Clay flocculation level with multivalent cations on some paddy soils in Bogor District, West Java, Indonesia

R A Chairunnisya*, D T Suryaningtyas and Iskandar
Departement of Soil Science and Land Resources, IPB University, Bogor, Indonesia
*Corresponding author: chairunnisyaayu@apps.ipb.ac.id

Abstract. The dispersion of clay on flooded and irrigated soils such as rice fields is a new challenge that must be solved. Dispersed clay will easily be carried away by water flow which makes the soil prone to erosion as an indirect effect of climate change. The implication of losing clay in the soil is the reduced fertility of the paddy soil. Therefore, flocculation of clay is important in order to prevent the flow of water from carrying it. This study aims to identify the degree of flocculation of clay in some paddy soils with multivalent cations differences in concentration and acidity. This study used six samples of paddy soil from Dramaga, Gunung Sari, and Gunung Sindur, Bogor District, West Java, Indonesia, which have 1:1 clay type, halloysite, and kaolinite. The clay flocculation level was observed at three pH levels by giving multivalent ions with predetermined concentration ranges. The results showed that there was no significant difference in the level of flocculation of kaolinitic and halloysitic soils with different pH levels and multivalent cations concentrations.

1. Introduction
Climate change can increase heavy rainfall, causing accelerated erosion. Erosion events result in the transport of clay-sized soil and humus which is rich in nutrients needed by plants. Clay dispersion is a common issue in flooded and irrigated soils like rice fields [1]. Clay that does not flocculate can move freely with the flow of water. These tiny particles will then accumulate in drainage channels and other waterways. Clay loss (deflocculation of clay) on the soil is a well-known occurrence that harms both agriculture and the environment [2][3]. From an agricultural perspective, decreased fertility and soil productivity are problems caused by clay dispersion. Meanwhile, from the perspective of soil and water conservation, clay loss from the soil can be used as a parameter for erosion [4].

The clay dispersion was significantly affected by the ion concentration in the soil solution under aquatic conditions and the surface charge of the sorption complex [5]. The dispersibility is related to soil clay content, and it would increase for clay that did not form complexes with organic matter and in wet or moist soil conditions [6]. Clay deflocculation, also known as "zero strength," can be interpreted as a loss of soil inorganic colloids [7].

Flooding and draining during rice cultivation affect soil pH and clay dispersibility. Clay dispersion and flocculation are typically measured by saturating the clay in a Na\(^+\)-Ca\(^{2+}\) solution and then calculating the SAR value [4]. A study by Nguyen et al [8] used the test tube experiments method to test the ability of silicic acid to disperse iron-rich clay particles in suspension that requires high clay concentrations. To see the coagulation of clay at lower concentrations, Massaro et al [9] used the dynamic light scattering method.

Paddy soils in Indonesia are highly diverse in terms of soil type, mineral clay, and irrigation method. This difference undoubtedly affects the clay’s dispersibility or degree of flocculation. Clay dispersion is
closely related to the risk of erosion and nutrient loss, both of which have received a lot of attention. The objective of this study was to determine the level of clay flocculation in paddy soil by using multivalent cations with numerous concentrations and different levels of pH.

2. Material and method

2.1. Soil sampling
The soils for this study were collected using the randomized method from several rice fields in Gunung Sari (GSR), Dramaga (DRM), and Gunung Sindur (GSDR), Bogor Regency, at depths ranging from 0-25 cm. The soil samples were then air-dried and sieved with a 2 mm sieve, with the results used for preliminary soil analysis.

2.2. Soil analysis
Preliminary soil analysis was carried out based on Balai Penelitian Tanah technical guideline procedures and ISRIC soil analysis procedures. These analyses were performed in the laboratory to extract and determine the levels of each soil characteristic according to the extraction method as follows: soil pH (pH H₂O and pH KCl), CEC (NH₄OAc pH 7), soil organic carbon (Walkey-Black), soil texture, clay mineral (XRD), electrolyte conductivity, and dissolved cations (extract deionized water 1: 5).

2.3. Separation of clay fraction
Soil samples (approx. 20 g) were placed into a beaker glass and added to 50 mL of 30% H₂O₂ and 200 mL of water, then heated for 30 minutes to remove organic matter. Filled water up to a volume of about 1 L and let it stand for 3.5 hours. At the time, the sand fraction was at the bottom, the dust fraction was in the middle, and the clay fraction was on top. Clay was extracted by siphoning off at a depth of 5 cm from the suspension in beaker glass, then transferring it to evaporating porcelain and drying it overnight at 105°C.

2.4. Preparation of clay suspension
The flocculation was determined using solutions from pure analyzed salts such as CaCl₂, MgCl₂, AlCl₃, KCl, and NaCl. To investigate the effect of cations on clay flocculation, approximately 20 mg of clay fraction is added to a 10 mL solution. 10-100 mmol L⁻¹ for Na and K; 0.2-2.0 mmol L⁻¹ for Ca; 1-10 mmol L⁻¹ for Mg; 0.01-0.10 mmol L⁻¹ for Al. At pH 5.5, 6.0, and 6.5, the dispersion characteristics are determined. The pH is adjusted by adding 0.1 M HCl and 0.1 M NaOH.

2.5. Determination of flocculation properties
The flocculation properties were determined using the test tube method. The clay suspension was transferred to a test tube and dispersed in an ultrasonic bath for 15 seconds. The transmission of the sample was measured with a UV-VIS spectrophotometer at 600 nm after two hours at room temperature. The ion concentration that results in flocculation with the transmission of 50% (C₅₀ value) was used to compare the effectivity of different cations on flocculation [4].

2.6. Data analysis
The data obtained is presented in graphic form using the Origin 2016 application.

3. Result and discussion

3.1. Soil characteristics
Data of soil chemical, physical, and mineralogical properties are present in Table 1. Base saturation is high in GSDR₁ and GSDR₂ (85% and 96%), which may be related to their pH values (6.3 and 6.6). The number of base cations and soil reactions (pH) influence base saturation. In general, the relationship between base saturation and soil pH is linear [10]. The XRD analysis also revealed that halloysite and
kaolinite predominated in the soil samples. These 1:1 type clay have CEC values in the range of 20-60 cmol$_e$ kg$^{-1}$.

### Table 1. Chemical, physical and mineralogical characteristics of the soil.

| Components | DRM$_2$ | GSR$_1$ | GSR$_2$ | GSR$_3$ | GSDR$_1$ | GSDR$_2$ |
|------------|---------|---------|---------|---------|---------|---------|
| Texture (%) |         |         |         |         |         |         |
| Sand       | 1       | 14      | 23      | 18      | 3       | 8       |
| Silt       | 27      | 41      | 49      | 43      | 39      | 36      |
| Clay       | 72      | 45      | 28      | 39      | 58      | 56      |
| pH         |         |         |         |         |         |         |
| H$_2$O     | 5.8     | 5.6     | 4.5     | 5.1     | 6.3     | 6.6     |
| KCl        | 4.6     | 4.4     | 3.6     | 3.9     | 5.1     | 5.4     |
| ΔpH        | -1.2    | -1.2    | -0.9    | -1.2    | -1.2    | -1.2    |
| EC (ds m$^{-1}$) | 0.11   | 0.05    | 0.14    | 0.07    | 0.08    | 0.19    |
| Salinity (mg L$^{-1}$) | 56     | 25      | 71      | 35      | 41      | 94      |
| C$_{organic}$ (%) | 3.45   | 1.81    | 3.73    | 2.52    | 1.67    | 1.28    |
| K$^+$ (cmol. kg$^{-1}$) | 0.28   | 0.14    | 0.14    | 0.24    | 0.10    | 0.18    |
| Na$^+$ (cmol. kg$^{-1}$) | 0.37   | 0.32    | 0.25    | 0.24    | 0.21    | 0.29    |
| Ca$^{2+}$ (cmol. kg$^{-1}$) | 12.25  | 16.66   | 6.98    | 12.85   | 14.80   | 15.43   |
| Mg$^{2+}$ (cmol. kg$^{-1}$) | 2.47   | 3.60    | 2.06    | 3.70    | 4.14    | 4.29    |
| CEC (cmol. kg$^{-1}$) | 21.07  | 28.35   | 25.03   | 27.53   | 22.66   | 21.12   |
| Base Saturation (%) | 73     | 73      | 38      | 62      | 85      | 96      |

Note: [+] a little; [++] moderate; [+++] dominant; [(+)] minor.

#### 3.2. Effects of pH and cations on clay flocculation

The rate of pH, cation concentration, and cation valency gave different levels of clay flocculation. Figure 1, shows the variety in pH values, and Na$^+$ concentrations allow variations in the level of flocculation of the clay in DRM$_2$. The clay flocculation value of DRM$_2$ declines with decreasing Na$^+$ concentration and pH. Also, at pH 5.5 and 6.0, clay began to flocculate at a concentration of Na$^+$ 30 mmol L$^{-1}$. According to the graphs and data, halloysitic soils tend to disperse at lower Na$^+$ concentrations and pH. Soils with small CEC values but high Na$^+$ and K$^+$ content deflocculated easily. Goldberg et al [11] stated in the result that the value of critical coagulation concentrations in illite/kaolinite soils increases with increasing pH and SAR values. According to Abbaslou [2], the ability of clay to disperse with the same Na$^+$ concentration is related to a decrease in cation exchange capacity, specific surface area, and plasticity index.

The samples of GSR and GSDR (Figure 1.) also showed differences in flocculation values with the given concentration and pH treatment. At a concentration of Na$^+$ 20 mmol L$^{-1}$, most of the soil samples began to flocculate. The flocculation value decreased in GSR samples when Na$^+$ concentration was 50 mmol L$^{-1}$ at pH 6.5 and less than 50 mmol L$^{-1}$ for pH 6.0 and 5.5. The clay dispersed at concentration Na$^+$ 10 mmol L$^{-1}$ for GSDR$_1$ and GSDR$_2$. Both of the samples have transmission values of less than C$_{50}$.
Figure 1. Clay flocculation rates with various concentrations of Na\(^+\) and pH in all paddy soil samples.

In general, there is no significant difference in flocculation values between kaolinitic and halloysitic soils. When the Na\(^+\) concentration is low, the entire sample disperses (10-20 mmol L\(^{-1}\)). In their paper, Muller et al [12] stated that increasing the pH led to a rise in the flocculation value of kaolinitic soils due to an increase in surface charge. Hillel [13] reported that the expansion of the double layer, increased pH value, and sodium predominance could reduce flocculation levels. Basak et al [14] discovered that when exposed to high concentrations of electrolyte solutions, clay from all soils (1:1 and 2:1) became more flocculated. Agricultural soils with high Na\(^+\) and pH close to neutral require a higher concentration of electrolyte solutions to keep the soil flocculated.

The dispersion occurred at concentrations of K\(^+\) 10-30 mmol L\(^{-1}\) for DRM, GSR, GSR2, and GSR3 for each pH level (Figure 2). GSDR flocculated at a concentration of K\(^+\) 20 mmol L\(^{-1}\). Even though both K\(^+\) and Na\(^+\) are monovalent ions, K\(^+\) has a lower dispersive potential than Na\(^+\). Because of this, K\(^+\) has a higher flocculation rate than Na\(^+\). This result is in line with Marchuk and Marchuk's [15] statement that the dispersive potential of potassium is lower than sodium.

Despite having the same valence, divalent cations like Ca\(^{2+}\) and Mg\(^{2+}\) have different flocculation rates. According to the results, flocculation occurred at concentrations greater than 1.0 mmol L\(^{-1}\) Ca\(^{2+}\) in all samples (Figure 3). Ca\(^{2+}\) has a higher flocculating capacity than Na\(^+\) and K\(^+\), as is well understood. As the graph shows, the flocculation of clay at two mmol L\(^{-1}\) Ca\(^{2+}\), while it takes 20-30 mmol L\(^{-1}\) Na\(^+\) and K\(^+\) to flocculate clay. Since the higher ion valences are stronger to flocculate, and Ca\(^{2+}\) hydration is smaller than Na\(^+\), it reduced clay dispersion. The addition of organic materials or liming, which can increase the availability of Ca\(^{2+}\) to maintain soil stability, is required for agricultural practice on dispersible soils.
Figure 2. Clay flocculation rates with various concentrations of K$^+$ and pH in all paddy soil samples.

Figure 3. Clay flocculation rates with various concentrations of Ca$^{2+}$ and pH in all paddy soil samples.

Compared with Ca$^{2+}$, the divalent Mg$^{2+}$ shows that flocculation occurs in a concentration range of 3-8 mmol Mg$^{2+}$ L$^{-1}$ (Figure 4). It requires a higher Mg$^{2+}$ concentration to flocculate clay than Ca$^{2+}$, which needs only one mmol L$^{-1}$. Previous research has provided that Ca$^{2+}$ has a higher power to flocculate clay.
than Mg$^{2+}$. As well known, the Ca$^{2+}$'s hydration radius is slightly smaller than that of the Mg$^{2+}$ ion, resulting in a lower electrostatic force holding the Mg$^{2+}$ in the adsorption site \cite{16}.

**Figure 4.** Clay floculation rates with various concentrations of Mg$^{2+}$ and pH in all paddy soil samples.

**Figure 5.** Clay floculation rates with various concentrations of Al$^{3+}$ and pH in all paddy soil samples.
The ability of Ca$^{2+}$ to flocculate also depends on the level of acidity. At higher pH, the concentration of Ca$^{2+}$ required to flocculate also increases. Although the level of flocculation was similar in all treatments at the three acidity levels, a higher Ca$^{2+}$ concentration was expected to pass the C$_{10}$ value at pH 6.0 and 6.5. At higher pH, the OH$^-$ will interact with the clay's edge side, neutralizing or negatively charging it, making it easier to disperse [4]. According to Chorom and Rengasamy [17], competitive H$^+$ and Ca$^{2+}$ bonds form by soil functional groups, which affect the surface charge and soil chemical solutions. At low pH, the calcium released or exchanged for H$^+$ results in a smaller negative charge on the surface charge and accelerated flocculation [18].

Clay flocculation occurs in the trivalent cation, Al$^{3+}$, at 0.06 mmol L$^{-1}$ (Figure 5). Compared to monovalent and divalent cations, the Al$^{3+}$ concentrations required to flocculate clay are much lower. At pH 6.5, the clay flocculation level is higher than pH 5.5. Nguyen et al [4] demonstrated in their study that the addition of AlCl$_3$ solution proved to be the most effective in clay flocculation, even at pH 6, where most of the Al is present in solution as Al(OH)$_3$. This behaviour is related to the ion's valence, ionic radius, and the size of the Al$^{3+}$ ion's hydration layer.

Based on the obtained clay flocculation data, the implication for the agricultural sector and climate change is the need for the addition of soil improvement materials, such as lime in cultivation activities. The addition of lime (especially containing Ca$^{2+}$) is done not only to increase soil pH but also to maintain the stability of soil aggregates. This action is a preventive measure for the occurrence of clay dispersion due to flooding and/or clay loss due to increased intensity and duration of rainfall.

4. Conclusion
There was an insignificant difference in the level of clay flocculation in haloisitic soils and kaolinitic soils. The pH value and ions concentration in the soil solution or irrigation water are quite influential on the clay dispersion. Thus, the strength of the cation to flocculate the clay based on the results of this study is Al$^{3+}$ > Ca$^{2+}$ > Mg$^{2+}$ > K$^+$ > Na$^+$. Knowledge of clay dispersion/flocculation behavior is needed in preventing erosion on agricultural lands that are vulnerable to climate change, especially when there is an increase in the duration and intensity of rainfall.

References
[1] Nguyen M N, Dultz S, Tran T T T and Bui A T K 2013 Effect of anions on dispersion of a kaolinitic soil clay: A combined study of dynamic light scattering and test tube experiments. Geoderma 209 209–13
[2] Abbaslou H, Hadifard H and Ghanizadeh A R 2020 Effect of cations and anions on flocculation of dispersive clayey soils Heliyon 6 e03462
[3] Basga S D, Tsozue D, Temga J P, Balna J and Nguetnkam J P 2018 Land use impact on clay dispersion/flocculation in irrigated and flooded vertisols from Northern Cameroon Int. Soil Water Conserv. Res. 6 237–44
[4] Nguyen M N, Dultz S, Kasbohm J and Le D 2009 Clay dispersion and its relation to surface charge in a paddy soil of the Red River Delta, Vietnam J. Plant Nutr. Soil Sci. 172 477–86
[5] Nguetnkam J and Dultz S 2011 Clay dispersion in typical soils of north cameroon as a function of pH and electrolyte concentration L. Degrad. Dev. 25 153–62
[6] Schjonning P, de Jonge L W, Munkholm L J, Moldrup P, Christensen B T and Olesen J E 2011 Clay dispersibility and soil friability-testing the soil clay-to-carbon saturation concept Vadose Zo. J. 11 (1) vzj2011.0067
[7] Boardman J 2010 A short history of muddy floods Soil Science Society of America Journal 21 303-09
[8] Nguyen M N, Picardal F, Dultz S, Dam T T N, Nguyen A V and Nguyen K M 2017 Silicic acid as a dispersibility enhancer in a Fe-oxide-rich kaolinitic soil clay Geoderma. 286 8–14
[9] Massaro M, Riela S, Cavallaro G, Gruttadauria M, Milioto S, Noto R and Lazzara G 2014 Eco-friendly functionalization of natural halloysite clay nanotube with ionic liquids by microwave irradiation for Suzuki coupling reaction J. Organomet. Chem. 749 410–15
[10] Sudaryono S 2009 Tingkat kesuburan tanah Ultisol pada lahan pertambangan batubara Sangatta, Kalimantan Timur Jurnal Teknologi Lingkungan. 10 337–46
[11] Goldberg S, Kapoor B S and Rhoades J D 1990 Effect of aluminum and iron oxides and organic matter on flocculation and dispersion of arid zone soils Soil Sci. 150 588–93
[12] Müller R H 1996 Zetapotential und Partikelladung in der Laborpraxis (Wissenschaftliche Verlagsgesellschaft: Stuttgart)
[13] Hillel D 1998 Environmental soil physics: fundamentals, applications, and environmental considerations (United States of America: Academic Press/An Imprint of Elsevier)
[14] Basak N, Chaudhari S K, Sharma D K 2015 Impact of varying Ca/Mg waters on ionic balance, dispersion, and clay flocculation of salt-affected soils Communications in Soil Science and Plant Analysis. 46 827–44
[15] Marchuk S and Marchuk A 2018 Effect of applied potassium concentration on clay dispersion, hydraulic conductivity, pore structure and mineralogy of two contrasting Australian soils Soil and Tillage Research. 182 35–44
[16] Emerson W W and Chi C L 1977 Exchangeable calcium, magnesium and sodium and the dispersion of illites in water Soil Research 15 255–62
[17] Chorom M and Rengasamy P 1995 Dispersion and zeta potential of pure clays as related to net particle charge under varying pH, electrolyte concentration and cation type European Journal of Soil Science 46 657–65
[18] Kaya A 2006 Settling of kaolinite in different aqueous environment J. Marine Georesourc. Geotechnol. 24 203–18

Acknowledgement
The author expressed gratitude to Lembaga Pengelola Dana Pendidikan (LPDP), Indonesia which sponsored this research.