The influence of peat layer above sulphidic material on iron dynamic in wetland

A Fahmi*, A Hairani, and B Radjagukguk

1 Indonesian Swampland Agricultural Research Institute (ISARI), Jln Kebun Karet, Loktabat Utara, Banjarbaru, Kalimantan Selatan, Indonesia.
2 Soil Science, Agricultural Faculty, Gadjah Mada University, Yogyakarta, Indonesia.

*Corresponding author: fahmi.nbl@gmail.com

Abstract. Most of peatland in Indonesia are found on tidal swamp area, and most of them have sulphidic material as substratum. Iron (Fe) is the main metal cation which found in sulphidic material, its solubility increases with decreasing soil acidity. Peat layer is an organic material which high affinity on metal cation such as Fe. This review addresses Fe solubility dynamic due to depletion and disappear peat layer in peatland sulphidic material as substratum. Iron in peatland was origin from sulphidic material layer, the presence of Fe in peat layer was caused of Fe movement from sulphidic material to upper layer. The naturally disappear and depletion of peat layer may increase Fe²⁺ concentration in wetland.

Keywords: Iron, sulphidic material, peatland, and wetland.

1. Introduction
Iron represent the fourth most abundant elements in earth. Iron is an essential element in all organisms and is involved in various essential functions. Iron typically present as oxides, hydroxides, sulfides, carbonates and sulfates [1]. Each mineral form is strongly influenced by many environmental factors such as redox potential, pH, organic matter, soil moisture, microorganisms, and anions and its behavior.

Iron biogeochemical property is very complicated and related to many biotic and abiotic processes in nature. In swamp lands, Fe minerals are mostly found in the form as goethite (α - FeOOH), pyrite (FeS₂), lepidocrocite (γ - FeOOH), schwertmannite (Fe₁₆ O₁₆ (SO₄)₃ (OH)₁₀ 10 H₂O), ferrihydrite (Fe₃HO₈ 4 H₂O), jarosite (KFe₃(SO₄)₂ (OH)₆), siderite (FeCO₃), vivianite (Fe₃ (PO₄)₂), strengite (FePO₄) and trolite (FeS), [2, 3, 4, 5, 6, 7]. Minerals such as gutite, pyrite, and schwertmannite which available in acid sulfate soils are origin from sulfidic materials. The high solubility of Fe in swamp lands is toxic for plants and pollutes the surrounding environment.

Peat soils in the tropics are formed due to accumulation rate of organic matter is higher than its decomposition rate. During the accumulation process there is a tendency for differences in peat thickness based on its distance from rivers or sea [8]. Peat layer are generally found in layers as a reflection from the dynamics of environmental conditions during the its formation process.
According to Rieley and Page [9] the difference in peat thickness reflects peat age. The thicker of peat layer the older age of its age, each layer shows different constituent materials therefore each layer may show different properties. These properties can be seen in the form of the level of decomposition, and furthermore influence to the nature of their interactions with metals or nutrients [10].

Peat soils are mainly composed of organic matter, at least contain 18% or more organic-C if the mineral fraction contains 60% or more clay; or more than 12% if the mineral fraction contains no clay [11]. Peat soils are rich in humic substances such as humic acid and fulvic acid. These materials have an important role in properties of soil. This role is influenced by humification stage. Humic substances content increase with decomposition stage [12]. Humic material have a large affinity for metal ions in the soil, its ability is highly depending on the content of its functional moieties or its total acidity. Humic acid has lower total acidity values than fulvic acid, and the substantially larger molecules and more complexes structures of humic acid to be more effective than fulvic acid in complexation or chelation [13].

About 10.52 million ha of peatlands in Indonesia are found on tidal areas [14], most of them have sulfidic material layer underneath. Naturally, peat material and sulphidic materials are interacted to forms a dynamic balance according to other environmental factors. This means that peat has an important role in reducing solubility of Fe which origin from sulphidic materials. This paper is constructed to provide an overview on the dynamics of Fe solubility as a consequently the loss of peat layers in peatlands with sulphidic material substratum.

2. Research Methodology

The overview the influence of peat layer on dynamics of Fe solubility in wetland was constructed from first year observation which has published in [15] and data from the second-year observation. The data was collected from the results of study that conducted on three (shallow, moderate, and deep) ombrogen peatlands. In addition, on the present research additional observation were also conducted at peatly acid sulphate soil (PASS) and potential acid sulphate soil (ASS), shallow peatland which all of peat layers were removed (SP 0) and shallow peatland which partially of peat layers were removed (SP 0.5) (Figure 1). They were a reflection from “degraded peatlands”, in the term for peatland which peat layer was disappeared or depleted in naturally for PASS and ASS or consciously excavated by man for SP 0 and SP 0.5. They were spread in one area and each of them were separated by tertiary channels. The research area was idle land with mixed vegetation that dominated by rubbers and shrubs. The research location is in Pangkoh 9, Pulang Pisau Regency, Central Kalimantan. The study site is located about 10 km the west of the Kahayyan River and 20 km the east of the Sebangau River.

Soil samples were collected with peat auger for peat soil and Belgium auger type for mineral soil. Soil sampling points were taken based on the presence of an interlayer layer (the boundary layer between peat and mineral material) and soil profile conditions (figure 1). Therefore, the number of sample points were different for each site. The soil sampling depth were (in cm) 90 and 125 for SP 0; 50, 90 and 125 for SP 0.5 ; 25, 50 and 75 for PASS; 25, 50, 75, 95, 115 and 135 for Shallow ; 50, 100, 120, 135 and 155 for Moderate; 50, 150, 200, 225, 245 and 265 for Deep peatland, respectively (Figure 1). In each study site, sampling points were replicated three times.

Peat decomposition stage was determined with the Na-pyrophosphate index [16]. Based on those method, it was found peat sapric decomposition stage in upper layer of shallow peatland, whereas in moderate and deep peatland were found two type peat layers, i.e. sapric in the upper layer and hemic in the lower layer (Figure 1). Parameters observed in this study were Fe$^{2+}$ (extracted with 1 N NH$_4$OAc pH 4.8), organic-Fe (extracted with 0.1 M Na$_2$P$_2$O$_7$) and total-Fe (extracted with HClO$_4$ + HNO$_3$ + H$_2$SO$_4$). They were measured with an atomic absorption spectrophotometer (AAS) [17; 18]. All the parameters were observed on transition from wet to dry season (T), peak of dry season (DS) and peak of wet season (WS).
3. Results and discussion

Based on figure 2, there were dissolved-Fe\(^{2+}\) in peat layers of shallow, moderate, and deep peat land even though in low concentration. The presence of Fe\(^{2+}\) measured in the peat layer showed that Fe\(^{2+}\) in peat layer especially in the nearest layer of sulfidic material indicated that Fe\(^{2+}\) moved to uppermost layer [15]. According to Tan [13] Fe\(^{2+}\) was more mobile than Fe\(^{3+}\), it may be moved to the upper layer with ground water level movements due to tidal force or high rainfall. However, figure 2 showed that Fe\(^{2+}\) concentration in sulfidic material layer was higher than in peat layer, this fact caused by high content of Fe, especially pyrite FeS\(_2\) in these mineral layers. Previously, similar results have been reported by Haraguchi et al [19] who conducted research in the Paduran area, Pulang Pisau Regency.

Figure 2. Exchangeable Fe\(^{2+}\) in SP 0, SP 0.5, ASS, PASS, shallow, moderate, and deep peatland that observed on dry season (green), wet season (yellow) and transition from wet to dry season (white).
Table 1: The average percentage of Fe\(^{2+}\) and organic-Fe content from total-Fe on sampling points in shallow, moderate, and deep peatland for two-time observations.

| Sampling points | Fe\(^{2+}\) (%) | Organic-Fe (%) |
|-----------------|-----------------|---------------|
|                 | First year*     | Second year   | First year* | Second year |
| **Shallow peat**|                 |               |             |             |
| G.s\(_2\)       | 0.0             | 0.0           | 81.0        | 77.2        |
| G.s\(_1\)       | 1.7             | 0.0           | 77.0        | 68.9        |
| Int.s           | 2.2             | 0.1           | 21.7        | 43.7        |
| M.s\(_1\)       | 11.3            | 0.3           | 22.5        | 32.7        |
| M.s\(_2\)       | 2.3             | 2.2           | 80.0        | 53.0        |
| M.s\(_3\)       | -               | 2.1           | -           | 69.7        |
| **Moderate peat**|                |               |             |             |
| G.m\(_2\)       | 1.8             | 0.0           | 80.0        | 78.1        |
| G.m\(_1\)       | 7.9             | 0.2           | 84.7        | 43.3        |
| Int.m           | 1.3             | 0.6           | 76.7        | 38.3        |
| M.m\(_1\)       | 3.5             | 1.4           | 93.3        | 62.3        |
| M.m\(_2\)       | -               | 1.5           | -           | 92.3        |
| **Deep peat**   |                 |               |             |             |
| G.d\(_2\)       | 0.0             | 0.1           | 51.2        | 81.5        |
| G.d\(_1\)       | 0.0             | 0.2           | 87.7        | 32.3        |
| Int.d           | 8.0             | 0.2           | 44.0        | 46.6        |
| M.d\(_1\)       | 3.2             | 0.1           | 88.6        | 33.3        |
| M.d\(_2\)       | 2.7             | 2.0           | 95.4        | 84.0        |
| M.d\(_3\)       | -               | 1.3           | -           | 71.1        |

* [15]

The concentration of organic-Fe on the surface of ASS was lower than to PASS, shallow, moderate, and deep peatland. Low organic-Fe concentration related with the absence of peat layer on the surface of ASS. This condition indicated that peat layers has important role in suppressing Fe solubility in tidal soils, especially peatlands with sulphidic material substratum and acid sulphate soils that associated with peatlands. According to Harvey and McCormick [20] peatlands have an important contribution to changes in water and mineral quality in peatlands and surrounding areas.

The important role of peat layer over sulfidic material might be seen by comparing the data of Fe\(^{2+}\) concentration in PASS and ASS with data of Fe\(^{2+}\) in shallow, moderate and deep peatland (Figure 2). It is known that Fe\(^{2+}\) concentrations in the upper layer of PASS and ASS were consistently higher than shallow, moderate, and deep peatland. This condition confirmed the important role of peat layer as organic material on Fe solubility. This result is accordance with the statements of Karlsson and Persson [21] and Ye et al [22] that the cycle, solubility and mobility of Fe in soils was largely determined by the presence of organic matter in the soil.

There were no differences of Fe\(^{2+}\) and organic-Fe concentrations in SP 0 and SP 0.5 compared shallow (Figures 2 and 3). This suggests that peatland properties did not immediately change after their peat layer recent excavating. This condition related with shortly interval time between soil sampling and excavation. In addition, shallow, SP 0 and SP 0.5 were in flooded condition (data not shown) during those interval time leads geochemical reactions or microorganism activity were relatively similar.
Figure 3. Organic-Fe in SP 0, SP 0.5, ASS, PASS, shallow, moderate and deep peatland that observed on dry season (green), wet season (yellow) and transition from wet to dry season (white).

4. Conclusion
Based on observation results, the highest Fe$^{2+}$ concentration was in the sulphidic material layer. If peat layer was above sulphidic material layers, dissolved Fe$^{2+}$ can be found in it, and its concentration pattern is decrease with increasing peat thickness. The presence of Fe$^{2+}$ that measured in the peat layer is origin from sulphidic material layer. The solubility of Fe$^{2+}$ in the peat layer was determined by peat layer thickness, the disappeared or depleted of peat layer in naturally or consciously excavated by man has caused an increase in Fe$^{2+}$ concentration in wetland.

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