The role of peat decomposition stage on iron solubility and distribution in tidal swamps

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Abstract. Most peat layers laying above sulfidic materials have important role in the geochemical cycle in tidal swampland. Depletion of the peat layer increase metal solubility and acidity from sulfidic materials which then potentially polluting and decreasing the quality of the surrounding environment. The purpose of this review was to describe the influence of peat layer thickness and its decomposition stage on iron solubility and distribution in the profile of peat soils and acid sulphate soils located around peatlands. This paper used observational data from a number of articles on peatlands with varies thickness and acid sulphate soils. Peat decomposition stage has important role on the distribution of Fe, the movement and ability of complex formation with Fe. Most of the Fe ions in peatlands were in organic complex form, and organic–Fe concentration in sapric peat layer was higher than hemic peat layer.

1. Introduction
In Indonesia, most of peatlands are found in association with acid sulphate soil (ASS), which its total area is increasing over time due to the depletion or disappearance of peat layers laying above sulfidic layers. Peat fires at the dry season occurring almost every year has caused severe environmental damages and changes in the soil chemical properties, both peat and acid sulphate soils. Peat layers protect the underlying mineral soils from oxidation and dissolution of iron compounds that potentially contaminate the surrounding environment. Tropical peats is formed due to higher rate of organic matter accumulation than decomposition. Sorensen [1] estimated peat formation rate for Indonesian peatlands ranges from 1–2 mm year⁻¹. Several studies on tropical peatlands have emphasized that the peat formation of contemporary deposits has been a dynamic process, and the periods of alternating accumulation, depend dominantly on the factors that influence to soil formation process. Rieley and Page [2] stated that the difference in peat thickness and material reflects its different characteristics.

Peat is rich in humic and fulvic acids and, these organic compounds play important roles on metal element solubility and mobility in the soil. Specifically, their important role is determined by their functional moieties or total acidity. Orru et al. [3] stated that humic substances content is determined by the peat decomposition stage. More decomposed peat material produces higher humic acid than fulvic acid. In addition, the concentrations of humic and fulvic acids in peat layer are influenced by their mobility and molecular stability. According to Dinu [4], fulvic acid is more mobile and less stable than humic acid [5].

Iron (Fe) ion is the fourth most abundant element in the earth crust. Iron plays important role in biogeochemical cycles of many elements in natural environment, especially in wetland soils. Iron in
tidal swamp originates from sulphidic materials [6], and its solubility can vary with soil type. Acid sulphate soils typically have higher iron concentration than peat soils. Iron mobility varies with their forms where ferro (Fe\(^{2+}\)) is more mobile than ferri (Fe\(^{3+}\)) [7], and complex of Fe organic substance is more mobile than iron-hydroxide [8]. Furthermore, the mobility and solubility of an element or mineral determine their distribution in soil profile. In acid sulphate soil, high Fe\(^{2+}\) concentration leads to toxicity for plant while in peat soils, its low solubility leads to deficiency. The presence of a peat layer above sulfidic materials is a natural phenomenon that found in tidal swamps. In the terms of Fe solubility, the interaction of peat with Fe is an important phenomenon to study more deeply. Previously, Fahmi et al. [6] concluded that Fe\(^{2+}\) solubility in peatland is determined by peat layer thickness. Whereas this paper was constructed to provide an overview on iron distribution in the profile of peat and acid sulphate soils in relation to peat layer thickness and decomposition stage, in addition the recent paper will confirmed the dominant mechanism that occurred which lead higher organic–Fe concentration in the sulfidic material layers than in the peat layers.

2. Methodology
This paper used observational data from a number of articles on peatlands which vary in thickness and acid sulphate soils [6,9,10]. Fe data published in this papers were reinterpreted with different perspectives and theories to enrich or increase the repertoire of knowledge by comparing Fe data in ASS, peaty acid sulphate soil (PASS), and shallow, moderate and deep peatlands.

3. Role of peat decomposition stage on iron solubility and distribution
The highest Fe\(^{2+}\) concentration was found in mineral soil layer, located either below the peat layers of shallow, moderate and deep peatlands or in the top layers of ASS. Based on the presence of peat layer above sulfidic material layer, the Fe\(^{2+}\) was not detected in top layer of PASS, shallow, moderate and deep peatlands in addition there were no differences inorganic–Fe concentration measured in PASS, shallow, moderate and deep peatlands (figure 1) which suggested that peat layer thickness has no effect on Fe\(^{2+}\) concentration in soils with peat layer laying above them. Large content of organic compound in the peat layer leading Fe\(^{2+}\) was not detected because most of Fe ions were chelated by humic substances. This fact is revealed by data indicating most of the Fe in the peat layer was in organic form (table 1). These data are in line with the previous research conducted by Yonebayashi [11], who stated that most of the Fe in tropical peat soils is in complex form with organic compounds and only about 4–5% is in solubile and exchangeable forms.

Based on the sampling point position in soil profile, organic–Fe concentration in the peat layer (the closest point to the sulphidic material layer) from shallow peatland was higher than moderate and deep peatlands (figure 1), which means more Fe ion were chelated by humic material in shallow peat layer than moderate and deep peatland. It indicates that there is a different ability in complex formation of sapric and hemic peats to chelate Fe where, the chelating ability of peat materials is highly dependent on the humic acid content. It is known that peat decomposition stages at these point on shallow peatland was characterized as sapric peat, while peat decomposition stages on moderate and deep peatlands were characterized as hemic peat (figure 1 and 2). According to Salampak [12] humic acid is more abundant in sapric than hemic peats while fulvic acid content in hemic peat is more abundant than in sapric peat. Humic acid is more effective than fulvic acid in the complex formation [12,4].

For shallow, moderate, and deep peatlands and PASS, organic–Fe concentration in the sulphidic material layer was higher than that in the peat layer (figure 2). Fahmi et al. [9] observed that organic–Fe was only found in shallow, moderate, and deep peatlands, and was also reported in similar pattern. They stated that this fact can be explained in two mechanisms, which possibly simultaneously occur or one of them dominates. First mechanism, humic material leached from the peat layer to the mineral layer, and then forms a complex with Fe. The high binding capacity of organic matter in peat waters facilitates metal mobility [13]. The second mechanism, Fe from the sulphidic material layer moves to the upper layer (peat layer) then forms a complex, which then moves to the lower layer (sulphidic material layer). Fe may move vertically to the upper layer simultaneously with ground water level.
movement [7], capillary [14] or due to redox fluctuations [15]. According to Gorham and Janssens [16] the presence of Fe in the peat layer is an evidence of the Fe movement from the mineral layer to the peat layer (figure 3). Ye et al. [17] stated that the profile of dissolved iron is strongly influenced by the abundance of organic ligands. The increasing Fe concentration occurs due to mixing mineral materials and peat materials [18].

Table 1. The concentration and percentage of Fe$^{2+}$ and organic–Fe in ASS, PASS, and shallow, moderate and deep peatlands for three observations [6,9,10].

| Sampling points (cm) | Acid sulphate soil (ASS)* | Peaty acid sulphate soil (PASS) | Shallow peatland | Moderate peatland | Deep peatland |
|---------------------|---------------------------|---------------------------------|------------------|-------------------|---------------|
|                     | Wet season | Observation time | Dry season | Wet season | Observation time | Dry season | Wet season | Observation time | Dry season |
|                     | Fe$^{2+}$ org.-Fe | Fe$^{2+}$ org.-Fe | Fe$^{2+}$ org.-Fe | Fe$^{2+}$ org.-Fe | Fe$^{2+}$ org.-Fe | Fe$^{2+}$ org.-Fe | Fe$^{2+}$ org.-Fe | Fe$^{2+}$ org.-Fe | Fe$^{2+}$ org.-Fe |
| –15                 | 242 | 9.7 | 103 | 4.1 | 3 | 0.1 | 530 | 25.3 | 79 | 1.8 | 626 | 15 |
| –40                 | 1,051 | 19.5 | 177 | 3.3 | 20 | 0.5 | 873 | 21.7 | 404 | 3.9 | 1,039 | 10.2 |
| Peat layer          | –10        | 239 | 6.0 | 1,945 | 49.4 | 5 | 0.2 | 1,545 | 75.3 | 78 | 2.9 | 858 | 32.5 |
| –80                 | 792 | 5.6 | 5,860 | 42.1 | 18 | 0.2 | 4,492 | 62.3 | 266 | 1.2 | 3,758 | 17.7 |
| Mineral layer       | –40        | 41 | 1.2 | 528 | 16.4 | 4 | 0.1 | 1,562 | 67.0 | 39 | 1.2 | 604 | 18.8 |
| –80                 | 792 | 5.6 | 5,860 | 42.1 | 18 | 0.2 | 4,492 | 62.3 | 266 | 1.2 | 3,758 | 17.7 |
| –90                 | nd         | 0 | 223 | 25.7 | 87 | 1.3 | 709 | 10.7 | 14 | 0.6 | 875 | 40.4 |
| –110                | 103 | 4.4 | 1,810 | 77.7 | 223 | 1.0 | 5,024 | 24.3 | 54 | 1.9 | 1,514 | 55.1 |
| –135                | 509 | 4.7 | 10,146 | 94.6 | 322 | 1.5 | 6,225 | 29.5 | 170 | 1.3 | 7,808 | 64.0 |
| –50                 | nd         | 0 | 499 | 85.7 | nd | 0 | 118 | 38.1 | nd | 0 | 764 | 53.0 |
| –100                | nd         | 0 | 270 | 10.1 | nd | 0 | 116 | 4.1 | nd | 0 | 281 | 32.8 |
| –135                | 163 | 2.9 | 3,873 | 69.2 | 93 | 0.75 | 3,563 | 28.9 | 97 | 1.1 | 4,162 | 48.0 |
| –135                | 280 | 2.4 | 11,049 | 97.3 | 361 | 1.59 | 6,387 | 28.2 | 234 | 1.8 | 10,600 | 83.1 |
| –50                 | nd         | 0 | 186 | 64.9 | nd | 0 | 85 | 84.8 | nd | 0 | 1,360 | 80.5 |
| –150                | nd         | 0 | 0 | 0 | nd | 0 | 5 | 4.6 | nd | 0 | 7 | 0.7 |
| –200                | nd         | 0 | 42 | 37.8 | nd | 0 | 14 | 10.6 | nd | 0 | 161 | 30.5 |
| –245                | 139 | 5.7 | 2,323 | 95.7 | 64 | 0.8 | 2,711 | 36.9 | 15 | 0.2 | 6,419 | 83.4 |
| –265                | 263 | 2.4 | 10,377 | 95.7 | 86 | 0.6 | 3,325 | 23.1 | 185 | 1.3 | 9,920 | 69.8 |

Note: nd = not detected.
Figure 1. The concentration of Fe$^{2+}$ in ASS, PASS, shallow, moderate and deep peatland [6,9,10].

Figure 2. The concentration of organic-Fe in ASS, PASS, and shallow, moderate and deep peatlands [6,9,10].

Figure 3. The concentration Fe in peatland based on soil depth [16].
In addition, this phenomenon can also be explained by differences in the mobility level and molecular stability of humic and fulvic acids contained in the peat material. According to Dinu [4], fulvic acid is more mobile than humic acid, and Dou et al. [6] stated that humic acid molecules are more stable than fulvic acid. Therefore, it is argued that complex of Fe–humic acid deriving from sapric peat will accumulate at its formation point (sapric peat layer), while complex of Fe–fulvic acid originating from hemic peat becomes more mobile and accumulates in other layers. Based on those facts, the recent paper confirmed that the dominant mechanism or second mechanism occurred which lead higher organic–Fe concentration in the sulphidic material layer than in the peat layer, Fe from the sulphidic material layer moves to the upper layer (peat layer) and forms a complex, and then the complex moves to the lower layer.

4. Conclusions

It can be concluded that peat decomposition stages had important role on the distribution of Fe, and the movement and ability of complex formation with Fe. The organic–Fe complexes found in sapric peat are consistently accumulated more at the site of formation than Fe found in hemic peat. However, organic–Fe complexes are more mobile than Fe mineral which lead them to accumulate in lowest layer (sulphidic material).

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