Dynamics of acidity and electrical conductivity due to seawater amelioration in total reclaimed acid sulphate soils, South Kalimantan

V Mayasari and Y Lestari
Indonesian Swampland Agricultural Research Institute, Banjarbaru, Indonesia
E-mail: yulibalittra70@yahoo.com

Abstract. The objective of our research was to determine the effect of inundation using seawater on the pH and EC of acid sulphate soils. This research consisted of 2 stages, an incubation experiment carried out in the greenhouse, Indonesian Swampland Agricultural Research Institute (ISARI), Banjarbaru South Kalimantan and in the field of Handil, Maluka village, Bumi Makmur District, Tanah Laut Regency, South Kalimantan. The incubation experiment used several seawater concentrations of 0, 12.5, 25, 37.5 and 50%, with randomized complete design with 3 replications. The field experiment used a raise bed system with two treatment applications: (i) without brackish water and (ii) with brackish water. The results of the incubation experiment showed that the longer the incubation period and the higher seawater concentration caused a decrease in the soil pH while increasing EC values. Conversely, incubation of potential acid sulphate soils using well water (0% seawater) resulted in increasing soil pH and EC values. Field experiments showed that the application of brackish water on acid sulphate soil gave lower soil pH than that without brackish water. Contrary, EC values of acid sulphate soil applied with brackish water were higher than those without brackish water application.

1. Introduction
Utilization of acid sulphate soil for agricultural requires reclamation technology and proper management to obtain optimal results. Acid sulphate soil reclamation can be done in two ways, namely limited and total relocations [1]. Limited reclamation is the management of soil and water that prioritizes efforts to maintain pyrite in reduced conditions. Total reclamation creates the maximum possible oxidative atmosphere so that almost all active pyrites are able to be oxidized and the reclamation process is carried out until the pyrite content in the soil is <1% and no longer reactive.

The total reclamation of potential acid sulphate soils in swamp areas begins with constructing drainage channels to lower the groundwater level and soil moisture. Decreasing soil moisture will increase oxygen diffusion into the soil layer to oxidize it is pyrite [2]. One of the acid sulphate land management systems that can accelerate pyrite oxidation is the manufacture of raised bed. With this system, the types of land commodities that can be planted are more various. However, before the pyrite oxidation process subsides, it will still release soil acidity, and high Fe and Al concentrations.
An innovative technique to prevent the negative consequences of acid sulphate soils on the environment is amelioration using seawater by periodic inundation for a certain time followed by leaching. Acid sulphate inundation using high tide is low cost (cheap) and is a large-scale remediation technique being tried in north Queensland (North Queensland). This technology is particularly suitable for locations close to the sea where the elevation of acid sulphate soils is very close to sea level and agricultural land use has been abandoned [3].

Amelioration by tidal inundation from the ocean supplies the alkalinity of bicarbonate, which directly neutralizes the acidity of soil and surface water. The effect of restoring acid sulphate soils degraded by flooding of tides from the sea for five years regularly improves soil and water quality. Soil pH values increases by 2-3 units and titrated acidity values decrease by 40-50 µmol g⁻¹ in the sulfuric horizon [3].

The results of Indrawati's [4] research show that leaching acid sulphate soils with seawater can remove acids (such as H⁺, Al³⁺, Fe²⁺, and SO₄²⁻) from the soil and increase soil pH values to become higher than that of distilled water. This is caused by exchanging exchange cations in the exchange complex with ions in seawater. Seawater with high ion contents can function as an acid ion exchange material in the land exchange complex. The ability of seawater as an ion exchange is quite significant [5]. Therefore, seawater has a good prospect for extracting acid cations in the exchange complex of acid sulphate soil.

Leachate water EC values can be used as an indicator of the stability of the pyrite oxidation process. The pyrite oxidation process has subsided when the leachate water EC reaches a constant value of <0.5 mS [6]. The objective of our research was to determine the effect of inundation using seawater on the pH and EC values of acid sulphate soils.

2. Methodology

The research was carried out in the greenhouse of Indonesian Swampland Agricultural Research Institute, and the field in Handil Maluka Village, Bumi Makmur Subdistrict, Tanah Laut Regency at a geographic position of 03°34'38.1" S; 114°35'546" E.

2.1. The greenhouse experiment

The research used potential acid sulphate soil with sun dried condition from Jelapat Village, Tamban Subdistrict, Barito Kuala Regency, South Kalimantan (03°14'16.1" S; 114°31' 020" E). The experimental was arranged using a completely randomized design, with three replications. The treatments tested were different concentrations (0%, 12.5%, 25%, 37.5% and 50%) of seawater.

The research was begun by weighing as much as 4 kg of sun-dried acid sulphate soil that had undergone leaching oxidation and was placed in a pot and flooded with 10 L well water. Observations were made five times (at 0, 5, 10, 15, 20 days) after inundation. The observation variables were pH and EC values.

The observation data obtained were analyzed statistically using SAS Portable 9.31 software. Analysis of variance and the Duncan tests were carried out in order to find out the differences in and between treatments.

2.2. Field experiments

Two raised beds (surjan) were used for research with an area of 5 m x 51 m each, which firstly had been applied with 2% husk and left for eight months (November 2013-June 2014) in order to increase aeration for running well pyrite oxidation. Then 1 surjan was still being laid and the other one was leached using brackish water every week for three months (July-September 2014). Then the leached surjan was left alone for leaching out the salts by rainwater (October 2014-January 2015). Observation on pH and EC values was carried out monthly for five times by taking 10 samples on each observation time. The data obtained were then averaged and graphed using Excel.
3. Results and discussion

3.1. The greenhouse experiment

The chemical analysis results of acid sulphate soil and seawater used in this study are presented in table 1. Acid sulphate soil used in this study is classified as very acidic with available Al and H cations being classified as high. From table 1, it can also be seen that the seawater used for this study is dominated by Na⁺, in addition to the ions Ca²⁺, K⁺, Mg²⁺ and SO₄²⁻. Given the high concentration of Na⁺, Ca²⁺, K⁺ and Mg²⁺ ions, the ionic ability of seawater is also high (ionic strength), so it is hoped that seawater has the ability to be an ion exchange.

| Chemical properties | Acid sulphate soil (sun dry) | Sea water |
|---------------------|-----------------------------|-----------|
| pH H₂O              | 2.97                        | 6.83      |
| EC (mS cm⁻¹)        | 1.54                        | 25.90     |
| Available-Al (cmol kg⁻¹) | 9.69                      | -         |
| Available-H (cmol kg⁻¹) | 7.10                      | -         |
| K⁺ (ppm)            | 202.80                      | 3480.00   |
| Na⁺ (ppm)           | 3480.00                      |           |
| Ca²⁺ (ppm)          | 117.52                      | 117.52    |
| Mg²⁺ (ppm)          | 397.00                      | 397.00    |
| SO₄²⁻                | 57.26                       |           |

Statistical analysis showed that the difference in seawater concentration affected very significantly on the pH value of the stagnant water in the 1st to 5th observations (table 2). Table 2 shows that the increasing concentration of seawater, decreases the pH value of the flooding water. According to Indrawati [4], the ions contained in seawater have the ability to exchange H⁺ cation in the exchange complex, where the higher H⁺ cation concentration in the seawater the greater its exchangeability. As a result, the concentration of H⁺ in the soil solution (flooding water) increases, which in turn decreases the pH value of the flooding water.

| Seawater concentration (%) | Observation 1st | 2nd | 3rd | 4th | 5th |
|----------------------------|-----------------|-----|-----|-----|-----|
| 0                          | 2.79 a          | 2.74 a | 2.60 a | 2.63 a | 2.69 a |
| 12.5                       | 2.75 ab         | 2.70 b | 2.54 ab | 2.64 b | 2.62 b |
| 25.00                      | 2.72 bc         | 2.69 bc | 2.54 ab | 2.60 b | 2.60 b |
| 37.50                      | 2.71 c          | 2.67 c | 2.48 b | 2.56 c | 2.52 c |
| 50.00                      | 2.70 bc         | 2.67 c | 2.47 b | 2.48 d | 2.45 d |

Note: The numbers in the same column followed by the same letter are not different according to Duncan's test at the 1% confidence level.
The EC values of flooding water is very evident from seawater detection (table 3). Table 3 shows that the increase in seawater concentration, the higher the pool of water EC. This is due to the increasing concentration of Na⁺ and Cl⁻. The high ionic concentration in the soil results in increasing the EC value [7].

The results showed that soil pH value was <3. According to Shamshuddin [8], pKa Al = 5, which means that the higher the concentration of seawater, the pH of the standing air decreases, which means the concentration of H⁺ is increasing. Furthermore, H⁺ reacts with silicate compounds to form weak acid Si(OH)₂ and the silicate compound is destroyed which releases Al³⁺, K⁺, Na⁺, Ca²⁺, Mg²⁺ [1,9] and Fe²⁺ [1]. The process of crushing mineral lattice by H⁺ according to Maas [1] is as follows:

\[
\text{Silicate} + H^+ \rightarrow \text{Si(OH)}_4 + \text{Al}^{3+} + \text{Mg}^{2+} + \text{Ca}^{2+} + \text{Na}^+ + \text{K}^+ + \text{Fe}^{2+} + \text{Fe}^{3+}
\]

Besides, the high acidity can accelerate the decomposition process of Al-hydroxide which initially settles into exchangeable-Al. Therefore, the lower the pH value causes, the higher the dissolved cations of K⁺, Na⁺, Ca²⁺, Mg²⁺, Fe²⁺ and Al so that the EC value increases.

**Table 3.** Effect of inundation using different seawater concentrations on the EC value of acid sulphate soils, South Kalimantan.

| Seawater concentration (%) | 1st Observation | 2nd Observation | 3rd Observation | 4th Observation | 5th Observation |
|---------------------------|----------------|----------------|----------------|----------------|----------------|
| 0                         | 2.24 e          | 2.43 e          | 3.01 e          | 3.13 e          | 3.40 e          |
| 12.50                     | 4.22 d          | 4.43 d          | 5.66 d          | 6.02 d          | 6.12 d          |
| 25.00                     | 5.98 c          | 6.19 c          | 7.77 c          | 8.07 c          | 8.40 c          |
| 37.50                     | 9.58 b          | 9.80 b          | 13.01 b         | 13.56 b         | 14.13 b         |
| 50.00                     | 13.30 a         | 13.40 a         | 15.60 a         | 16.02 a         | 16.33 a         |

Note: The numbers in the same column followed by the same letter are not different according to Duncan's test at the 1% confidence level.

The effect of flooding time on pH and EC values is shown in figures 1A and 1B. Figure 1A shows that at the beginning, the flooding decreased the pH values of the water until the 3rd observation (15 days after flooding), and increased and then decreased them again in the 4th – 5th observations except for the treatment of 0% seawater concentration. This is thought to be related to the cation exchange process between seawater and acid cations in the exchange complex. The longer the flooding, increases the acid cations such as H⁺, Al³⁺ and Fe³⁺ so that the pH value of the stagnant water decreases. The increase in the pH values of the stagnant water was probably due to the neutralization process of H⁺ by carbonate ions contained in seawater.

The electrical conductivity (EC) value of acid sulphate soil water increases with the length of inundation time. This shows that the longer inundation, causes the higher dissolved ion concentration. Because the pH values of flooding water were <3.5, the increases in EC value were probably due to the increased concentration of Al³⁺ coming from the destruction of silicate minerals [8] or the decomposition of Al-hydroxide [11].
Figure 1. Effect of flooding acid sulphate soil using different seawater concentrations on pH value (A) and EC value (B).

3.2. Field experiments

The location of this research is around 2 km away from the sea, so according to local farmers during the dry season they often get seawater runoff (brackish water). The climatic data on the amount of rainfall and rainy days from July 2014 to January 2015 were taken from the Kurau Subdistrict Observation Post, Tanah Laut Regency, South Kalimantan which was the closest observation post from the research location.

Watering on the total reclaimed acid sulphate soil with brackish water was carried out in July-September 2014. During this period, the monthly rainfall ranges from 88-108 mm which are classified as low to moderate and the number of rainy days is 6-7 days month⁻¹. After the application of brackish water at the October 2014-January 2015, the land is left exposed to rainwater with the aim of leaching acidic cations resulting from pyrite oxidation, extraction by seawater from trapping sites and Cl⁻ contained in seawater. Graphs of rainfall and rainy days can be seen in figures 2A and 2B.

Figure 2. Rainfall and rainy days at the study location from July 2014 to January 2015 [12,13].
The dynamics pH values of acid sulphate soil applying without the application of brackish water were not significantly different. Since July to September 2014, the soil pH values had decreased. It was suspected because of lower rainfall so the H⁺ concentration was higher causing a decrease in the soil pH. Furthermore, at the beginning (in October) of the leaching process, the soil pH was lower than September. This was due to the accumulation of acid cations, especially H⁺, as the result of pyrite oxidation or the cation exchange dissolved by rainwater. On the figure 2, it can be seen that increasing rainfall occurs (in November 2014 to January 2015) (figure 2A) and followed by an increase in soil pH (figure 3A).

Figure 3 also shows that the application of brackish water reduces soil pH values. According to Lestari et al. [14], that inundation of acid sulphate soils by seawater can increase the concentration of dissolved H⁺ and Al³⁺.

The dynamic EC values of acid sulphate soil applying brackish water were similar with those without applying brackish water. Figure 3B shows that the EC values of acid sulphate soil treated with brackish water are lower in August than those in July to October, and then the values decrease. In that of without brackish water application, the soil EC values increase until November 2014 and then decrease (figure 3B). The accelerating agents of the EC value occurrences were the increasing concentration of ions (anions + cations) as results from pyrite oxidation. Meanwhile, there is a decrease in EC value due to decreased ion concentration resulted by rainwater leaching. In general, EC values of acid sulphate soil watered with brackish water are higher than those without applying brackish water due to the addition of those ions contained in seawater.

**4. Conclusions**

The results showed that the higher seawater concentration decreased the pH values of the inundation water, but it increased the EC values of inundation water. The pH value of inundation water fluctuates with the length of inundation time, however, EC increases with increasing length of inundation. The dynamic values of soil pH and EC in the field affected by applied brackish water were not different. With
those without brackish water application. Application of brackish water caused reducing soil pH and increasing EC values.

References

[1] Maas A 1989 Genesis, classification and reclamation of potential acid sulfate soils in South Kalimantan, Indonesia PhD Thesis State University of Ghent, Belgium

[2] Cook F J, Dobos S K, Carlin G D and Miliar G E 2004 Oxidation of pyrite in acid sulfate soils: in situ measurement and modeling Soil Research 42(6) 499–507

[3] Johnston S, Keene A, Bush R, Burton E and Sullivan L 2009 Remediation of coastal acid sulfate soils by tidal inundation: Effectiveness and geochemical implications Proceedings of 18th NSW Coastal Conference Ballina, NSW 3-6 November, East Coast Conferences Coffs Harbour NSW

[4] Indrawati U S Y V 2001 Pengaruh air laut sebagai amelioran terhadap beberapa sifat kimia tanah sulfat masam (in Bahasa) Thesis Program Pasca Sarjana Universitas Gadjah Mada Yogyakarta

[5] Maas A, Sutanto R and Purwadi T 2000 Pengaruh air laut terhadap oksidasi pirit dan tanah hara tanah sulfat masam (in Bahasa) Jurnal Ilmu Tanah dan Lingkungan 2(2) 41–45

[6] Maas A 2003 Peluang dan konsekuensi pemanfaatan lahan rawa pada masa mendatang (in Bahasa) Pidato Pengukuhan Jabatan Guru Besar pada Fakultas Pertanian Universitas Gadjah Mada

[7] Murtianto H 2010 Studi kualitas air tanah untuk pengembangan wisata di kawasan Parangtritis, Bantul Daerah istimewa Yogyakarta (in Bahasa) Journal geografi GEA 10(2)

[8] Shamshuddin J and Auxtero E A 1991 Soil solutions composition and mineralogy of some active acid sulfate soils in Malaysia as affected by laboratory incubation with lime Soil Scince 152(5) 365–375

[9] Sudarsono 1996 Pengelolaan Tanah dan Air dalam Pengembangan Sumberdaya Usahatani Berkelanjutan dan Berwawasan Lingkungan (in Bahasa) Makalah disajikan dalam Pelatihan Pelaksanaan Penelitian dan Pengembangan Pertanian Integrated Swamps Development Project (ISDP) Palembang

[10] Shamshuddin J, Muhrizal S, Fauziah I and Husni M H A 2004 Effect of adding organic materials to an acid sulfate soil on the growth of coca (Theobroma cacao L.) seedlings Science of the Environmental 323 33–45

[11] Yuliana E D 2012 Jenis mineral liat dan perubahan sifat kimia tanah akibat proses reduksi dan oksidasi pada lingkungan tanah sulfat masam (in Bahasa) Jurnal Bumi Lestari 12(2) 327–337

[12] BPS 2015 Kecamatan Kurau Dalam Angka 2015 (in Bahasa) Badan Pusat Statistik Kabupaten Tanah Laut

[13] BPS 2016 Kecamatan Kurau Dalam Angka 2016 (in Bahasa) Badan Pusat Statistik Kabupaten Tanah Laut

[14] Lestari Y, Ma’as A, Noor M and Susanto A 2016 Prosiding Seminar Nasional Dies Natalis Fakultas Pertanian, Universitas Gadjah Mada, Yogyakarta