

DISTRIBUTION PROFILE OF IRON FRACTIONS IN ACID SULFATE SOIL FROM SECONDARY SWAMP FOREST – MERAUKE PAPUA

Yohanes B.J. Rusmanta^{1,*}, Ahyar Ahmad¹, Indah Raya¹ and Bachrul Ibrahim²

¹Department of Chemistry, ²Department of Soil Science
Hasanuddin University, Indonesia

E-mail: ruspapua@yahoo.com (*Corresponding Author)

Abstract: Acid sulfate soils (ASS) have become a problem for rice farming in Merauke Regency of Papua Province. Newly opened rice fields that used to be swamp, secondary swamp forest or primary swamp forest usually have soil acidity problems. This research had been conducted to find out the soil fractions of acid sulfate soil at secondary swamp forest environment. So, the iron fraction distribution profile in ASS can be described in more detail. The benefit is the determination of problem-solving strategies to be more precise. In this study, a series of sequential analyzes were performed to find the iron fractions in the soil. The profile of iron fractions in this study consisted of fraction I or EFLE, fraction II or acid reducible, fraction III or organic oxidizable, and fraction IV or resistant. Different solvents were used sequentially to extract iron from the sample, but to measure iron used AAS. Sampling was conducted from secondary swamp forests located in the Kumb River border area. The result is in secondary swamp forest (SSF), high total iron concentrations in the upper layer and decreased steadily to a depth of 50 cm. In the secondary forest (SF), total iron concentrations tend to be flat and slightly increased at a depth of 30 - 50 cm. Iron concentration of AR fraction is the most of the other fraction. The strategy to overcome the acid sulfate problem in this place is to stop water coming from iron-rich swamps. Then prevents iron oxidation from secondary mineral fraction (AR) by addition of organic materials. After that, planting plants that are phyto-remediator to reduce the amount of iron in the soil.

Keywords: acid sulfate soil (ASS), iron fraction in soil, sequential extraction techniques (SET).

1. Introduction

Acid sulfate soil are soil which are severely acidic, or have the potential to become acidic, as a result of oxidation of iron sulphide (van Breemen, 1973). The iron sulfide are most commonly in the form of pyrite (FeS_2) but may also include marcasite (FeS_2), greigite (Fe_3S_4) and mackinawite (FeS) (Bush and Sullivan, 1997; Bush et al., 2004; Burton et al., 2008a). Acid sulfate soil (ASS) reduce groundwater quality, because they are acidic and contain excessive amounts of metals (Claff, et al. 2011), especially iron and aluminum (Osterholm and Astrom 2002). ASS also interfere with biological life and destroy infrastructure (Sammut, et al., 1995). Sources of acid or hydrogenium ions and metal ions are derived from ASS leaching when oxidized and washed (Kinsela, Collins and Waite 2011).

ASS problem can be solved in various ways, ranging from amelioration is by fertilizer containing phosphate, to give a good irrigation system, until phytoremediation (Johnston, Slavich and Hirst 2005). Each type of these efforts has advantages and disadvantages. Amelioration requires a high cost because it takes a lot of ameliorant to overcome the problem of excess acid per hectare (Claff, et al. 2011). Provision of a good irrigation system and phytoremediation takes a long time (Indraratna, et al. 2006).

Iron minerals are ubiquitous in ASS environments (van Breemen, 1973; Bigham et al., 1996; Bush and Sullivan, 1997; Åström and Corin, 2000; Fanning et al., 2002, Bush et al., 2004; Boman et al., 2008; Burton et al., 2008a), and exert a major influence on biogeochemical processes (Bigham et al., 1996; Jones et al., 2006). Iron transformations also greatly affect and often control the cycling of trace metals and other contaminants (Burton et al., 2008b). As such, an understanding of iron behavior in ASS can provide insight into redox processes, biogeochemical pathways and the mobility of trace elements (Claff, et al. 2011).

In this study, we used sequential extraction techniques (SET) introduced by Badri and Aston (Badri and Aston 1984) and used by Naji et al (Naji, Ismail and Ismail 2010). In this study, we measured iron concentrations in four fractions in three different types of land. The first type of land is a secondary swamp forest that is submerged to a depth of 2 meters during the rainy season, the second type of land is the same type of forest that is submerged to a depth of 1 meter during the rainy season, and the third type is secondary forest that is not submerged during the rainy season. The results are used to confirm the iron content in each fraction of each soil layer and each type of landscape. The result is to give a more complete picture of the iron fractions in the soil in different soil types, so that it can be determined what remediation techniques are suitable for use.

2. Methodology

2.1. Description of the Sampling Sites

The soil samples consist of three locations taken from the banks of the Kumb River in the District of Kurik Merauke Regency. The distance between the three locations is about 100 meters each. The first location (A) and the second one (B) are in the secondary swamp forest which is dominated by the *Melaleuca cajuputi* trees. The place is waterlogged as high as 1 to 2 meters in the rainy season, while in the dry season the place is dry. The third location (C) as a benchmark, taken from the edge of the secondary swamp forest which is slightly inundated during the rainy season. The dominating plant is no longer the *Melaleuca cajuputi* trees, but rather has been mixed with several *Acacia* trees.

2.1. Sampling

Samples were collected using plastic pipe instead of ring soil sampler. PVC pipes with diameter of 2 inches and length of 5 cm each for topsoil and 10 cm for subsoil. Samples are numbered according to the sample point, the repetition, and the sample depth is 0-5cm, 5-10cm, 10-15cm, 15-20cm, 20-30cm, and 30-40cm, up to 40-50 cm. Soil samples were put into plastic bags to prevent contamination and were immediately taken to the laboratory to be characterized and analyzed.

3.1. Samples Analysis

First, sample characterization is measured water content and pH. The two are sequentially extraction according to those introduced by Yap known as sequential extraction techniques or SET (Badri and Aston 1984, and Najji et al 2010). Then the first extraction with sodium acetate solvent produce extracts of metals that are easily, freely, leachable and exchangeable (EFLE). The second extraction with hydroxylamine ($\text{NH}_2\text{OH}\cdot\text{HCl}$) results in metals classified in the Acid Reducible (AR) fraction or metals bound to secondary minerals. The third extraction using H_2O_2 solvent produces a metal fraction bound to organic compounds. Finally, the fourth step is the sample destruction of the remaining third step using HNO_3 and HClO_4 .

3. Result and Discussion

3.1. pH

The pH measurement results are shown in Table 1. The pH value indicates that the soil sample is very acidic, ranging from 3.5 to 4.8 on top soil layer (0-20 cm) and pH 4.2 - 5.5 on deeper soil layer (20 - 50 cm).

Table 1: pH in Secondary Swamp Forest (SSF) and Secondary Forest (SF) Soils

Depth (cm)	pH at SSF 2	pH at SSF 1	pH at SF
0 – 5	3.5	3.6	4,0
5 – 10	3.5	3.5	4.1
10 – 15	4.2	4.8	4.2
15 – 20	4.8	4.8	4.4
20 – 30	4.7	5.4	4.2
30 – 40	5.5	5.4	4.8
40 – 50	5.5	5.5	5.2

3.2. Distribution of Iron Fractions

The measurement of iron fractions is shown in Table – 2. The concentrations of iron fractions vary within each depth and location of sampling.

Table 2a: Distribution of iron as EFLE fraction in different depth of soil and type of forest soil

Depth (cm)	SSF 2 ($\mu\text{g Fe/g}$)	SD	SSF 1 ($\mu\text{g Fe/g}$)	SD	SF ($\mu\text{g Fe/g}$)	SD
-5	191	116	564	229	245	124
-10	59	11	467	150	258	98
-15	193	40	125	70	210	66
-20	271	82	174	93	287	89
-30	399	186	198	56	208	54
-40	482	233	104	28	127	40
-50	672	389	47	10	118	19

Iron EFLE fractions are at a level indicating that the soil is acid sulphate soil (Ebimol, et al. 2017). The iron concentration of the EFLE fraction of SSF is much higher than the EFLE iron concentration of secondary forest (SF), at a depth of soil 0-10 cm. Usually a layer of 0-5 cm is an organic layer and a layer of 5-20 cm is top soil. This indicates that weathering of secondary minerals and organic materials occurs mostly in the organic layer and upper of topsoil layers in secondary swamp forests (SSF). In the SF and subsoil of SSF, weathering occurs tend to be evenly distributed. EFLE iron also comes from other places carried by water when the location is inundated. That makes the EFLE iron concentration in SSF-2 higher than in SS-1 and SF.

Table 2b: Concentration of Iron as Fraction II (*Acid Reducible*) in different depth of soil and type of forest soil

Depth (cm)	SSF 2 ($\mu\text{g Fe/g}$)	SD	SSF 1 ($\mu\text{g Fe/g}$)	SD	SF ($\mu\text{g Fe/g}$)	SD
0 – 5	32167	10525	17900	5635	3773	1093
5 – 10	11400	4107	12987	6221	3460	1378
10 – 15	1873	597	9673	3685	2340	702
15 – 20	3280	1470	5467	1484	1341	606
20 – 30	1387	457	9740	7247	786	212
30 – 40	1343	359	144	117	1025	309
40 – 50	434	93	199	55	1075	187

Iron fraction II (Acid Reducible) has the highest value among all fractions. The highest value is located in SSF-2, which is flooded the longest followed by SSF-1 that is in shorter flood and location SF that is not inundated. This large concentration occurs in the uppermost layer (0 – 5 cm) SSF-2 and the second highest is in the location of SFF-1. Iron in the form of AR fraction is also derived from erosion occurring in other locations and sedimentation processes that occur in this location.

Table 2c: Concentration of Iron as Fraction III (*Oxidisable Organic*) in different depth of soil and type of forest soil

Depth (cm)	SSF 2 ($\mu\text{g e/g}$)	SD	SSF 1 ($\mu\text{g e/g}$)	SD	SF ($\mu\text{g Fe/g}$)	SD
-5	8563	5141	8620	4413	1342	540
-10	6933	3984	5450	2631	1325	435
-15	5433	2151	2890	1537	405	138
-20	2763	1202	2970	1028	355	139
-30	4337	1449	1735	927	874	286
-40	1343	457	2377	742	476	172
-50	4233	1368	1577	514	124	40

Iron as a fraction III bound to organic compounds in the soil is highest in the uppermost layer at the SSF-2 site and follows at the site of SSF-1. This happens because the process of decomposition of biomass that comes from the leaves of the forest continuously. Iron tends to bond with organic compounds present in the biomass and form complex compounds (Claff S. R., 2011). In all layers, the iron concentration of fraction III in SSF is higher than that of SF. this indicates that the biomass decomposition process is more common in SSF than in SF.

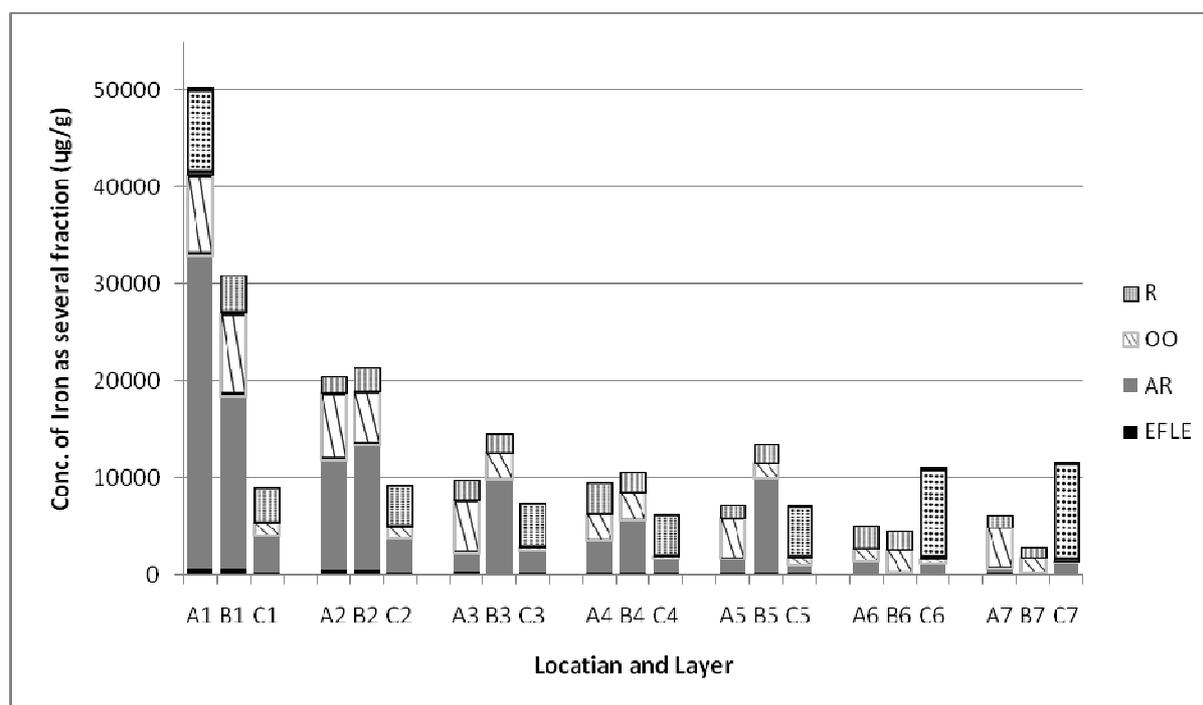
Table 2d: Concentration of Iron as Fraction IV (*Resistant*) in different depth of soil and type of forest soil

Depth (cm)	SSF 2 ($\mu\text{g e/g}$)	SD	SSF 1 ($\mu\text{g e/g}$)	SD	SF ($\mu\text{g Fe/g}$)	SD
0-5	8880	5262	3883	2084	3760	1107
5-10	1628	749	2577	1148	4283	1495
10-15	2117	1217	1823	566	4437	1461
15-20	3217	1692	2010	1025	4313	770
20-30	1315	424	1785	817	5370	1982
30-40	2483	815	1870	529	9483	3708
40-50	1267	237	1085	260	10460	2514

At layers 5 to 50 cm, iron fraction IV (Resistant) in SF is higher than in SSF. Resistant fraction indicates primary minerals in the soil. Highest concentration of this iron fraction in layer 30 – 50 cm of Swamp Forest (SF) mean primary minerals that rich in iron still have not been composed or wheatered. whereas a rather high iron concentration in layer 1 of SFF-2 indicates a sedimentation process.

Table 3: Concentration of total iron in different depth of soil and type of forest soil

Depth (cm)	SSF 2 ($\mu\text{g e/g}$)	SSF 1 ($\mu\text{g e/g}$)	SF ($\mu\text{g Fe/g}$)
0-5	50160	30957	9122
5-10	20438	21482	9326
10-15	9821	14512	7391
15-20	9534	10623	6295
20-30	7234	13458	7237
30-40	5228	4496	11110
40-50	6122	2907	11779



Figure– 1: Concentration of total iron as 4 fractions (EFLE, AR, OO, and R) in Different Depth (1 = 0-5cm; 2 = 5-10cm; 3 = 10-15cm; 4 = 15-20cm; 5 = 20-30cm; 6 = 30-40cm; 7 = 40-50cm) and Forest Type (A = SSF-2; B = SSF-1; and C = SF)

Highest concentration of total iron layer 1 (0-5cm) of Secondary Swamp Forest – 2 (SSF-2) soil is 50,160 $\mu\text{g/g}$. Second highest concentration of total iron is 30.957 $\mu\text{g/g}$, layer 1 of SSF-1 soil. For comparison data, total iron in vertisol soil Serbia is 68.428 $\mu\text{g/g}$ (Jelig, et al., 2011). The high total iron concentration in Secondary Swamp Forest (SSF) soil in layers 1 and 2 and continues to decline with increasing depth, indicates a sedimentation process. In other words, iron comes from somewhere else and settles in SSF-2 and SSF-1 soil. Both places are inundated during the rainy season. SSF-2 was inundated about 2 meters while SSF-1 was flooded up to 1 meter deep. When the dry season, both places are dry. Iron concentration in SF is tend to flat then slightly increase at 30 – 50 cm layer. In secondary forest (SF) there is no sedimentation process because it is not waterlogged even in the rainy season.

The possible strategies can be applied to overcome the acid sulfate soil problems in this place. We can inhibit the entry of acidic water from swamp. We can also created some new waterways that supply fresh water from different sources. Another strategy is to enrich organic materials in the soil. After that, we can apply the phytoremediation strategies to remedy excess of iron and others metals from the field.

4. Conclusion

Water puddle plays a role in the sedimentation process, which will form the first fraction of iron on the ground surface. This is what accelerates the formation of actual acid sulfate soil. Sulfuric acid in secondary swamp forests (SSF) undergoes a process of weathering primary minerals containing iron more rapidly than those occurring in secondary forests (SF). The strategy to overcome the acid sulfate problem in this place is to stop water coming from iron-rich swamps. Then prevents iron oxidation from secondary mineral fraction (AR) by addition of organic materials. After that, planting plants that are phyto-accumulator to reduce the amount of iron. The highest total iron concentrations in secondary swamp forest (SSF) are in the upper layer and decrease steadily to a depth of 50 cm. In the secondary forest (SF), total iron concentrations tend to be flat and slightly increased at a depth of 30 - 50 cm. Iron concentration in the form of AR fraction is the most of all types of fractions.

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