A comparison of cation exchange capacity of organic soils determined by ammonium acetate solutions buffered at some pHs ranging between around field pH and 7.0

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Abstract. Cation exchange capacity (CEC) and exchangeable cations are among two of the most important measures for determining soil characteristics and soil quality. There are various methods of measuring CEC, including the ammonium acetate method of Schollenberger and Dreiblebis (1930) which is buffered at pH 7.0 and the barium chloride-triethanolamine method of Mehlich (1938) which is buffered at pH 8.2. These CEC measurements can result in values very different from the CEC of the soil at its field pH (effective CEC or CECe), especially in acidic soils, such as organic soils, with pH-dependent CEC. Therefore, the focus of this article is the comparison of CEC of organic soils obtained using the different pH level of the extraction solution. Five organic soil and two mineral soil samples were used in this experiment. The variables tested were CEC and exchangeable cations using ammonium acetate solutions buffered at several pHs; field pHs (acidic) of 3.8, 4.2, 4.8 and neutral (7.0). Each soil sample and pH level were replicated three times. The decomposition rate of the five organic soil samples was determined using the pyrophosphate color method, which proved to be sapric. The results indicate a positive relationship between pH and CEC value, the higher the pH buffer the much higher the CEC measured. There was a considerable difference of CEC values produced from the varying pHs of extraction solution. However, the pH of the extraction had no substantial effect on measured exchangeable cations. Keywords: CEC method, exchange sites, field pH, pH-dependent charge

1. Introduction
Recently, organic soil has been used for many agricultural activities such as oil palm and industrial forest plantations. Therefore, up until today there has been extensive research on the chemical, physical, and biological characteristics of organic soils, and how they respond to agricultural activities. Cation exchange capacity (CEC) and exchangeable cations are among two of the most important measures for determining soil characteristics and soil quality. CEC is a significant chemical property of soil, which reflects the buffer system in soils. Exchange reactions control the equilibrium between solid and liquid phases in soils, reducing fluctuations in ion concentrations which result from agronomic and other practices [1]. CEC is a measure of the negative charges carried by soil particles which fall into two
different categories: permanent and variable charges. These distinct categories determine the best method to measure the CEC since the CEC value may be highly sensitive to the method used.

There are various methods for CEC determination, two of which are the ammonium acetate method of Schollenberger and Dreibleis (1930) which is buffered at pH 7 and the barium chloride-triethanolamine method of Mehlich (1938) which is buffered at pH 8.2. These CEC measures can result in values which are not representative of the CEC of the soil at its field pH (effective CEC or CECe). This is especially true for acidic soils, such as organic soil which has pH-dependent CEC. As organic soil has a variable charge, these two methods would inflate the CEC value, giving an inaccurate result. The extraction solution would lead the organic soil pH to the pH value of the solution itself. The magnitude of the error incurred in the CEC measurement depends on the difference between the pH value of the soil and the extraction solution [2].

The intended use of the CEC data is important as a base for selecting the CEC determination method. For soil classification purposes, CEC is often measured at a standard pH and ammonium acetate buffered at pH 7 as the recommended procedure. In mineral soils, the usage of this buffered ammonium acetate method is widely accepted even for the soil quality interpretation purpose. However, for organic soil, pH 7 is too far above the field pH that theoretically will overestimate the CEC. Therefore, the aim of this study was to present the different CEC value of organic soils extracted by ammonium acetate solutions buffered at several pHs; field pHs (acidic) of 3.8, 4.2, 4.8 and neutral (7.0).

2. Materials and Methods
This experiment was conducted in the Laboratory of Soil Science and Land Resources Department, IPB University from March – June 2019. Ammonium acetate solutions buffered at four different pH (pH 7.0, 4.8, 4.2, 3.8) were used to extract seven soil samples with three replications for each buffered solution. Thus, there were 84 experimental units in this research.

2.1 Materials
There were five organic and two mineral soil samples collected from six locations. The organic soil samples were obtained from Ogan Komering Ilir Regency, Siak Regency, and Selatpanjang Regency in Sumatra and Katingan Regency in Kalimantan. The mineral soil samples were taken from Cianjur Regency and Bogor Regency, West Java. The solution used for the extraction was ammonium acetate buffered at four different pH (pH 3.8, 4.2, 4.8 and 7.0), 80% ethanol, and 1 N sodium chloride. The solution for distillation was 50% sodium hydroxide, 2% boric acid and 0.1 N chloride acid.

2.2 Methods
Soil samples were air-dried and passed through a 2.0 mm sieve before being analyzed. Five grams of soil sample was added into a centrifuge tube. Then, 30 ml ammonium acetate solution was added to the centrifuge tube, and shaken thoroughly for 30 minutes then allowed to stand overnight. Next, the sample was centrifuged for 10 minutes and the leachate was filtered with Whatman paper in a 100 ml volumetric. This process was repeated three times until the leachate reached 90 ml. Then, the leachate was diluted with 10 ml of ammonium acetate to reach a total volume of 100 ml. This leachate solution was used to measure exchangeable cations in the soil. Sodium and potassium were determined using a flame photometer. Calcium and Magnesium were determined using an atomic absorption spectrophotometer.

The remaining soil sample was washed with four separate additions of 30 ml of water; 15 ml of water and 15 ml of 80% ethanol; 30 ml of 80% ethanol; and 30 ml of 80% ethanol, to remove excess ammonium. Each washing process was conducted by shaking the sample for 30 minutes and centrifuging for 10 minutes. The leachate from this process was discarded. Then, to extract the adsorbed ammonium in the soil sample, 30 ml of 1 N sodium chloride was added to the centrifuged tube, shook for 30 minutes and filtered the leachate with Whatman paper in a 100 ml volumetric. This process was done 3 times until the leachate reached 90 ml. The leachate was diluted using 1 N sodium chloride until
the volume reached 100 ml. The concentration of ammonium in sodium chloride extract was determined by distillation.

The distillation process was conducted by adding 10 ml of 50% sodium hydroxide; 10 ml of the extract, and using 10 ml of 2% boric acid in a container. The obtained extract was titrated using 0.1 N chloride acid and the CEC was calculated as follows;

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CEC\left(\text{me/100gram}\right) = \frac{(a - b) \times 0.1 \times v \times MCF \times 100}{w \times al}
\]

a : titer volume of 0.1 N HCl for the sample (ml);
b : titer volume for the blank (ml);
v : volume of the extracting solution (ml);
MCF : moisture correction factor;
w : weight of the sample (g);
al : sample aliquot (ml);

The decomposition rate of the organic soil was determined by miscellaneous pyrophosphate color. One gram of sodium pyrophosphate was dissolved in 4 ml of water in a 30 ml container. Then, approximately 2.5 cm³ of moist soil sample was added into the solution, mixed and allowed to stand overnight. On the following day, the sample was mixed and the chromatographic paper was inserted into the sample to a one cm depth using tweezers. The paper strip was allowed to be wetted to 2 cm height above the slurry surface. The paper strip was removed with tweezers and the excess dry paper was cut off the strip to leave only the portion that was in contact with the soil. Then, the strip was placed in a piece of blotting paper and pressed gently with tweezers to make even contact. The color was determined by comparing the paper strip to Munsell color charts.

3. Result

3.1 Soil Characteristic
Table 1 presented the characteristics of the five organic soil samples. pH of the organic soil samples was ranging from 3.44 to 3.52, which indicated the acidic condition in the soil. Ash content was measured in this experiment and showed that the results were ranging from 2.23% to 13.25%. Soil sample from Siak Regency had the highest amount of ash content. Pyrophosphate color analysis to determine the decomposition rate of the five organic soil samples showed that all of the soil samples had a dark color. According to the Munsell color chart, the color value of the soil was ranging from 6 to 7, meanwhile, the color chrome ranged from 4 to 6. Table 2 showed two soil samples from Siak Regency were light yellowish brown, whereas the soil samples from Katingan and SelatPanjang Regency were very pale brown. The soil sample from Ogan Komering Illir Regency was brownish yellow.

| Sample                        | pH  | Ash content (%) | Pyrophosphate color |
|-------------------------------|-----|-----------------|---------------------|
| S1 (Ogan Komering Illir Regency) | 3.44 | 6.14            | 10YR 6/6            |
| S2 (Siak Regency)             | 3.46 | 13.25           | 10YR 6/4            |
| S3 (Siak Regency)             | 3.51 | 4.45            | 10YR 6/4            |
| S4 (Katingan Regency)         | 3.45 | 2.23            | 10YR 7/4            |
| S5 (Selatpanjang Regency)     | 3.52 | 3.96            | 10YR 7/4            |

3.2 CEC of soil samples
The results show a linear relationship between the CEC of the organic soils and pH of the extraction solution, as for all five samples the CEC increases as the pH of the solution escalates. According to Table 1, the escalation rate of CEC between pH 4.8 and 7.0 were ranging from 68.09% to 93.95%. The CEC of soil sample from Selatpanjang Regency at pH 3.8 and 7.0 were 41.72 me/100 gram and 130.26 me/100 gram, which increased more than 200%. Based on CEC result in general, sample from Siak Regency had the lowest escalation rate, whereas the soil sample from Selatpanjang Regency had the highest escalation rate.

**Table 2. CEC of soil samples with different level of pH extraction solution**

| Sample                                | CEC (me/100 gram) | pH 3.8 | pH 4.2 | pH 4.8 | pH 7   |
|---------------------------------------|-------------------|--------|--------|--------|--------|
| Organic soil sample:                  |                   |        |        |        |        |
| S1 (Ogan Komering Illir Regency)      |                   | 40.79  | 49.96  | 72.40  | 126.44 |
| S2 (Siak Regency)                     |                   | 33.64  | 36.70  | 47.91  | 80.53  |
| S3 (Siak Regency)                     |                   | 42.51  | 54.24  | 63.03  | 107.01 |
| S4 (Katingan Regency)                 |                   | 42.40  | 52.10  | 72.69  | 126.00 |
| S5 (Selatpanjang Regency)             |                   | 41.72  | 47.83  | 67.16  | 130.26 |
| Mineral soil sample:                  |                   |        |        |        |        |
| M1 (Cianjur Regency)                  |                   | 27.13  | 29.60  | 30.30  | 33.47  |
| M2 (Bogor Regency)                    |                   | 32.34  | 33.08  | 33.08  | 38.28  |

The same method was conducted on two mineral soil samples from two different locations. Results confirmed that the measured CEC of the two mineral soil samples did not considerably increase as the solution pH escalated. Table 2 showed that the escalation rates of the two soil samples extracted at pH 3.8 and 7.0 were less than 25%. The CEC of Cianjur Regency soil measure at pH 3.8 was 27.13 me/100 gram and 33.47 me/100 gram at pH 7.0. The escalation rate of CEC for this soil is 23.37% respectively.

### 3.3 Exchangeable Cations

In general, the exchangeable cations extracted from four different pH of extraction solutions were not considerably different as stated in Figure 1. Exchangeable sodium from five organic soil samples tended to be constant. Soil sample from Selatpanjang Regency had the highest decreasing rate of exchangeable sodium, however the value decreased around 0.74 me/100gr. Exchangeable potassium on samples which were extracted with pH 4.8 solution tended to decrease. The highest decreasing value of exchangeable potassium was from 1.79 me/100 gram to 1.36 me/100 gram, which was below 25%. The exchangeable calcium decreased as the pH’s deflation of the extraction solutions. The highest decreasing value of exchangeable calcium was from 18.13 me/100 gram to 10.90 me/100 gram. On the other hand, the exchangeable magnesium was fluctuating.
4. Discussion

Pyrophosphate color analysis was conducted to determine the decomposition rate of organic soils samples. It showed that the decomposition class of the organic soils samples used in this experiment was sapric. Sapric materials are defined by PCI < 4 [3]. PCI is defined as the color value minus chroma to generate a single number for classifying the decomposition rate [4]. The CEC of sapric materials is normally higher than in fibric or humic materials.

The standard method for CEC measurement on soils in the laboratory is conducted with a pH 7.0 solution for soil extraction. Schollenber & Dreibelbis (1930) used buffered salt (ammonium acetate) at pH 7 because at that time, CEC measurement was mostly conducted in western Europe, Russia, and the western and mid-western USA, where the soil pH in these locations was mostly neutral to alkaline [2]. In contrast, the results showed that all organic soil samples used in this location were acidic, as the pH are presented on Table 1. As organic soil has pH dependent charge, the charge will certainly increase when the pH is escalated and the measured CEC will increase as well. Therefore, it is promptly
understandable that this method would not be suitable for organic soils having field pH ranges from 3 to 4. Considering this, the measurement of organic soils CEC would be best conducted with an extraction solution which has the same pH range with the soil pH in field condition to ensure that the laboratory analysis result is representative of the field condition.

The result of this experiment showed that the pH of the extraction solution affected the result of CEC measurement in the laboratory. The CEC values increased as the pH of the extraction solution escalated. [5] Stated that the ammonium extraction with high pH led to a higher pH in acid soil suspensions, leading to an increase in the negatively charged sites of organic matter. The results of this experiment were in line with Ciesielcki and Sterckemen’s findings; showing that organic soils CEC measurement with high pH extraction solution resulted in a higher value of CEC. CEC measured on pH 3.8 and 4.2 had a lower value gap than CEC measured on pH 4.8 and 7.0. In general, the CEC value gap between pH 3.8 and 4.2 was below 25%, whereas the CEC value gap between pH 3.8 and 7.0 was up to 212%. Measurements taken using high pH will not give representative results of CEC in the field condition and lead to incorrect data analysis. Therefore, the most suitable pH to measure the CEC of organic soil are either 3.8 or 4.2. However, extraction solution with pH 3.8 is a troublesome work. For this reason, pH 4.2 is the most recommended pH for the extraction solution.

The experiment on exchangeable cations showed that the pH of the extraction solution had no substantial effect on the result. The result of exchangeable cations was similar for all the pH values. The exchangeable potassium was not drastically affected by the pH because the ability of ammonium acetate to extract potassium is dependent on the concentration of ammonium ions and not on the pH of the suspensions [5]. Identical remarks have been made by [6]. The effectiveness of K extraction by ammonium ions is well known. Exchangeable calcium tended to decrease as the pH of the extraction solution escalated. The highest decreasing value of exchangeable calcium belongs to soil from Siak Regency, from 18.13 me/100 gram at pH 3.8 to 10.90 me/100 gram at pH 7.0. On the other hand, exchangeable magnesium tended to fluctuate as the highest value gap was from 7.78 me/100 gram to 5.23 me/100 gram.

In this experiment, different pH extraction solutions were also used for CEC measurement on mineral soils. The pH of mineral soil used in this experiment were 6.11 and 5.10. The result showed that the pH of extraction solution had no substantial effect on the result of CEC measurement. This was the expected result as the mineral soils used in this experiment did not have a high pH-dependent charge. Therefore, the CEC measurement method on mineral soils should be conducted based on charge categories in the soil.

5. Conclusion
CEC of organic soils increases in line with the escalation of the pH of the extraction solution. Therefore, CEC of organic soil should be determined at pH 4.2 to gain the most accurate result which is representative of the field condition. The different pH level of the extraction solution did not have a substantial effect on exchangeable cations on organic soil.

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