



HYDROMORPHIC SOILS AND THEIR CHEMICAL REACTIONS

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Abstract: In flooded soil, the O₂ diffusion is extremely low, implying a soil considered anoxic. With the lack of O₂ as the final electron acceptor of carbon oxidation by the microbial community, the transfer of these is directed to alternative acceptors. The ions that receive electrons have their redox state altered, generating increasingly reduced species. These reactions change the chemical behavior of the ions, resulting in the dissolution and precipitation of different compounds. Thus, the present review sought to compile the main chemical characteristics involved in hydromorphic soils.

Keywords: Soil chemical balance; gleization; hydromorphism; electron secondary acceptors; flooded soils.

INTRODUCTION

Numerous names are given to hydromorphic soils in the most diverse classification systems found around the world (Huang *et al.*, 2011; WRB, 1998; Soil Survey Staff, 1999; EMBRAPA, 2018). Briefly, hydromorphic soils are characterized by water saturation in their pores, with or without the presence of surface water, resulting from the elevation of the water table or by impediment to drainage as a result of concretionary or consolidated material of low hydraulic conductivity (Duchaufour, 1977; Kaur *et al.*, 2020).

Soil hydromorphism derives from long periods of flooding or the occurrence of several prolonged wetting cycles, which imply profound redox, physical and biological changes (Sousa *et al.*, 2019; Zhang and Furman, 2021; Hong *et al.*, 2016; Yuan *et al.*, 2020). In soils with aerobic or oxic characteristics, the macropores are in equilibrium with O₂ and other gases from the atmosphere and pedosphere (e.g., CO₂ and N₂) (Kirk, 2004; Lindsay, 1979). On the other hand, in hydromorphic soils, the constant state of saturation restricts the diffusion of O₂ in its porous network, leading to the formation of a medium with little or no presence of O₂ in the layer's furthest from the flooded surface (Kirk, 2004; Kehew, 2000; Conrad, 2020).

The absence of O₂ or its limitation in flooded soils generates a new state of chemical and biological equilibrium (Van Breemen and Burman, 2002). First, O₂ limitation forces the transition of facultative anaerobic bacteria to act anaerobically, in addition to expanding the community of exclusively anaerobic bacteria (Hong *et al.*, 2016). To sustain the microbiological community, an intense

depolymerization and fixation of organic carbon (OC) occurs in the microbial mass, transferring electrons from the organic substrate to some receptor element (Reusch and Burger, 1973; Strawn *et al.*, 2020). Therefore, the absence of O₂ as an electron acceptor in flooded soils implies the use of other substitute chemical elements (Sousa *et al.*, 2019).

Among the alternative electron acceptors, iron is the main one due to its abundance in soils (Sousa *et al.*, 2019; Rennert, 2018). Upon receiving electrons from the OC metabolized by the microbiota, the chemical receptors alternative to O₂ have their oxidation state altered, generating changes in the expressions of color and ion mobility (Zhang and Furman, 2021; Van Breemen and Burman, 2002). Therefore, the coloration established in the hydromorphic soil is grayish, coming from Fe⁺³ ions reduced to Fe⁺², with strong expression of the neutral color of clay minerals and very low chroma, with or without mottling resulting from the segregation of Fe and Mn (EMBRAPA, 2018). However, a long time of flooding or saturation cycles is required for strong changes in the redox potential to occur (Yuan *et al.*, 2020; Gotoh and Patrick, 1974).

Flooded soils are found in several regions of the globe, usually in regions of alluvial deposits; or in plains of recent late Pleistocene-Holocene formations, marked by the intense action of ferrollysis on the E horizon (Van Breemen and Burman, 2002). Therefore, they are soils of intense agricultural use for rice production thanks to natural flooding or facilitated water management (Yuan *et al.*, 2020; Hemati Matin and Jalali, 2017). Thus, this review seeks to encompass the main properties and chemical characteristics that occur in hydromorphic soils.



MATERIAL AND METHODS

The review was produced based on the compilation of studies and research in scientific journals and books available on scientific dissemination platforms on the chemical balance of flooded soils and their interactions with minerals and microbiological activity.

RESULTS AND DISCUSSION

Hydromorphic soils are characterized by the process of gleization, resulting from temporary or permanent water stagnation, which led to changes in the redox potential, with a predominance of grayish color expression (Van Breemen and Burman, 2002; EMBRAPA, 2018). This coloration comes from the loss of expression of pigmenting chemical elements, such as Fe^{+3} present in solution and in iron oxide clay minerals, due to their reduction after O_2 depletion (Duchaufour, 1977; Vodyanitskii and Minkina, 2019).

In liquid media, the O_2 diffusion coefficient is four times lower than in gaseous atmospheres (Kirk, 2004). In the case of submerged soils, the amount of O_2 can still be kept close to 10.0 mg L^{-1} in the first 50 cm, as the release of O_2 by algae during photosynthesis, however, drops to $<1.0 \text{ mg L}^{-1}$ at 100 cm depth (Marschner, 2021). However, in the porous soil network, as it is completely filled with water, O_2 diffusion is about 320 000 times lower than in aerated pores (Colmer and Flowers, 2008). Therefore, in this condition, electron transfer predominates to chemical species capable of replacing O_2 as the electron acceptor terminal (Strawn *et al.*, 2020).

Despite this, small concentrations of O_2 diffused in the surface water layer can keep it in an oxidized state enough for oxidation reactions to occur (Kirk, 2004; Zhang and Furman, 2021). In the absence of oxygen in soils, redox changes occur between two systems with different redox potential (Sousa *et al.*, 2019). Biological activity plays a selector role in alternative electron acceptor terminals to O_2 , which normally depend on the generated energy potential and availability of ions in solution (Sahrawat, 2004; Strawn *et al.*, 2020). This preference in electron transfer from OC oxidation is established as follows: $\text{O}_2 > \text{NO}_3^- > \text{Mn}^{4+} > \text{Mn}^{3+} > \text{Fe}^{3+} > \text{SO}_4^{2-} > \text{CO}_2 > \text{H}^+$ (Strawn *et al.*, 2020; Ponnampuruma, 1972).

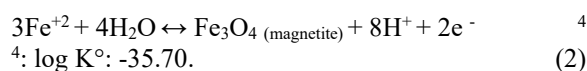
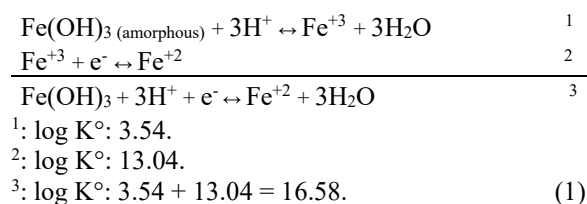
Reoxidation of soil chemical species prevails in the opposite order of reduction, as, for example, Fe^{+2} ions in solution need much lower O_2 activity than Mn^{+2} to return to their oxidized state (Van Breemen and Burman, 2002; Zhang and Furman, 2021). However, the occurrence of redox reactions depends on environmental factors that stimulate the microbial community. If there is stagnation of water and soil organic matter (SOM) in the environment, however, the climate is cold enough to limit microbial activity, the consumption of O_2 is low and does not generate an

anoxic environment with abundant electron transfer (Strawn *et al.*, 2020).

The order of electron acceptor terminals and the amount of energy obtained by biological activity varies based on access to the acceptor element (Sahrawat, 2004; Ponnampuruma, 1972). Those structural elements in more consolidated and well-crystallized minerals will have a lower electron-accepting capacity (Lovley, 1991). For example, in the more crystallized iron oxides, such as goethite (FeOOH), the structural Fe^{+3} has a lower potential to receive electrons than this same ion presents in the ferrihydrite structure (Strawn *et al.*, 2020; Rennert, 2018), a mineral with a lower degree of crystallization (Schwertmann, 1958; Klein and Dutrow, 2012).

The presence or contribution of SOM by aquatic plants, fauna and organic acids carried by water from surrounding regions are the main suppliers of oxidizable OC for obtaining energy from the microbial community (Strawn *et al.*, 2020; Sahrawat, 2004). SOM decomposition is the main source of electrons in flooded soils. With the oxidation of structural carbon transferring its electrons to the electrosphere of ions, such as Fe^{+3} , accompanied by a reduction in the activity of free H^+ in solution (Van Breemen and Burman, 2002; Ponnampuruma, 1972).

In this way, the pH of hydromorphic soils is stabilized at values close to neutrality (7.0), thanks to the consumption of protons during electron transfer between the redox pairs (Parent *et al.*, 2008) (Equation 1). However, the increase in pH is buffered by the precipitation of magnetite when the Fe^{+2} activity exceeds the solubilization limit of this mineral, and as a consequence of its formation there is intense H^+ release (Mello and Perez, 2019; Equation 1 and 2).



Source: Adapted from Mello and Perez (2019) and Lindsay (1979).

Soils when flooded show different behavior in terms of changes in their pH. For example, temporarily flooded acidic soils show strong peaks of pH reduction and elevation, while in calcareous and sodic soils the pH decline is gradual (Hemati Matin and Jalali, 2017). These changes in pH are also related to increased CO_2 activity by biological respiration and HCO_3^- formation, which occur more intensely in acidic soils at the initial moments of flooding (Ponnampuruma, 1972; Kirk, 2004). However, acidic or calcareous soils



stabilize pH in the neutral range for up to 12 weeks after flooding (Hemati Matin and Jalali, 2017).

Based on the pH stability value of hydromorphic soils, the determination of the standard oxidation-reduction potential of electron acceptors becomes more expressive when used at pH 7.0 than, in comparison, the equilibrium constant and the standard redox potential of chemical reduction reactions (Sousa *et al.*, 2019) (Table 1). That is, the activity of H⁺ and electrons (pe) are closely linked, and both should be used in the evaluation of the redox state of the soil (James and Brose, 2011). For such a condition, the use of pe + pH solubility diagrams fit the ideal determination of the stability limits of minerals and ions in the soil (Lindsay, 1979; Brookins, 1988).

Table 1. Summary of redox half-reactions of chemical species in hydromorphic soils.

| Chemical reaction | | |
|---|----------------------------------|--------|
| | log K ^o | 105,15 |
| NO ₃ ⁻ + 6H ⁺ + 5e ⁻ ↔ 1/2N ₂ + 2H ₂ O | Eh ⁰ (V) | 1,240 |
| | Eh ₇ ⁰ (V) | 0,744 |
| | Eh ₇ (V) ¹ | 0,220 |
| ----- | | |
| | log K ^o | 41,66 |
| MnO ₂ + 4H ⁺ + 2e ⁻ ↔ Mn ⁺² + 2H ₂ O | Eh ⁰ (V) | 1,229 |
| | Eh ₇ ⁰ (V) | 0,403 |
| | Eh ₇ (V) ¹ | 0,200 |
| ----- | | |
| | log K ^o | 17,91 |
| Fe(OH) ₃ + 3H ⁺ + e ⁻ ↔ Fe ⁺² + 3H ₂ O | Eh ⁰ (V) | 1,057 |
| | Eh ₇ ⁰ (V) | -0,182 |
| | Eh ₇ (V) ¹ | 0,120 |
| ----- | | |
| | log K ^o | 41,08 |
| SO ₄ ⁺² + 10H ⁺ + 8e ⁻ ↔ H ₂ S + 4H ₂ O | Eh ⁰ (V) | 0,303 |
| | Eh ₇ ⁰ (V) | -0,213 |
| | Eh ₇ (V) ¹ | -0,150 |

Notes: log K^o: equilibrium constant. Eh⁰: standard redox potential. Eh₇⁰: standard oxidation-reduction potential at pH 7.0.¹ Approximate values of the reduction potential controlled by the chemical species in flooded soils (Ponnamperuma, 1972).

Source: Adapted from Sousa *et al.* (2019), Zhang and Furman (2021) and Ponnamperuma (1972).

It is worth mentioning that if a redox pair in a reaction is in a much higher concentration than the other ions, the concentration of the reduced and oxidized species are little influenced in the equilibrium, thus, the electrical potential of the soil is controlled by the dominant redox pair in a given moment (Kirk, 2004).

Thus, when the reduced ion that controls the electrical potential of the soil is mostly consumed, the electrical potential of the soil starts to be controlled by the chemical species of lower electrical potential (Table 1), thus reestablishing a new state of electrical balance of the soil, however, at a lower level than the previous one (Strawn *et al.*, 2020; Sousa *et al.*, 2019). In well-developed tropical soils, the abundance of iron oxides

favors the establishment of Eh₇ closes to that of Fe²⁺ when soils are under flooding (Sousa *et al.*, 2019; Table 1). However, the different species of Fe minerals present in the soil intensify the reduction of structural Fe⁺³ in different Eh₇ bands. The amorphous Fe – Fe(OH)₃, inorganic mineral form of low crystallinity (Schwertmann, 1958) – more abundant in soils in flooded areas, initiates the reduction of Fe⁺³ ions to Eh₇ ≤ -0.071 V, while, in goethite it occurs at values ≤ -0.23 V (James and Brose, 2011; Mello and Perez, 2019).

The reduced chemical species can act as an electrical buffer in the soil, although they depend on the amount of available and free ion, complexation, sorption, precipitation and dissolution (Kirk, 2004). Sousa *et al.* (2019) describe that the ions, when reduced, start to compose large proportions of the exchange complex. For the authors, when the reduced ions in solution, for example, those of Fe⁺², are oxidized, the exchangeable complex restores the equilibrium releasing proportionally the amount of reduced ions in order to restore the electrical potential of the soil. This process occurs until all the Fe⁺² is oxidized in solution (Kirk, 2004).

Chemical processes in hydromorphic soils

The variations in the decrease of the electrical potential of the soil depend on the type and amount of SOM, the available electron acceptors, temperature and time of flooding (Sparks, 2003). In soils with 60% pore space filled with water, anaerobic microbial activity is increased, and aerobic activity is reduced until it becomes negligible as the soil is fully soaked (Sahrawat, 2004; Zhang and Furman, 2021).

Compared to oxic condition soils, initially, the OC metabolized by the microbial community in flooded soils are the fractions with greater solubility, such as carbohydrates, amino acids and sugars, disaccharides and non-recalcitrant molecules (Kristensen *et al.*, 1995). However, SOM decomposition in flooded environments is limited due to the low net energy gain from microbial activity (Strawn *et al.*, 2020; Marschner, 2021). Therefore, there is the accumulation of organic material or peat bogs (Figure 1) (Bockheim, 2021).



Figure 1. GLEISSOLO HÁPTICO (EMBRAPA, 2018) with accumulation of organic matter on the surface horizon.

Source: Authors (2022).



The increase in pH in flooded soils accelerates the decomposition of SOM by promoting its desorption from the inorganic surface of clay minerals and oxides (Grybos *et al.*, 2004; Said-Pullicino *et al.*, 2021). Simultaneously, there is a reduction of Fe and Mn minerals that contribute to the decline of complexation and adsorption of ions in solution, including potentially toxic ones (Kirk, 2004; Rinklebe *et al.* 2016). This is due to the increased availability and mobility of Fe⁺² in solution, implying the intense formation of Fe-SOM complexes (Yuan *et al.*, 2020; He *et al.*, 2005). With Fe-blocked SOM sites, the adsorption of trace elements such as Ar, Zn, Cu, Th, Cd, As and La in areas of hydromorphic soils is limited (Olivie-Lauquet, 2001; Strawn *et al.*, 2020; Wang *et al.*, 2022). Plants grown in these environments can suffer phytotoxicity, phytoextracting these elements by allocating them in shoots and grains (He *et al.*, 2005; Hockmann *et al.*, 2018).

The intensity of SOM degradation directly influences nitrogen species in flooded environments and the complexation of metallic elements, such as Fe and Mn (Kirk, 2004; Vodyanitskii and Minkina, 2019). In waterlogged rice planting soils, SOM can supply up to 75% of all the nitrogen required by plants (Sahrawat, 2004). In these environments, there is little or no transformation of mineralized NH₄⁺ from SOM to NO₃⁻ in the subsurface, maximizing its concentration in the soil solution (Ponnamperuma, 1972; Gu *et al.*, 2019). In low redox potential environments (based on the solubility diagram pe + pH, considering the pH at 7.0), if pe + pH varies from 4.0 to 9.0, the nitrogen species present, as a priority, include: NO₂(g), NH₃(g) and N₂O₄(g); when the site is extremely reduced, from pe + pH < 3.5, the NH₄⁺ ions become the most stable (Lindsay, 1979).

If NO₃⁻ is present at a level sufficient to control the electrical potential (Table 1) and has organic substrates, this will be the priority chemical species in the reception of electrons from microbial activity (Kirk, 2004; Ponnamperuma, 1972). As a result, NO₃⁻ can be transformed into more volatile forms of N into Eh₇ ≤ 0.70 V (James and Brose, 2011; Strawn *et al.*, 2020), like the gases N₂ and N₂O, in a process called denitrification (Bremner and Shaw, 1958; Castaldelli *et al.* 2019). This process intensifies due to changes in the concentration gradient. The NH₄⁺ released from the SOM mineralization diffuses from the lower subsurface and the zone of its highest concentration to the surface of the water layer, oxidized zone and of lower concentration (Figure 2), where it then converts to NO₃⁻ and returns in the oxidized form to the subsurface where its concentration is lower, and finally, denitrification occurs (Sousa *et al.*, 2019; Allen *et al.*, 2010; Sahrawat, 2004; Sousa, 2006).

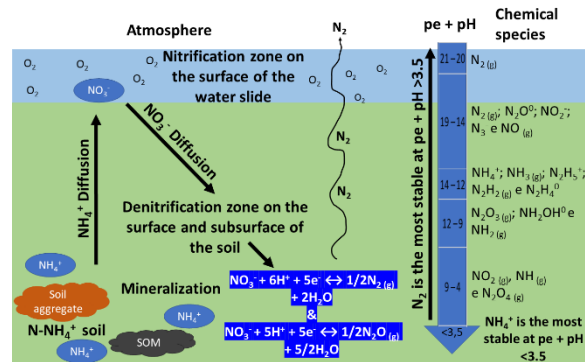
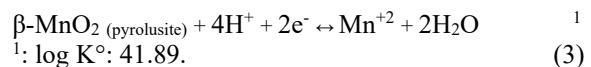


Figure 2. Scheme of nitrification and denitrification in hydromorphic soils.

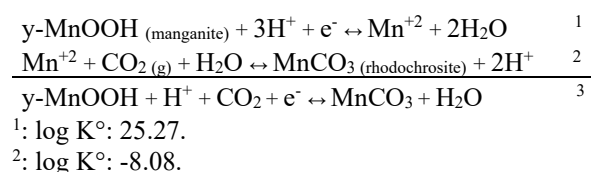
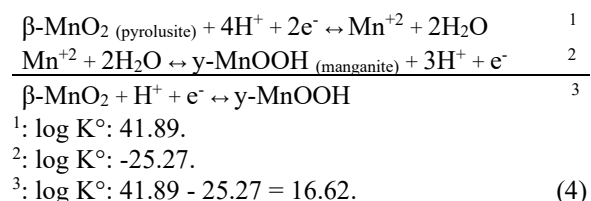
Source: Adapted from Sousa (2006) and Lindsay (1979).

The reduction of NO₃⁻ coincides with that of Mn⁺⁴ until most of its ions or its redox buffering capacity is exhausted (Sousa *et al.*, 2019). If the environment becomes more reduced, the Mn oxides and, later, the Fe oxides become the alternative electron acceptors (Table 1). The reduced forms Mn⁺² and Fe⁺² is more soluble and mobile than the oxidized forms, and in flooded environments there is strong dissolution of Fe Mn mineral phases, which increases the activity of these elements in the soil solution (Kirk, 2004; Ponnamperuma, 1972; Wahid and Kamalam, 1993) (Equation 1 and 3).



Source: Adapted from Lindsay (1979).

Despite this, the activity of Mn⁺² ions tends to decrease in the soil, mainly due to complexation reactions in SOM, adsorption in the exchange complex and precipitation in insoluble minerals (Sousa *et al.*, 2019; Ponnamperuma, 1972). At pe + pH of 16.62 (pH at 7.0), pyrolusite is dissolved, with Mn⁺⁴ being reduced to Mn⁺² and subsequently being precipitated into inorganic manganite mineral (Lindsay, 1979; Equation 4). Furthermore, part of the Mn⁺² in soil solution can be precipitated in the form of MnCO₃ (rhodochrosite) (Equation 5) as the CO₂ activity produced by the activity of microbial communities and roots increases (Lindsay, 1979; Marschner, 2021).

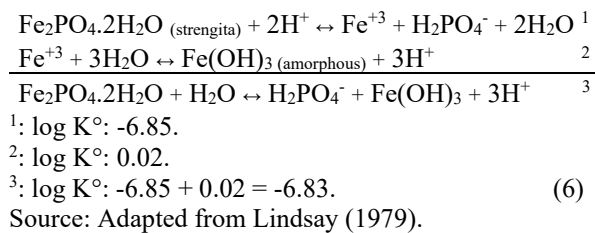




$$^3: \log K^\circ: 25.27 - 8.08 = 17.19. \quad (5)$$

Source: Adapted from Lindsay (1979).

On the other hand, the reduction of Mn and Fe ions present in the structures of oxides and hydroxides is slow due to the limited surface area (solid-solution) and the slow diffusion of water through the porous network of aggregates and concretions (Strawn *et al.*, 2020). Therefore, the reduction of ions and destruction of these minerals in hydromorphic soils takes a long time, especially for the more stable iron oxides, such as goethite (Vodyanitskii and Minkina, 2019; Yuan *et al.*, 2020). In the case of Fe minerals, those with the highest log K° and the lowest crystallization tend to be the most easily dissolved in waterlogged soils, for example, the convention of amorphous Fe in magnetite (Mello and Perez, 2019). With the solubilization of minerals and Fe and Al oxyhydroxides in flooded soils to maintain the Fe⁺³ activity in balance, phosphate ions (Equation 6) and sulfates are also released from the minerals, increasing their availability (Hemati Matin and Jalali, 2017; Lindsay, 1979).



In hydromorphic soils, the water table fluctuation establishes cyclic oxidation-reduction zones, mainly for Fe (Vodyanitskii and Minkina, 2019; Said-Pullicino *et al.*, 2021). Throughout these several continuous cycles, clay minerals are gradually destroyed by the action of ferrolysis (Brinkman, 1970). Brinkman (1970, 1979) proposes ferrolysis starting with the saturation of the cation exchange complex (CEC) of clays by Fe⁺² during flooding, followed by the following steps: hydrolysis of Fe⁺³ at oxic moments of the soil, acidification of CEC and desilication by the solubilization of clay minerals (Figure 3). This pedogenetic process favors the presence of a B horizon that is more clayey than the A horizon, with the intermediate E of a whitish color, designated as albic E (Soil Survey Staff, 1999; EMBRAPA, 2018).

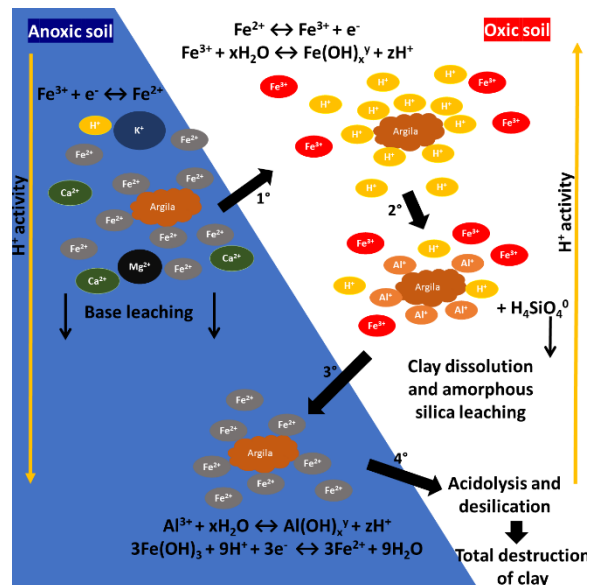


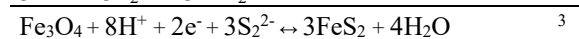
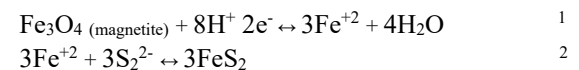
Figure 3. Summarized example of the action of ferrolysis on a clay mineral fragment present in temporarily flooded soils or with an oscillating water table. (1) CEC saturation of clay by Fe⁺²; (2) reoxidation of the reduced iron ions, followed by their hydrolysis, with the H⁺ produced saturating the CEC of the clay mineral, which leads to its instability and dissolution in silica and also to the convention in clay saturated by Al⁺³; (3) clay is again subjected to the flooding cycle and its CEC is saturated by Fe⁺², and the Al⁺³ is displaced to the soil solution and undergoes hydrolysis; and (4) total solubilization of the clay particle occurs by acidolysis and silica leaching. Source: Adapted from Brinkman (1970, 1979).

With the supply of structural Fe⁺³ in minerals and in solution decaying close to the lower limit of electron reception, sulfate ions become the main chemical species to be reduced (Strawn *et al.*, 2020; Ponnampereuma, 1972; Zhang and Furman, 2021). At pe + pH close to 4.0, (where the pH was kept at 7.0), S increases in the polyanion state, for example: S₂⁻², S₃⁻², S₄⁻³ and S₅⁻⁴; with pe + pH < 3.13 and pH above 7.0, the transformation of SO₄⁻² into S⁰ (Rhombic S) (Lindsay, 1979). Sulfides can form ionic pairs with ions in solution, giving rise to H₂S and metallic sulfides (Zhang and Furman, 2021; Rinklebe *et al.*, 2016). Weber *et al.* (2009) reported that 56% of the Cu adsorbed to SOM was converted to Cu_xS precipitate within 16 days after the flood, with part of these salts establishing themselves as colloidal particles that can adsorb Pb and Cd. In the case of H₂S, its production intensifies in Eh₇ ≤ -0.21 V (James and Brose, 2011).

In flooded acidic soils, SO₄⁻² activity is initially increased by solubilizing the Fe and Al oxides that retain them in the exchange complex, proceeding with their slow reduction until disappearing in a few months (Hemati Matin and Jalali, 2017; Sousa *et al.*, 2019; Ponnampereuma, 1972). In alkaline soils, for



example, the total reduction of 1.56 cmol_e dm⁻³ of SO₄²⁻ occurred within 6 weeks (Ponnampertuma, 1972). Along with the decline in the amount of SO₄²⁻ ions in the soil, the concentration of Fe⁺² also decreases, due to the formation of insoluble FeS_x minerals (Strawn *et al.*, 2020; Mello and Perez, 2019) (Equation 7).



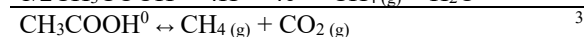
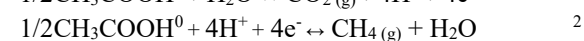
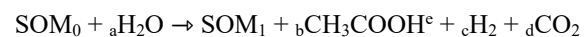
¹: log K^o: 35.70.

²: log K^o: 3 x (26.93).

³: log K^o: 35.70 + 3 x (26.93) = 116.49. (7)

Source: Adapted from Mello and Perez (2019).

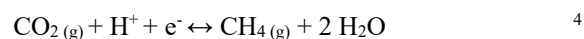
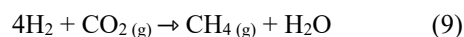
In extremely reduced environments (Eh₇ -0.24 V and/or pe + pH < 3.0, considering pH at 7.0), with low availability of secondary electron acceptors, SOM fermentation becomes necessary for the obtaining energy for anaerobic microorganisms (Strawn *et al.*, 2020; Lindsay, 1979; James and Brose, 2011). For this to occur, the hydrolysis and decomposition of SOM in flooded areas requires the syntrophic cooperation of anaerobic bacteria and methanogenic *Archaea* (Dušek *et al.*, 2020; Conrad, 2020). Thus, these microorganisms act on the dissimilation of organic substrates into acetic acid, alcohol, formic acid and CO₂, which are then converted into CH₄ and acetate (Lindsay, 1979) by the methanogenic microbiota (Dušek *et al.*, 2020). This process can be seen in equations 8, 9 and 10 below.



¹: log K^o: -7,20.

²: log K^o: 15,72.

³: log K^o: -7,52 + 15,72 = 8,52. (8)



⁴: pe⁰ = -4,13. (10)

Source: Adapted from Lindsay (1979) and Kirk (2004).

Degradation of SOM to CH₄ should start after all secondary electron acceptors have been depleted, such that the ΔG (Gibbs free energy) of the CH₄ producing depolymerization is less than that of those redox reactions at the alternative electron acceptor terminals. (Conrad, 2020). Therefore, the production of CH₄ is not very expressive in environments of pe + pH > 7.0 (Lindsay, 1979). The methanogenesis step is also accompanied by increased Fe⁺² activity, as there are not high amounts of H₂S to produce FeS_x minerals (Strawn *et al.*, 2020; Kehew, 2000).

In swamps, where methanogenesis is intense and there is a high input of SOM, a high amount of CH₄ gas is released to the atmosphere through boiling or bubbles, coming from a strong cloud of gas with enough pressure to break the pressure of the column of water over the gas accumulation zone (Bridgham *et al.*, 2013; Dušek *et al.*, 2020). The accumulated CO₂ produced by microbial activity can also be released in large proportions by this same process (Sousa *et al.*, 2019).

In hydromorphic soils of pe + pH > 4.0 (considering neutral pH), the CO₂ released by root respiration and by the soil microbiological community can reach levels of 0.0003 to 0.3 atm, given the low diffusion of CO₂ in water (Dušek *et al.*, 2020; Lindsay, 1979). The CO₂ dissolved in flooded soils has a direct impact on the pH and on the activity of the species HCO₃⁻, as it acts on the solubilization of soil minerals due to the greater acidity of the water and the potentiation of hydrolysis (Sousa *et al.*, 2019; Zu *et al.*, 2022). In flooded calcareous soils, for example, the CO₂ activity is much higher than in non-calcareous mineral soils, because there is high dissolution of CaCO₃ (Hemati Matin and Jalali, 2017).

In regions of soils with more recent formations or with low intensity of weathering, such as bivalent environments, if temporary water stagnation occurs and hydrolysis is potentiated by the greater acidity of the water, an intense dissolution of minerals rich in basic cations occurs (Van Breemen and Burman, 2002; Turk *et al.* 2011). Parts of these bases can be leached and concentrate in the subsurface horizon when part of the water is percolated, saturating it with carbonate minerals (Turk *et al.* 2011; Strawn *et al.*, 2020).

CONCLUSION

The chemical balance established in hydromorphic soils is directly related to the availability of organic substrate for the action of the microbial community, the intensity of electrons to be transferred to the final receptors and the chemical species available to control the electrical potential of the soil. NO₃⁻, Mn⁴⁺, Fe³⁺ and SO₄²⁻ ions are the main alternative electron acceptors when O₂ is depleted in the soil solution. As the electrical potential of the soil is reduced, a certain chemical species starts to control the electrical potential of the soil and also to buffer it, until all its still oxidized amount is available. With the reduction of ions and elements in mineral phases, the soils of flooded environments acquire a grayish color, with neutral expressions of clay minerals, with or without mottles of Fe and Mn. In extremely reduced environments (pe + pH < 3.0, considering the pH at 7.0) and with the depletion of alternative electron acceptors, the fermentation of organic substrates and



methanogenesis become the main sources of energy for the soil microbiological community.

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