Distribution of pyrite depth and soil properties in fresh water swampland in North Candi Laras Sub-district, South Kalimantan Province

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Abstract. One of the challenges of swampland utilization for agricultural uses is the existence of pyrite (FeS$_2$), especially in the topsoil. The aim of this research was to study the distribution of pyrite position with depth and soil properties in fresh water swampland in North Candi Laras Sub-district, Tapin Regency, South Kalimantan Province. Pyrite layer was determined by using hydrogen peroxide (H$_2$O$_2$) and its unique reaction was marked by foam existence with soil pH <2.5. Ten soil samples analyzed to determine physical and chemical properties. The result of this research showed that pyrite depth varied from 25 cm to >100 cm. The depths of pyrite material were grouped into 25 to 50 cm, 51 to 75 cm, 76 to 100 cm, and 101 to 150 cm. The closer to the river, pyrite depth in the soil was deeper. The pyrite depth affected soil pH and cations. Soils containing pyrite material were very acidic with an average field soil pH 4.0 to 4.5. Cation Ca, K, Na levels were higher with the shallower pyrite depth in the soil, meanwhile Mg was almost same in all pyrite depth groups. The information of pyrite position within the soil is useful for controlling water table management to prevent pyrite oxidation.

1. Introduction
Swampland utilization for agricultural uses is one of the efforts made by the government to achieve food sovereignty. This step is also to offset agricultural land reduction in Java Island due to conversion of the agricultural land to non-agricultural land [1]. Swampland is part of the wetland ecosystem which is characterized by shallow or inundated groundwater level. Swampland is grouped into tidal and non-tidal swamp (fresh water swamp). Tidal swamp is influenced by ebb and flow of the sea and the river water. Fresh water swamp is affected by rainwater that falls in the local or surrounding and upstream areas [4].

One of the challenges of swampland utilization for agricultural uses is existence of pyrite (FeS$_2$). High levels of pyrite in topsoil can limit swampland utilization [5]. Pyrite is formed in soils originating from marine deposits in seawater or brackish that contain organic matter and sulphate-reducing bacteria. The bacteria reduce sulphate to sulphide in an anaerobic environment, such as the following reaction [6].

$$\text{Fe}_2\text{O}_3 + 4 (\text{SO}_4)^2^- + 8 \text{CH}_2\text{O} + \frac{1}{2} \text{O}_2 \rightarrow 2\text{FeS}_2 + 8 (\text{HCO}_3^-) + 4\text{H}_2\text{O}$$
Pyrite becomes dangerous if oxidized because it causes high acidity. The oxidation of pyrite produces sulfuric acid and jarosite mineral which interfere plant growth due to high acidity [7-9]. Pyrite oxidation occurs when acid sulphate soils are drained. Groundwater level will drop due to draining so that oxygen enters the soil horizon which causes the pyrite oxidized by the following reaction:

$$2 \text{FeS}_2 + 7 \text{O}_2 + 2 \text{H}_2\text{O} \rightarrow 2 \text{Fe}^{2+} + 4 (\text{SO}_4)^{2-} + 4 \text{H}^+$$

Pyrite oxidation produces iron, sulfate, and hydrogen [10,11]. Ion H⁺ was released through that reaction causes acid soil pH. In addition, acid soil pH also causes high availability of Fe and Al in the soil. The result of research in tidal swampland in Banyuasin [12] showed that the lower the pH, the higher Fe and Al availability. High Fe and Al content can poison plants. Furthermore, high levels of Fe and Al can bind P elements in the soil so they are not available for plants.

Based on the description above, the information of the pyrite depth needs to be known to prevent oxidized pyrite, especially during soil tillage. The study aims to determine the distribution of pyrite depth and soil properties in fresh water swampland in North Candi Laras Sub-district, Tapin Regency, South Kalimantan Province.

2. Materials and methods

This research was conducted in North Candi Laras Sub-district, Tapin Regency. Research areas are located between two major rivers, namely Nagara and Barito River. The two rivers greatly influence soil characteristics and properties in research area. Landforms in research area consisted of alluvial and fluvio marin landforms. Soil parent materials consisted of smooth alluvium (clay and silt), a little sand, marine deposits and thin organic matter. Soils in research area were dominated by Inceptisols, Entisols, and Histosols [14].

The average rainfall rate of North Candi Laras Sub-district area is 2,403 mm [15]. North Candi Laras Sub-district is categorized into C3 climate with six wet and five dry months [16]. Soil temperature regime in study area was isohyperthermic. Soil moisture regimes were udic and aquic. According to geological map sheets of Banjarmasin (1713) and Amuntai (1712), research area has an alluvium geological formation (Qa) which was composed of kaolinite clay deposits, sand filled dust, peat, gravel, and loose chunks from river and swamp deposits. River and swamp sediments consisted of clay, sand, mud, silt, and organic [17,14].

Soil observation was conducted using a peat auger with a length of 150 cm. Pyrite layer was determined by testing the soil of each layer using hydrogen peroxide (H₂O₂). The presence of pyrite in the soil was indicated by foam and soil pH of the reaction was <2.5. The layer which showed the pyrite was recorded. The observation of pyrite depth was carried out as many as 100 observation point to determine distribution of pyrite depth in the study location.

Ten soil samples were taken from each layer to determine physical and chemical properties. Sample testing was carried out in the laboratory of Soil Research Institute. Soil samples analysis included soil pH, organic carbon, total N, potential P and K, available P, exchangeable bases, cation exchange capacity (CEC), base saturation, and pyrite content. Soil pH measurement used 1:5 H₂O extractor to measure active (actual) acidity and 1 N KCl extractor to measure reserve (potential) acidity. Measurement of organic carbon used the Walkley and Black method and total N used the Kjeldahl method. Potential P and K was determined by 25% HCl extract which would dissolve various forms of phosphate and potassium compounds close to the total P and K levels. Exchangeable bases were measured by Atomic Absorption Spectrophotometer (ASS) for Ca and Mg and flame photometer for K and Mg. Measurement of exchangeable bases and cation exchange capacity (CEC) used 1 N NH₄OAC pH 7. Base saturation was calculated based on the number of bases divided by CEC and multiplied by 100% [13].
3. Results and discussion

3.1. Distribution of pyrite depth

Pyrite depths in the study area varied from 25 cm to >100 cm. Figure 1 shows its distribution. The pyrite depths were grouped into four classes, namely G1 (25 to 50 cm), G2 (51 to 75 cm), G3 (76 to 100 cm), and G4 (101 to 150 cm). Distribution of pyrite depths are presented by figure 1.

![Figure 1. Map of pyrite depths distribution.](image-url)

In the northern of study location, pyrite depths were more varied than the southern part. In the southern, pyrite depths were dominated by depth of 51 to 75 cm and 76 to 100 cm. However, the soils which is closer to the river had usually a deeper pyrite layer than soils that is further from the river. In the southern part of study location which is showed in figure 1, pyrite depth of G3 category (76 to 100 cm) was located closer to the river than pyrite depth of G1 category (25 to 50 cm) and G2 category (51 to 75). It happened because shallow pyrite layer near the river has been buried by river sediment. Otherwise, soils that were further from the river had shallower pyrite depths. In the middle to southern of study location, pyrite depths were dominated by G3 category (76 to 100 cm). Both of the rivers in study location influenced the variation of pyrite depths. In the northern part, the distance between Barito River and Niagara River is wider than in the southern part of the study area. In other hand, in the southern, the distance of the two rivers was closer till to the point where they originated from. The close distance between two rivers caused the flanked land to be exposed to high tides from the two rivers which carried a lot of sediment from the upstream, so that the sediment covers the pyrite layer which was once shallow. Therefore, pyrite layer in study location was deep and it was grouped into two categories which is G3 (76 to 100 cm) and G4 (101 to 150 cm) category. Based on the landform, the deep pyrite layer was found in levee landform, while shallow pyrite layer was found in medium swampland which the distance was further from the river.

3.2. Soil morphology properties

Soils were observed in the field based on the specific morphological properties, namely color, texture, pyrite depth, drainage, and others. Soils color were dominated by dark brown and yellowish dark brown with 7.5 YR to 10 YR hue. The color of the top soil was darker than sub soil. Soils texture were
dominated by clay, but in top soils were dominated by silty clay. Several observations were organic soil with sapric maturity and peaty clay, which is a mixture of peat and clay deposits.

**Table 1.** Morphological and physical attribute of pedons observed.

| Pedon | Depth (cm) | Matrix Color | Texture/maturity | pH field | Pyrite depth | pH foam (H$_2$O$_2$) | Drainage       |
|-------|------------|--------------|-----------------|----------|--------------|---------------------|-----------------|
| P1    | 0 - 13     | 7.5 YR 3/1   | Sapric          | 4.5      | 58           | 2.0                 | poorly drained  |
|       | 13 - 33    | 7.5 YR 3/2   | Peaty clay      | 4.0      |              |                     |                 |
|       | 33 - 58    | 10 YR 5/2    | C               | 4.0      |              |                     |                 |
|       | 58 - 125   | N5           | C               | 4.0      |              |                     |                 |
| P2    | 0 - 25     | 10 YR 7/2    | SiL             | 4.5      | 25           | 2.0                 | poorly drained  |
|       | 25 - 125   | N5           | C               | 4.0      |              |                     |                 |
| P3    | 0 - 30     | 10 YR 3/1    | Sapric          | 4.5      | 55           | 2.0                 | poorly drained  |
|       | 30 - 55    | 10 YR 3/3    | Sapric          | 4.0      |              |                     |                 |
|       | 55 - 100   | N5           | C               | 4.0      |              |                     |                 |
| P4    | 0 - 15     | 10 YR 3/3    | SiC             | 4.0      | 75           | 2.0                 | poorly drained  |
|       | 15 - 35    | 10 YR 4/2    | SiC             | 4.0      |              |                     |                 |
|       | 35 - 75    | 10 YR 5/1    | C               | 4.0      |              |                     |                 |
|       | 75 - 120   | 5 GY 5/1     | C               | 4.0      |              |                     |                 |
| P5    | 0 - 12     | 10 YR 3/2    | SiC             | 4.0      | >120         | -                   | poorly drained  |
|       | 12 - 30    | 10 YR 3/1    | SiC             | 4.0      |              |                     |                 |
|       | 30 - 57    | 10 YR 4/1    | SiC             | 4.0      |              |                     |                 |
|       | 57 - 90    | 5 Y 6/1      | C               | 4.0      |              |                     |                 |
|       | 90 - 120   | 2.5 Y 5/1    | C               | 4.0      |              |                     |                 |
| P6    | 0 - 15     | 10 YR 4/2    | SiC             | 4.0      | 120          | 2.0                 | poorly drained  |
|       | 15 - 52    | 10 YR 4/1    | SiC             | 4.0      |              |                     |                 |
|       | 52 - 90    | 10 YR 5/1    | C               | 4.0      |              |                     |                 |
|       | 90 - 120   | 10 YR 6/1    | C               | 4.0      |              |                     |                 |
| P7    | 0-20       | 10 YR 5/3    | C               | 4.0      | >120         | -                   | somewhat poorly drained |
|       | 20-50      | 10 YR 5/2    | C               | 4.0      |              |                     |                 |
|       | 50-80      | 10 YR 4/2    | C               | 4.0      |              |                     |                 |
|       | 80-120     | 10 YR 4/3    | C               | 4.0      |              |                     |                 |
| P8    | 0-20       | 10 YR 23/1   | C               | 4.0      | >120         | -                   | very poorly drained |
|       | 20-50      | 10 YR 4/1    | C               | 4.0      |              |                     |                 |
|       | 50-80      | 10 YR 4/2    | C               | 4.0      |              |                     |                 |
|       | 80-120     | 10 YR 5/2    | C               | 4.0      |              |                     |                 |
| P9    | 0 - 24     | 7.5 YR 3/2   | C               | 4.0      | >120         | -                   | poorly drained  |
|       | 24 - 53    | 7.5 YR 5/2   | C               | 4.5      |              |                     |                 |
|       | 53 - 82    | 7.5 YR 3/1   | C               | 4.0      |              |                     |                 |
|       | 82 - 120   | 7.5 YR 4/2   | C               | 4.0      |              |                     |                 |
| P10   | 0 - 16     | 10 YR 3/1    | SiL             | 4.5      | 98           | 2.0                 | poorly drained  |
|       | 16 - 47    | 10 YR 4/1    | SiC             | 4.0      |              |                     |                 |
|       | 47 - 79    | 10 YR 5/1    | SiC             | 4.0      |              |                     |                 |
|       | 79 - 98    | 10 YR 6/1    | C               | 4.0      |              |                     |                 |
|       | 98 - 120   | 10 YR 7/1    | C               | 4.0      |              |                     |                 |

Remarks: Texture = SiC (Silty Clay), C (clay), SiL (Silty Loam).
The drainage condition of the observed soils could be categorized into poorly drained, somewhat poorly drained, and very poorly drained. In general, soil observed was in a wet condition (aquic) which was indicated by soil poorly drained (table 1). In this condition, pyrites were identified by its dark green color. Soil layer contained pyrite when was poured by H$_2$O$_2$ and the measured foam pH was 2 (table 1). Oxidized pyrite layer produced jarosite. Jarosite is a straw yellow, covering of the soil pores [18]. Some of samples (P5, P7, P8, P9) did not react to the hydrogen peroxide, but in the chemical analysis results there was a small amount of pyrite. Pyrite levels were also thought to be found at a depth of $>120$ cm so that there was a little amount in the upper layer. Morphological and physical attribute of pedons were presented in table 1.

3.3. Soil chemical properties

Acidity of the soil which contained pyrite was presented in table 1. The soil which contained pyrite was very acidic with an average pH 3.4 to 4.4. Based on table 1, soils which contained higher pyrite has pH value $<4$. In the second layer of P2, soil pH is 3.9 due to pyrite content which was on 3.69% level. Whereas, pH value in the first layer of P2 is 4.2 because of pyrite content was on 0.02% level. P1, P3 and P4 also have the same conditions. The higher of pyrite content resulted the lower the pH. The low soil pH was indicated by the presence of oxidized pyrite or jarosite [19]. Soils with pyrite depth 101-150 cm (P7, P8, P9) has lower pH than soils with pyrite depth $<100$ cm. That could be happened because pyrite levels were getting higher along with the deeper of soil depth, so that when the soil was dried, oxidized pyrite caused soil became very acidic. However, in the field condition, the shallower pyrite layer was easier to oxidize. According to Sutandi et al. [7], the shallower pyrite depth causes the lower soil pH. The decrease of soil pH occurs due to drainage so that pyrite was oxidized to produce H$^+$ ion and causes low soil pH.

The highest organic carbon was found in P1 and P3 with pyrite depth 51 to 75 cm. The pyrite depth did not influence organic carbon. The highest organic carbon was in P1 and P3 due to their parent material which is derived from organic matter (peat material). In general, organic carbon content in topsoil of all pedons were higher than subsoil. Total N value was higher in soil with pyrite depth 51 to 75 cm. Total P$_2$O$_5$ content in the observed soil was higher than total K$_2$O content. It was caused by phosphor fertilization. The highest P$_2$O$_5$ and K$_2$O levels were in soil whose pyrite depth was 25 to 50 cm and 51 to 75 cm as compared to soil with pyrite depth $>75$ cm. The soils CECs were moderate to high and were very high in P1 and P3 that caused organic carbon in both of them were very high. The CEC value can be increased by applying organic matter [20]. P1 and P3 were organic soil so that they had a high organic matter content. Base saturation level which was dominant was low. The lowest base saturation was in P8 and P9 in the soil with depth G4 (101 to 150 cm). It was due to low soil pH which caused low base saturation. Whereas, the highest base saturation was in P5 with the same pyrite depth.

The levels of exchangeable bases are presented in figure 2. The highest Ca levels are found in the soil in G2 (51 to 75 cm) and G1 (25 to 50 cm) category. The exchangeable Mg levels of all pyrite depth groups were almost the same, but there was one observation point (G4) which had highest Mg content. The highest K content existed in G1 pyrite depth category, while in the other pyrite depth category, the K content was same. The highest Na levels was found in the soil in G1 (25 to 50 cm) and G4 (101 to 150 cm) pyrite depth category. The Na content in G4 category varied due to more observation points. Based on the criteria for assessing soil fertility [21], the levels of exchangeable bases in the observation point were different. The Ca content was classified as very low and had a value $<2$ cmol$_c$kg$^{-1}$. Meanwhile, the Mg content was grouped as moderate (1.1 to 2.0 cmol$_c$kg$^{-1}$) to high (2.1 to 8.0 cmol$_c$kg$^{-1}$). K content was classified as low with a value of 0.1 to 0.3 cmol$_c$kg$^{-1}$. Na content was categorized as low (0.1 to 0.3 cmol$_c$kg$^{-1}$) to moderate (0.4 to 0.7 cmol$_c$kg$^{-1}$). The low levels of the exchangeable bases in the shallow pyrite depths soil were caused by pyrite oxidation which producing H$^+$ ions which were acidic. The number of H$^+$ ions caused the exchangeable bases to be released from the absorption complex and washed so that the levels of exchangeable bases in the upper layer were less than the lower layer [7].
Table 2. Chemical properties of pedons observed.

| Pyrite depth groups | Pedon | pH H2O | C (%) | N (%) | P2O5 (mg/100g) | K2O | CEC of Soil (Cmol/kg) | Base Sat. (%) | Pyrite (%) |
|---------------------|-------|--------|-------|-------|----------------|-----|----------------------|---------------|------------|
| G1 (0-25 cm)        | P2    | 4.2    | 0.24  | 0.02  | 66             | 11  | 11.51                | 21            | 0.02       |
|                     |       | 3.9    | 3.86  | 0.21  | 20             | 11  | 27.46                | 17            | 3.69       |
| G2 (51-75 cm)       | P1    | 4.4    | 27.55 | 0.99  | 214            | 10  | 50.75                | 12            | 0.83       |
|                     |       | 4.4    | 30.04 | 0.98  | 113            | 6   | 58.37                | 11            | 0.80       |
|                     |       | 4.3    | 7.41  | 0.29  | 12             | 6   | 32.58                | 13            | 0.21       |
|                     |       | 3.8    | 4.07  | 0.20  | 13             | 9   | 27.15                | 12            | 1.14       |
| G2 (51-75 cm)       | P3    | 4.4    | 47.13 | 1.65  | 63             | 7   | 72.97                | 5             | 1.15       |
|                     |       | 4.2    | 30.38 | 0.99  | 16             | 7   | 48.05                | 5             | 0.99       |
|                     |       | 3.5    | 6.92  | 0.26  | 21             | 9   | 29.94                | 8             | 5.85       |
| G2 (51-75 cm)       | P4    | 3.4    | 3.24  | 0.20  | 13             | 5   | 29.90                | 9             | 0.79       |
|                     |       | 4.0    | 2.34  | 0.16  | 13             | 7   | 21.30                | 14            | 0.05       |
|                     |       | 3.9    | 2.35  | 0.17  | 13             | 6   | 26.72                | 13            | 0.02       |
| G3 (76-100 cm)      | P10   | 4.3    | 3.71  | 0.22  | 18             | 7   | 24.81                | 27            | 0.15       |
|                     |       | 4.2    | 3.10  | 0.19  | 17             | 6   | 23.76                | 24            | 0.20       |
|                     |       | 4.3    | 2.34  | 0.16  | 17             | 5   | 24.02                | 25            | 0.20       |
| G4 (101-150 cm)     | P5    | 4.2    | 4.47  | 0.24  | 41             | 5   | 26.09                | 42            | 0.37       |
|                     |       | 4.1    | 2.23  | 0.16  | 18             | 5   | 24.31                | 35            | 0.13       |
|                     |       | 4.0    | 1.85  | 0.13  | 18             | 5   | 23.57                | 41            | 0.15       |
|                     |       | 4.0    | 1.53  | 0.11  | 18             | 5   | 22.89                | 44            | 0.33       |
| G4 (101-150 cm)     | P6    | 4.0    | 6.08  | 0.33  | 27             | 6   | 29.20                | 7             | 0.53       |
|                     |       | 4.0    | 2.06  | 0.15  | 12             | 5   | 25.82                | 12            | 0.32       |
|                     |       | 3.9    | 1.15  | 0.10  | 11             | 6   | 24.71                | 14            | 0.16       |
| G4 (101-150 cm)     | P7    | 3.8    | 5.62  | 0.28  | 43             | 8   | 29.90                | 12            | 0.91       |
|                     |       | 3.8    | 3.44  | 0.18  | 20             | 5   | 26.83                | 12            | 0.62       |
|                     |       | 3.6    | 4.62  | 0.23  | 42             | 4   | 28.92                | 11            | 1.01       |
| G4 (101-150 cm)     | P8    | 4.0    | 8.94  | 0.37  | 39             | 6   | 34.54                | 7             | 0.33       |
|                     |       | 3.9    | 2.91  | 0.18  | 16             | 7   | 28.31                | 8             | 0.02       |
|                     |       | 4.0    | 2.47  | 0.16  | 9              | 5   | 26.36                | 10            | 0.17       |
| G4 (101-150 cm)     | P9    | 3.7    | 4.95  | 0.24  | 17             | 5   | 27.87                | 8             | 0.24       |
|                     |       | 3.7    | 3.61  | 0.20  | 14             | 5   | 24.06                | 7             | 0.11       |
|                     |       | 3.8    | 4.33  | 0.23  | 22             | 5   | 27.26                | 8             | 0.12       |

3.4. Implications of land containing pyrite for agriculture

Land containing pyrite can be used for agricultural purposes but the information of pyrite depth is needed. Pyrite in the soil will not be dangerous if it is under waterlogging conditions. The information of pyrite position within the soil is useful for controlling water table management to prevent pyrite oxidation. Pyrite can appear to the surface if the soil tillage is too deep, so to prevent this, farmers need to know the pyrite depth in their land. According to Enio et al. [19] research, land containing pyrite can be oxidized when it is drained during cultivation. The oxidation of pyrite releases H ions which cause acidity that is followed by the release of toxic metals in the soil, such as Al3+ and Fe3+ which can kill plants and aquatic life.
4. Conclusions
The pyrite layer depth in the observed location soil was affected by its distance from the river. The closer to the river, the deeper the pyrite layer position. Landform in swamp area can be used as reference for pyrite depth mapping. Soil color in study area were dominated by dark brown and yellowish dark brown with 7.5 YR to 10 YR hue. Soil texture in study area were dominated by clay. Soil observed was in a wet condition (aquic) which was indicated by soil poorly drained. Soils which contained higher pyrite had low pH value. Soils with pyrite depth 101 to 150 cm has a lower pH than soils with pyrite depth <100 cm. N total content were moderate. Total P2O content in the observed soil was higher than total K2O. The levels of Ca, K, Na cation were higher with the pyrite depth in the soil getting shallower, while Mg was almost the same in all pyrite depth groups. Soil containing pyrite can be used for agricultural purposes but the user has to keep the pyrite in reduced condition.

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