

Hydroxylated green rust as inhibitors of denitrification in hydromorphic soils?

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Hydromorphic soils are not always saturated by water. During the dry season, the watertable can decrease and some horizons can then be aerated. During this period, oxihydroxides such as lepidocrocite or goethite are found in soils under temperate climate. When soil are saturated with water, dissolved oxygen is rapidly exhausted in the soil solution and the microflora use other electron acceptors. The sequence of soil component reduction classically demonstrated by numerous authors starts with the reduction of nitrate when they are present in soil solution. Then, when this source is exhausted, Fe(III) of iron oxihydroxides is reduced to Fe(II). This sequence is based on the calculation of critical potential (Sposito, 1981). In soils located in agricultural catchment, nitrates are always present in solution at the beginning of autumn when soils become saturated with water. Therefore, they are first reduced and Fe(III) is reduced when nitrate concentration reaches zero. A new compound was recently discovered in hydromorphic soil (Trolard *et al.*, 1997): hydroxylated green rust. This compound is a mixed Fe(II)-Fe(III) hydroxide, and the ratio between Fe(II) and Fe(III) depends of the degree of

reduction of the soil. It appears in soils when Fe(II) is released in solution. Thermodynamic calculations report that in three different sites Fe(II) in solution was in equilibrium with this hydroxylated green rust in hydromorphic soils (Genin *et al.*, 1997). The critical potential of the couple $\text{Fe}_3(\text{OH})_8/\text{Fe(II)}$ is very closed and superior from that of nitrate/nitrite. Therefore a competition can exist between these two couples in the process of electron acceptors for microflora. One of this place was a site located in a small intensive agricultural catchment submitted to high input of organic nitrogen. The temporal dynamics of nitrate and Fe(II) concentrations in soil solution were simultaneously monitored.

Preservation of the soil solution

Special attention was paid to preserve the physico-chemical characteristics of the soil solution to avoid the oxidation of Fe(II) to Fe(III) prior to the in situ measurements of pH, Eh and Fe(II) concentration. This preliminary step should be respected in any geochemical study in reduced environments.

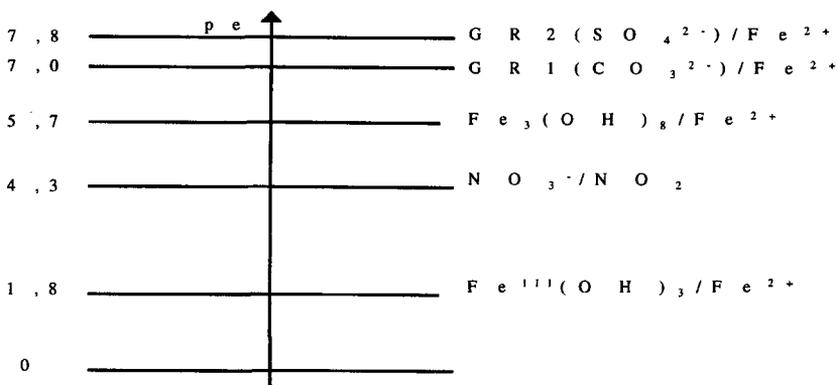


FIG. 1. Sequence integrating hydroxylated green rust.

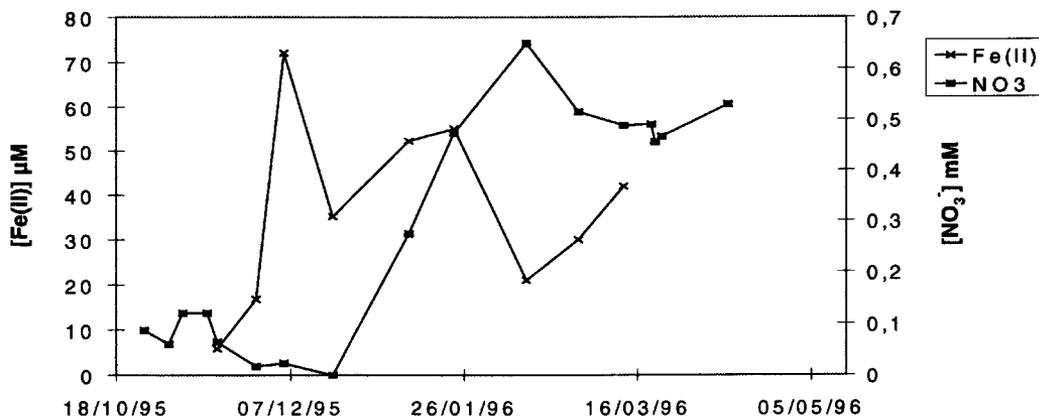


FIG. 2. Seasonal variations of nitrate and Fe(II) concentrations.

Seasonal dynamics of Fe(II) and nitrate concentrations

Figure 2 presents the dynamics of nitrates and Fe(II) in the Sg horizon (50 cm). Three steps can be defined. During the first step, nitrate concentration decrease and reach zero. Then, Fe(II) starts to increase in the soil solution, and hydroxiled green rusts precipitate in soils. The Fe(II) concentration is in equilibrium with the mineral $\text{Fe}_3(\text{OH})_8$.

During the last step, nitrate concentration increases in soil solution. They are issued from the mineralization and leaching of the organic fertilizer spread on the upper cultivated parcell at the beginning of autumn. As hydromorphic soils are open system, the horizon are crossed by flux of water charged with pollutants or dissolved oxygen. During this last stage, simultaneously increase of nitrate and Fe(II) concentrations is observed. The environment is therefore still reduced, but nitrate seem to be protected; they are not denitrified. The microflora seems to use preferentially the mixed hydroxiled green rust than nitrate as electron acceptors.

Conclusion

The denitrification in hydromorphic soils can be inhibited by the formation of a hydroxiled green rust which competes with nitrate as electron acceptors. This compound appears in soil when Fe(II) is released. The denitrification can be maintained as long as $\text{Fe}_3(\text{OH})_8$ is absent: the presence of a small supply of nitrate should prevent its formation by preventing the dissolution of oxydes such as goethite or lepidocrocite.

References

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