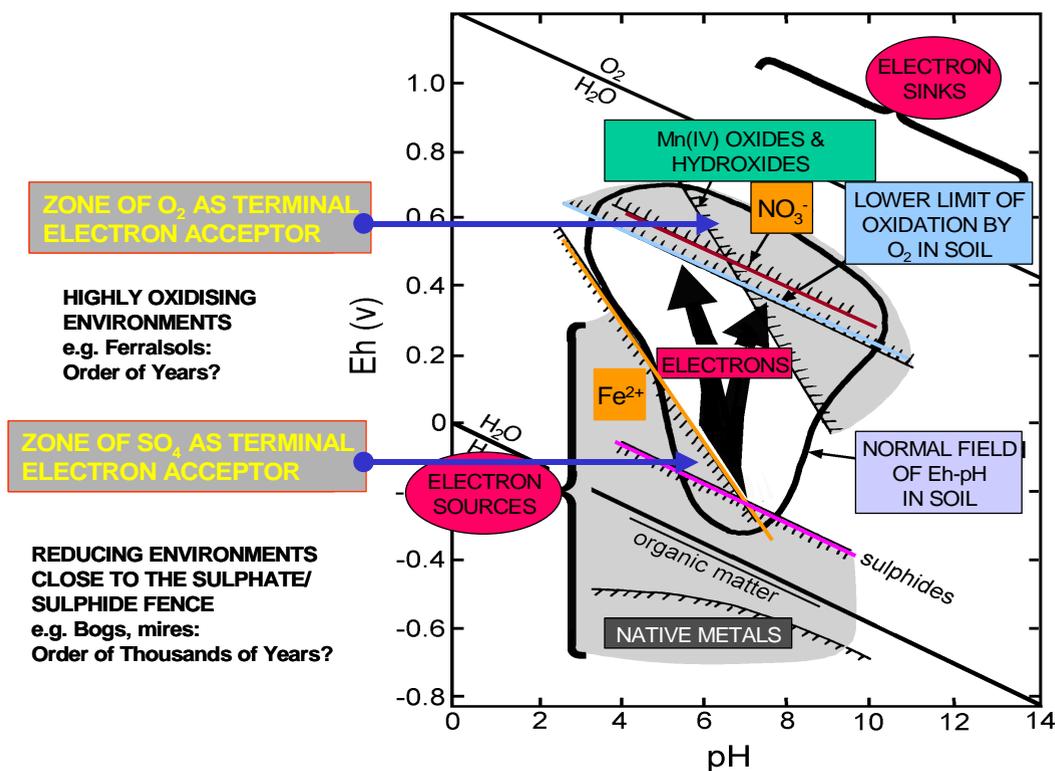

FIGURE 5. Residence times of organic matter.

In effect, reservoirs of long residence time such as bogs and mires, are not really achievable except by the slow natural processes that form deposits of this nature. The reservoirs of shorter residence times represented by soils are the only ones potentially available for any kind of anthropogenic management of carbon sequestration on the land surface. A longer residence time may be engineered in the soil by liming to produce calcium carbonate. However, since lime is produced by the decarbonation of limestone, the process would give no net gain. A net gain could be effected by the formation of an iron or manganese carbonate at low Eh (see Table 5 and Figure 6). Hydromorphic conditions would be a pre-requisite.

TABLE 5. Carbonate formation as an alternative.

Rhodochrosite
$CH_2O + 2MnO_2 + 2H^+ = MnCO_3 + Mn^{2+} + 2H_2O$
Siderite
$CH_2O + 4FeOOH + 6H^+ = FeCO_3 + 3Fe^{2+} + 6H_2O$
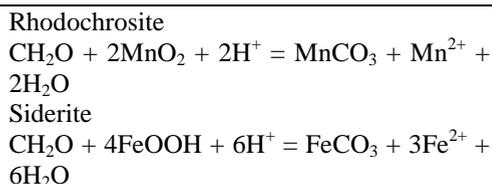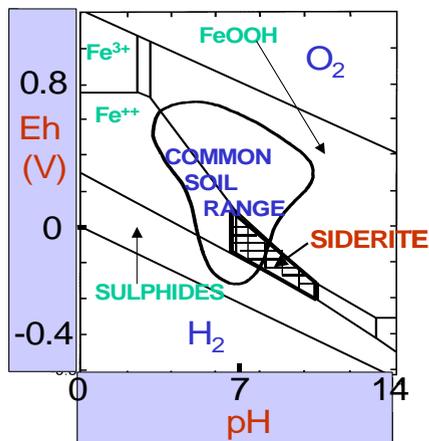
FIGURE 6. Predominance field of siderite. Phase boundaries drawn with respect to Fe activity of 10^{-6} and P_{CO2} of $10^{-3.5}$ bars. Siderite field expands to higher Eh and lower pH as P_{CO2} increases.

DISCUSSION

Soils and wetlands have been suggested as possible sinks for carbon present in the atmosphere as CO_2. There is no doubt that such deposits function in this way. Destruction of part of this sink by burning and havesting of the land biomass (especially by deforestation for example) has been partly responsible for the increase in atmospheric CO_2 over the last 250 years. Re-establishment of the land biomass by reforestation and other land management practices is a viable way of removing the ecological footprint represented by such destruction. Realistically, however, turning the clock bacl in this way is an unlikely proposition – the human population has doubled two and a half times since the Industrial Revolution started, and may double at least once more in the present century.

Also implicated in the historically recent increase in atmospheric CO_2, is the burning of fossil fuels. This offers a different problem to any plans for sequestering carbon in soils. The carbon in fossil fuel deposits has a natural residence time in the lithospheric reservoir, which is largely a function of the rate of erosion necessary to expose a deposit to the weathering environment. Typically, it is of the order of tens of millions of years. Burning fossil fuels adds this old carbon to the atmosphere rapidly, and if the soil sink is all that is available to take up this new influx, the uptake can only be ephemeral. A reservoir with residence times of decades cannot hope to replace a reservoir with residence times of 10^7 years.

Finally, the possibility of storing carbon as an iron carbonate would be viable, but the kinds of pedological environments where this phase would be stable – gleyed and wetland environments – are not readily susceptible to management for these purposes. Moreover, hydromorphic environments of this kind lead to conditions where methane may be generated – a far more potent greenhouse gas than CO_2.

CONCLUSIONS

The foregoing analysis leads to the following conclusions:
1. OM is the most reduced part of the Earth's exogenic environment.
2. In breaking down in the environment, OM acts as an electron pump.
3. In the presence of oxygen or oxygen-bearing electron acceptors, OM returns CO_2 to the atmosphere.
4. Depending upon the redox conditions, OM represents a residence time for carbon of as little as a year, to no more than a few thousands. Since C from fossil fuels has a residence time in the geological reservoir of the order of ten millions of years, burning such fuels can be looked upon as a semi-permanent addition of CO_2 to the atmosphere.
5. The formation of carbonate in soil offers the possibility of converting atmospheric CO_2 into longer term storage, but carbonates that would allow a net gain

on residence time, such as siderite, form under water-saturated conditions that are difficult to manage.

6. Furthermore, such an environment is likely to release methane, a more potent greenhouse gas than CO_2, to the atmosphere.

7. Other techniques of carbon sequestration (deep burial in the much large marine reservoir for example), probably offer more cost-effective means of controlling atmospheric CO_2.

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