Distribution of Al, Fe, and Si oxides in three soil orders in dryland of Aceh Besar, Indonesia

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Abstract. The Al, Fe, and Si fractions in the soil are often associated with silicate minerals and hydroxide oxide fractions. The composition of these minerals in the soil is influenced by the degree of weathering and soil development. This study investigated the content and distribution of Al, Fe, and Si oxides in three soil orders (Inceptisols, Ultisols, and Oxisols) on dryland in Aceh Besar, Indonesia. Soil samples were collected in the layers of soil horizon of each profile. The content of Al, Fe, and Si in the soil was extracted with two selective solvents, namely sodium dithionite-citrate solution to determine the forms of Al, Fe and Si free and ammonium-oxalate to determine the forms of Al, Fe, and Si amorphous. The content of Al, Fe, and Si in the extract was measured by AAS. The results showed that the content and distribution of Al, Fe, and Si oxides of soil in the dryland of Aceh Besar varied between soil orders and also differed between horizons. The dithionite-extractable Al ranged from 0.02% to 13.14%, the dithionite-extractable Fe ranged from 1.01% to 4.08%, while the dithionite-extractable Si ranged from 0.62% to 4.29%. The oxalate-extractable Al ranged from 2.09% to 6.44%, the oxalate-extractable Fe ranged from 0.23% to 1.62%, while the oxalate-extractable Si ranged from 1.37% to 18.5%. The content of Fe oxides varied from 0.42% to 3.64%, while the index of crystallinity of Fe ranged from 0.11 to 0.79. The distribution of Al, Fe, and Si in the extract was measured by AAS. The results showed that the content and distribution of Al, Fe, and Si oxides of soil in the dryland of Aceh Besar varied between soil orders and also differed between horizons. The dithionite-extractable Al ranged from 0.02% to 13.14%, the dithionite-extractable Fe ranged from 1.01% to 4.08%, while the dithionite-extractable Si ranged from 0.62% to 4.29%. The oxalate-extractable Al ranged from 2.09% to 6.44%, the oxalate-extractable Fe ranged from 0.23% to 1.62%, while the oxalate-extractable Si ranged from 1.37% to 18.5%. The content of Fe oxides varied from 0.42% to 3.64%, while the index of crystallinity of Fe ranged from 0.11 to 0.79. The distribution of Al, Fe, and Si oxide at several soil orders on dryland Aceh Besar district was very diverse. The distribution of Al- and Fe-oxide were not consistent with the depth of the soil, while Si-oxide tends to decrease with increasing soil depth. The sequential of Fe crystallinity index from low to high is Oxisols < Ultisols < Inceptisols which means that Oxisols is more developed than Ultisols and Inceptisols.

1. Introduction

Dryland has considerable potential to be developed for agriculture, but the use of dryland has found many problems and constraints. The problem with dryland in humid tropical regions is a lack of water during the dry season, acidic soil reactions, inadequate nutrients, low of cation exchange capacity and base saturation, as well as erosion-sensitive soil conditions which are the most dominant environmental constraints in the area [1]. The physical properties of soil on dryland are not good, namely bad soil structure, low soil moisture, soil aeration is somewhat hampered, and the low of water holding capacity [2]. Mineral composition on dryland such as Inceptisols, Ultisol, and Oxisols is dominated by several types of secondary minerals (clay minerals) which are often found in the soils including kaolinite, halloysite, montmorillonite, iron and aluminum hydrous-oxides (gibbsite, goethite, and others) and increasing Al content in the subsoil layer [3].

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These secondary minerals often produce variable-charged soils which tend to be positively charged at low soil pH [4], so that they have low soil chemical quality because they have low clay activity which is characterized by a low soil CEC and sum of cations [5]. The results of the research conducted by [6] in some locations in Aceh showed a low level of soil fertility. The low level of soil fertility is very closely related to the composition of minerals contained in it, and this condition depends on the parent material or soil type. Therefore, information about the composition of soil minerals is essential to evaluate.

Methods for identifying soil mineral types and compositions have been widely developed such as physical methods with x-ray diffraction (XRD), differential thermal analyzer (DTA), infrared spectroscopy, and scanning electron microscopy (SEM) [7]. The use of chemical methods with a selective solvent method has also been used to identify crystalline and amorphous fractions of soils [8]. However, each of these methods has advantages and disadvantages. Analysis of soil mineral with physical methods such as XRD and SEM is usually more expensive compared to chemical methods, so chemical methods are now widely used as an alternative by analyzing the fractions of Al, Fe, and Si with three extracting solutions such as dithionite-citrate [9], ammonium oxalate [10], and sodium pyrophosphate [11]. The DS solution (dithionite-citrate) used to extract Al, Fe, and Si-oxides to show the presence of crystalline and non-crystalline minerals [12]. Al, Fe, and Si cations in the soil generally vary according to soil type and in soil profiles also differ between horizons. By using Al, Fe, and Si fractions with various extractions, it can be determined the composition of crystalline and amorphous minerals as well as the index of the thermality of iron compounds [8, 13]. This paper aims to present the content and distribution of the Al, Fe, and Si oxide fractions on three soil orders in the dryland of the Aceh Besar District.

2. Materials and Methods

2.1. Materials
Materials used in this study includes a map of soil types scale 1: 250,000, geological maps of Aceh Besar scale of 1: 500,000, chemicals for field identification that consists of a solution of peroxide (H₂O₂), hydrochloric acid (HCl), distilled water, and chemicals for laboratory analysis such as Na-dithionite, citrate acid, oxalic acid ammonium, and the standard solution Fe, Al, and Si, and other chemical reagents.

2.2. Methods
This study was conducted using a descriptive method that is based on field observations and laboratory analyzes. Field surveys were carried out for observing soil profiles and identifying soil orders and taking soil samples for analysis in the laboratory. This study focused on three soil orders found in dryland in Aceh Besar district, Indonesia, namely: Inceptisols, Ultisols, and Oxisols. Soil samples of the Inceptisols (Oxyaquic Dystrudept) were taken from the Gaseue Data village of Seulimum subdistrict (05°20'16.1"N; 95°34' 5.8" E), Ultisols (Typic Kandiaquults) taken from Jalin village, Jantho subdistrict (05° 16’ 58.41”N; 095°37’ 51.82” E), and Oxisols (Plinthic Kandiudox) taken from Suka Mulya village, Lembah Seulawah subdistrict (05° 27’19.4” N; 95° 46’ 19, 2” E).

2.3. Identification of Soil Order
Identification of soil order or soil subgroup was conducted by observation of soil morphological properties in the fields based on soil observation guidelines and analysis of soil samples in the laboratory [14]. The soil samples of each profile of three soil orders were taken at horizon layers of each type (subgroup) of soil. Soil samples taken from the field before being analyzed were first dried for 1 week, then crushed and sifted using 2.0 sieves for analysis of soil texture and using a 0.5 mm sieve for analysis of routine soil chemical properties such as pH, organic C, total N, available P, total of P₂O₅ and K₂O, exchangeable cations (Ca-exch, Mg-exch, K-exch, and Na-exch), cation exchange capacity (CEC), base saturation (BS), exchangeable aluminum and hydrogen (Al-exch and H-exch) and electrical conductivity (EC). Methods and procedures for soil analysis are based on the
procedures issued by the Bogor Soil Research Center [15]. The properties of the soil are used as supporting data for the assessment of fertility status and identification of soil subgroups.

2.4 Extractions of Al, Fe, and Si

Identify the fractions of Al, Fe, and Si at each soil horizon, soil extracted with solutions of dithionite-citrate (Al$_d$, Fe$_d$, and Si$_d$) and ammonium-oxalic acid (Al$_o$, Fe$_o$, and Si$_o$). The dithionite-citrate solution is used to identify the forms of free fractions of Al, Fe, and Si at each layer of soil horizon by extracting soil using a 0.1 M sodium dithionite-citrate solution [9]. The analysis procedure for Al, Fe, and Si-dithionite was: 0.5 g of soil sample was put into a 250 ml plastic bottle and then added 50 ml of extractant (sodium dithionite-citrate 0.1 M solution) using a volumetric pipette and shaken for 12 hours with a shaker machine. After shaking, 25 mL of the suspension is decanted into the centrifuge tube and then centrifuged for 15 minutes at 2500 rpm, then filtered with Whatman 42 paper and the supernatant solution is stored in a dark bottle. Furthermore, 5x and 20x dilutions were carried out for the measurement of Al, Fe, and Si with atomic absorption spectrophotometer (AAS) at wavelengths of 248.3, 309.3, and 251.6 nm, respectively.

The ammonium-oxalate solution was used to identify the form of amorphous fractions of the soil by using a solution of 0.2 M ammonium oxalate pH 3.8 [10]. The procedure is to extract 0.5 g of soil samples with ammonium oxalate solution for 4 hours, then centrifuged and the content of Al, Fe, and Si is measured by AAS. The analysis procedure of Al, Fe, and Si dithionite-citrate and ammonium oxalate extracts used an analysis guide according to the one published by Buurman [16]. The form of crystalline oxide Fe was determined by calculating the difference between Fe-dithionite and oxalate extract (Fe$_d$-Fe$_o$), while Fe crystallinity index is calculated from the ratio between Fe oxalate extract and Fe dithionite extract (Fe$_o$/Fe$_d$) and the percentage of soil ferrihydrite content was determined from the content of Fe$_o$ multiplied by 1.7 [17].

3. Results and Discussion

3.1. Description and characteristics of soil

Table 1 shows that based on the results of the profile observation and analysis showed that the Gaseu Inceptisols data have an arrangement of horizons Ap, AB, BA, Bw, BC, C, with a 100 cm solum thickness, have a udic and isohyperthermic soil regime. This soil has only recently developed and formed from acidic sediment developed because there are hilly topography to mountainous and formed above and composed of mixed minerals in the form of gibsite, metahalloysite, and feldspar [18]. These inceptisols are characterized by the cambic horizon, have a medium (medium) texture, while Ultisols Jantho, and Lembah Seulawah Oxisols are two soil orders which have developed and have an argillic horizon (for Ultisols) and oxic horizon (for Oxisols). Both of these soil orders, the thickness of the soil solum is relatively deep (80 - >120 cm) and is containing a mixture of minerals between feldspar, calcite, gibsite, and goethite.

| Soil order | Soil subgroup | Soil texture | Soil horizon | Soil regime | Soil mineralogy |
|------------|---------------|--------------|--------------|-------------|----------------|
| Inceptisols| Oxyaquic Dystrudepts | Medium       | Ap, AB, BA, Bw, BC, C | Udic, IHP | Mixed         |
| Ultisols  | Typic Kandiaquults | Medium      | Ap, AB, BA, Bt$_1$, Bt$_2$ | Udic, IHP | Kaolinitic    |
| Oxisols   | Plinthic Kandiudox | Medium    | A, AB, BA, Bo$_1$, Bo$_2$ | Udic, IHP | Ferritic      |

IHP = isohyperthermic

3.2. Content of Al, Fe, and Si dithionite

The results of the analysis of the content of Al, Fe, and Si soil at various layers of the horizon extracted with a solution of dithionite-citrate and ammonium-oxalate and the content of oxide fractions can be seen in Table 2.
3.2.1. Al-dithionite (Al_d). Table 2 shows that the content of Al-dithionite (Ald) in the Inceptisols of Gaseu Data at each horizon of Ap, AB, BA, Bw, BC, C ranges from 0.18% to 0.92% and tends to increase with increasing soil depth and varies from low to medium on the horizon. This variation indicates that the process of soil horizon formation also influences the transformation of minerals which causes differences in the composition of Al-dithionite soil compounds. The results of a similar study on toposequence of dryland in the Bogor (West Java) showed that the content of Al extracted with dithionite in the Inceptisols was low at 0.87% on the Ap horizon and 0.89% at the Bw horizon, while on the horizon Bw2 and Bw3 Al_d values are not measurable, because the Al in the form of being bound to organic matter [19].

The content of Al-dithionite (Al_d) in Jalin Ultisola at the five layers of the horizon Ap, AB, BA, Bt1 and Bt2 varied from 10.61% to 13.14%. This shows a variation in the content of Al-dithionite at each layer of the horizon, whereas in the dryland in Sawah Lunto and Sijunjung (West Sumatra), it shows that Ultisols contain Al_d ranging from 14.03% to 22.16%, and the content tends to decreases with increasing soil depth [20]. Al-dithionite content in Lembah Seulawah Oxisols at five horizon layers of Ap, AB, BA, Bo1, and Bo2 ranges from 4.45% to 8.87%. The Al_d content is higher when compared to the results of study on Oxisols in Saree (Gunung Seulawah) of Aceh Besar district which found that the Al content extracted with dithionite-citrate varied from 0.95% to 1.12% and its value tended to decrease at deeper depths [21]. The different content of Al_d between these Oxisols is related to the soil genesis process [22].

3.2.2. Fe-dithionite (Fe_d). Table 2 shows that the Data Gaseu Inceptisols have Fe-dithionite (Fe_d) content at six layers of the horizon of Ap, AB, BA, Bw, BC, C, indicating values that are not much different, ranging from 1.21-2.01%. This Fe_d content is lower than the results of a similar study conducted on toposequence in the Bogor (West Java, Indonesia), which showed that the content of Fe-dithionite in Inceptisols ranged from 4.93% at the Ap horizon and 4.36% at the Bw2 horizon, while at the Bw2 and Bw3 horizons the Fe_d value is not measurable (very low) [19]. The difference in Fe content is due to the composition of the parent material differences between the two locations. Inceptisols of Data Gaseu are formed from sedimentary rock which is dominated by quartz sand so
that the Fe content is lower. Possible other factors that lead to higher Fe₄ content in Inceptisols of Bogor because in this region the soil is more developed because it has higher rainfall.

Fe-dithionite (Fe₄) content in Ultisols of Jalin ranges from 1.01% to 2.10%. This Fe₄ value tends to decrease from the Ap horizon to Bt₁ and after that increases again. The results of a study on Ultisols in the Saree (Gunung Seulawah) of Aceh Besar District showed that the content of Fe-dithionite increased at the surface horizon of 4.89% to 5.31% and decreased at deeper depths of soils [21]. Furthermore, there are the Oxisols of the Lembah Seulawah containing Fe-dithionite in the five layers of the horizon of A, AB, BA, Bo₁, Bo₂, ranging from 2.19% to 4.08% or relatively low. The Fe₄ content in this soil profile tends to increase at deeper soil depth, especially at the Bo₁ and Bo₂ horizons as the character of the "oxic" horizon. The results of a similar study on Fe-dithionit in Aceh Besar, showed that the content Fe₄ in Oxisols increased from 4.35% to 5.10% along with the increase the depth of the soil [21]. The content of Fe oxide in Oxisols is higher than the other soil orders because Oxisols are categorized as old soil with a further level of development, so the content of Fe oxides in Oxisols is high. The high Fe oxide high on the soil horizon, especially at the A horizon, has the potential to reduce the availability of some nutrients such as phosphates and sulfates due to fixation.

3.2.3. Si-dithionite (Si₄). Table 2 also shows that Si-dithionite (Si₄) content in the Inceptisols of Data Gaseu ranges from 1.30% to 3.70%, and there is an increase at the deeper of soil depth. The availability of Si in the soil, especially in the tropics, is meager due to the desilication process, which is the chemical transfer of silica out of the soil solum due to leaching, so that concentration of Fe and Al increases [23]. However, the availability of Si is also influenced by the distribution of parent materials, climate, and land management. Si-dithionite content in Ultisols of Jalin ranges from 0.62% to 4.29% and increases with increasing soil depth. In the Oxisols of Lembah Seulawah, Si₄ content ranging from 2.14% to 3.60% and tends to vary within the soil profile. From the upper layer of the Ap horizon to the BA horizon, the Sid content initially tends to increase, but at the Bo₁ and Bo₂ horizons the value tends to decrease again. Si content dissolved from the soil increases with increasing temperature [24]. This is related to the level of weathering of rocks or parent materials containing silicate minerals. The higher the temperature, the higher the level of weathering. Fluctuations in Si₄ content in the soil also depend on the process and the level of development of the soil [25, 7].

3.3. Content of Al, Fe, and Si oxalate

The oxalate extraction used to identify the forms of soil components in amorphous and humus complex forms [17]. In the soils, the amorphous material is often associated with a parent material of volcanic or pyroclastic material. These amorphous fractions consists of allophane minerals, imogolite, ferrhydrite, and Al, Fe and Si oxides which have a very high affinity for soil phosphate anion [26].

3.3.1. Al-oxalate (Alₙ). Table 2 shows that the content of Al-oxalate (Alₙ) in the profile of three soil orders in dryland of Aceh Besar District varied from 2.08% to 6.49% and was classified as low to moderate. The highest content of Al-oxalate was found in Oxisols of Lembah Seulawah, and the lowest was found in Inceptisols of Data Gaseu. In the Inceptisols, the content of Al-oxalate (Alₙ) at horizons of Ap, AB, BA, Bw, BC, C ranges from 2.05-5.36%. In Ultisols of Jalin with horizons of Ap, AB, BA, Bt₁, Bt₂, the content of Al-oxalate (Alₙ) ranges from 4.89% to 5.82% and is classified as medium rate. From this value shows that Alₙ content is relatively almost the same between the horizon layers. Furthermore, in Oxisols of Lembah Seulawah with horizons of A, AB, BA, Bo₁, Bo₂ varies from 4.27% to 6.44. Alₙ content in the soil profile tends to decrease from the top to the bottom layer to the parent material (>125 cm). Based on the data of Al-oxalate, it can be said that the Alₙ content in Oxisols of Lembah Seulawah is higher than Alₙ in Ultisols of Jalin and in Inceptisols of Data Gaseu or their values are sequential: Oxisols> Ultisols> Inceptisols. This shows that the content of the amorphous fraction in Oxisols of Lembah Seulawah is higher than that of Ultisols of Jalin and Inceptisols of Data Gaseu. Oxisols of Lembah Seulawah are formed from volcanic tuffs which have decayed further so that the form of the amorphous fraction is higher. In Ultisols of Jalin and Inceptisols Data Gaseu, the parent material consists of sedimentary rocks dominated by quartz so that the content of the amorphous fraction is lower.

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3.3.2. Fe-oxalate (Fe<sub>o</sub>). The content of Fe-oxalate (Fe<sub>o</sub>) in three soil orders of Aceh Besar dryland also varies from 0.23% to 1.62%. This data indicated that the Fe<sub>o</sub> content is relatively not much different between soil order and all the contents are classified as low (<2.0%). In Table 2 it can be seen that the Fe-oxalate (Fe<sub>o</sub>) content in the profile of Data Gaseu Inceptisols ranges from 0.40% to 0.82% and its value tends to decrease on horizon at the bottom. In Ultisols of Jalin, Fe<sub>o</sub> content varies from 0.23% to 1.62% (very low to low) and in Ultisols showed that the content of Fe<sub>o</sub> decreases at deeper the soil depth, but at a depth of 97 cm or the Bt<sub>2</sub> horizon, the value increases again to 1.62%. This shows that in the Bt<sub>2</sub> layer, there has been a change in mineral composition because it’s close to C horizon (parent material). Furthermore, in Oxisols of Lembah Seulawah, it is seen that the Fe<sub>o</sub> content ranges from 0.24-0.65% and this value is relatively not much different between the horizon layers and relatively low because it is less than 2.0% [27].

3.3.3. Si-oxalate (Si<sub>o</sub>). The content of Si-oxalate (Si<sub>o</sub>) in the three soil orders in dryland of Aceh Besar District varies from 1.37% to 18.5% or varies from low to very high. This data shows that the Si<sub>o</sub> content between the soil orders is very varied. Table 3 shows that the Si<sub>o</sub> content in the soil profile on Ultisols of Jalin was higher than that of Si<sub>o</sub> in the other two soil orders which were followed by Oxisols of Lembah Seulawah, and the lowest was in the Inceptisols of Data Gaseu. In the Inceptisols, Si<sub>o</sub> content is relatively small (1.37-3.26%), while in the Ultisols are very high (14.7-18.5%) and also in the Oxisols of Lembah Seulawah (6.37-9.04%). The variation in the content of Al, Fe, and Si oxalate is caused by differences in soil parent material because of differences in the level of soil development.

3.4. Crystallinity of Fe Oxides
Iron oxide (Fe crystalline) in the soil is in the form of crystalline, and noncrystalline and composition of these minerals in the soil depend on the level of soil development and composition of the parent material [28]. Table 3 also shows that the content of Fe oxide (Fe<sub>d</sub>-Fe<sub>o</sub>) fraction in the three soil orders from dryland of Aceh Besar is rather varied between the soil order and between the horizons. In Inceptisols of Data Gaseu, Fe oxide content ranges from 0.66% to 1.21%. The highest content on the soil profile of Inceptisols at BA horizon and the lowest on the AB horizon. In Jalin Ultisols, the content of Fe oxide ranges from 0.42% to 1.54% and the highest is found at the Ap horizon, while the content of Fe oxide in the Oxisols of Lembah Seulawah ranges from 1.95% to 2.48% and the highest is also found in the A horizon. The highest content of Fe oxide fraction is Oxisols of Lembah Seulawah, while in Inceptisols of Data Gaseu and Ultisols of Jalin, the content of the crystalline fraction of Fe oxide is relatively low.

Furthermore, based on the data in Table 3 also shows that the crystallinity index of iron (Fe<sub>o</sub>/Fe<sub>d</sub>) also varies between soil orders. In the Data Gaseu Inceptisols, the values ranged from 0.26 to 0.54, whereas in Jalin Ultisols ranged from 0.18 to 0.79 and in Lembah Seulawah Oxisols ranged from 0.10 to 0.21. This Fe crystallinity index is one indicator of the level of soil development [28]. If the index of crystallinity of Fe <0.10, the soil belongs have developed very rapidly, whereas if the value ranges from 0.10 to 0.35, then soil is classified as developed, and if the value is 0.35 to 0.55, then the soil is classified as developing or undeveloped soil, respectively [17]. Based on the above criteria, it can be said that Oxisols of Lembah Seulawah is more developed than Ultisols of Jalin and Inceptisols of Data Gaseu. The ferrihydrite content in each layer of soil horizon in the three soil orders in dryland of Aceh Besar District also varies between soil orders.

3.5. Distribution of Al, Fe, dan Si

3.5.1. Distribution of Al-, Fe-, dan Si-dithionite. Distribution of Al, Fe, and Si dithionite (free form) according to soil depth in three soil orders (Inceptisols, Ultisols, and Oxisols) in dryland of Aceh Besar District can be seen in Figure 1.
Figure 1. Distribution of Al, Fe, and Si-dithionite in three soil orders in the dryland of the Aceh Besar District

Figure 1 shows that the distribution of the content of Al-, Fe-, and Si-dithionite varies between orders and depth of soil. Distribution pattern of Al-dithionite in the soil profiles are relatively similar between soil orders and but the content of Al-dithionite of each soil order is different. Al-dithionite content in Ultisols of Jalin was higher than in Oxisols of Lembah Seulawah and Inceptisols of Data Gaseu the content in Ultisols more than in Oxisols and Inceptisols. The content and distribution pattern of Fe-dithionite between Inceptisols of Data Gaseu and Ultisols of Jalin is relatively the same, which does not change with increasing soil depth, whereas in Oxisols of Lembah Seulawah tends to increase with increasing soil depth even from a depth of 0-40 cm, but after that increased until it reached the parent material (C horizon). Figure 1 also shows that the content of Fe-dithionite in the Oxisols of Lembah Seulawah is higher than the content of Fe-dithionite in the Inceptisols of Data Gaseu and Ultisols of Jalin. The Si-dithionite content in all soil orders tends to increase at deeper soil depth, especially in the Data Gaseu Inceptisols and in the Jalin Ultisols whereas in the Lembah Seulawah Oxisols fluctuate somewhat, which initially increases, but at a depth of 40 cm decreases again at deeper of the soil. This difference in the content and distribution patterns of Al, Fe, and free Si is a phenomenon that is common in most soils which are influenced by factors of soil formation [25].

3.5.2. Distribution of Al-, Fe-, and Si-oxalate. The distribution of Al, Fe, and Si oxalate (amorphous form) in soil profile in three soil orders (Inceptisols, Ultisols, and Oxisols) in dryland of Aceh Besar District can be seen in Figure 2. Figure 2 shows that the Al-oxalate distribution, according to the soil depth, is different between three soil orders (Inceptisols, Ultisols, and Oxisols). In Inceptisols of Data Gaseu, Al-oxalate is relatively unchanged according to depth, whereas in Oxisols of Lembah Seulawah tend to decrease with increasing depth to 125 cm depth. Figures 2 also shows that after 120 cm, the content of Al-oxalate has almost the same value between soil orders. The distribution of Fe-oxalate in Inceptisols of Data Gaseu tends to decrease at a depth of 35 to 45 cm, after which it does not change. In Ultisols of Jalin, the Fe-oxalate content is relatively unchanged with depth, whereas in Oxisols of Lembah Seulawah it tends to decrease to a depth of 100 cm and after that, an increase occurs. The distribution of Si-oxalate in Inceptisols of Data Gaseu tends to increase with increasing depth, as well as the Ultisols of Jalin and Oxisols of Lembah Seulawah, but the Si-oxalate contents in Ultisols of Jalin and Oxisols of Lembah Seulawah are higher when compared to Inceptisols of Gaseu.
Figure 2. Distribution of Al, Fe, and Si-oxalate on three soil orders in dryland of Aceh Besar District

The contents of Al, Fe, and Si-oxalate is a representation of the forms of amorphous fraction and the complex humus fraction in soil. These forms are generally formed from the weathering of material fragments of volcanic material. These materials are initially rich in silica and aluminium and when decaying tend to form amorphous aluminosilicate minerals with varying Si and Al ratios [17]. Among the minerals included in this mineral group are allophane and imogolite and this form is mostly found in the Andisols [29]. However, if further weathering occurs, amorphous fractions will be formed which are dominated by Al in the form of gibbsite (Al (OH)₆). This form is often found in orders of Inceptisols, Ultisols, and even Oxisols [1, 30, 31].

3.5.3. Fe-oxide, crystallinity index, and ferrihydrite. The distribution of Fe-oxide, Fe crystallinity index (Feₒ/Fe₉), and ferrihydrite in three soil orders according to soil depth in dryland of Aceh Besar District can be seen in Figure 3. Figure 3 shows that the distribution patterns and changes in Fe-oxide content in Inceptisols of Data Gaseu and Ultisols of Jalin are relatively same and the values tend not to change at deeper soil depth, whereas in the Oxisols of Lembah Seulawah, the pattern of changes in Fe-oxide tends to increase at deeper depth up to 120 cm, and the content of Fe-oxide in the Oxisols of Lembah Seulawah is higher than the content of Fe-oxide in the other soil orders. This shows that the Oxisols of Lembah Seulawah is one of the more developed soils so that the iron oxide fraction in soil is increasingly dominant. Figure 3 also shows that the value Feₒ/Fe₉ or Fe crystallinity index in Oxisols of Lembah Seulawah is smaller than the values (Feₒ/Fe₉) in Inceptisols of Data Gaseu and Ultisols of Jalin. This shows that the crystalline form of iron minerals is more dominant in Oxisols than Ultisols and Inceptisols. Although different in number, but the pattern of distribution in the soil is relatively no different. The pattern of distribution of ferrihydrite according to the depth of soil between soil orders occurs a little variation, but the average content of ferrihydrite is not so different.
3.6. Correlation between Al, Fe, and Si fractions

The distribution of crystalline Fe, Fe<sub>o</sub>/Fe<sub>d</sub> (Fe crystallinity index) and ferrihydrite in three soil orders according to soil depth in dryland of Aceh Besar District can be seen in Figure 4. In the figures shows a significant correlation between the content of Fe-dithionite and Fe-oxide. This indicates that the dithionite-citrate extraction can be used to identify iron fraction proportionally can predict the forms of soil crystalline Fe or Fe oxyhydroxides in soils because this solution can extract forms of free soil fractions which include crystalline minerals, amorphous minerals and complex-humus fractions which are bound to metal [3]. A significant correlation also occurs between Al-dithionite and Si-oxalate. The relationship is positively linear, which means that the higher the content of Al-dithionite, the higher the content of Si-oxalate. This shows that the composition of Al and Si in the soil is very closely related to the formation of minerals, especially silicate minerals [7]. The relationship that is linearly correlated also occurs between the ratio of Fe<sub>o</sub>/Fe<sub>d</sub> and Fe-oxalate. This can be explained that with the increase in Fe-oxalate, the Fe<sub>o</sub>/Fe<sub>d</sub> also increases. Increasing the value of Fe<sub>o</sub>/Fe<sub>d</sub> shows the content of mineral crystalline is getting lower so that the amorphous fraction will be increasingly dominant [17, 31].

Based on the results of regression analysis and the correlation it was also found that there was no real correlation between Al-oxalate and Si-oxalate. This shows that Si and Al cations in the soil are often competing for ions, especially in the formation of amorphous minerals. If the Al content is high, the Si cation will usually be desolated so that the comparison with Si will be smaller. The results of the analysis also show that the content of soil Fe-oxide is inversely related to the Fe crystallinity index. It can be explained that with increasing soil Fe-oxide fraction, the crystallinity rate of iron compounds will increase or the Fe<sub>o</sub>/Fe<sub>d</sub> index decreases, as well as the soil ferrihydrite content, does not correlate with the Fe crystallinity index [28].

Dryland in Aceh (Indonesia), especially in Aceh Besar District is dryland consisting of various types of soil orders, including Inceptisols, Ultisols, Oxisols, Andisols, Entisols and others [32]. The formation of various soil orders occurs because, in the dryland of Aceh Besar, there are various types of parent materials with very varied topography. With several land orders, the composition of soil minerals can also vary according to the process of soil formation. In soil, especially in the humid tropical region, soil minerals are generally dominated by silicate minerals and oxyhydroxides fractions formed from aluminium, iron, silicate, oxygen, calcium, potassium, and sodium ions [5]. The composition and arrangement of these elements continue to change as the processes of soil formation occur. According to [30], soil minerals can be grouped into forms that have crystalline structures and
amorphous forms, as well as forms that bind to soil humus complexes. These forms can be partially identified using x-ray diffraction (XRD), thermal differential analysis (DTA), infrared spectroscopy, and using selective chemical dissolution (SCD) as has been widely used by researchers [3, 21, 33].

Figure 4. Correlation between the content of Al, Fe, and Si with soil fractions in dryland of Aceh Besar District

Selective chemical solvents are a common term used in the analysis of soil minerals using chemical solutions that are selective to extract semi-quantitative mineral components from soil and sediments [7, 5]. There are three extraction systems that are commonly used to identify soil mineral components, namely: (a) dithionite-citrate solution, (b) solution of ammonium-oxalic acid, and (c) sodium pyrophosphate solution [17]. Dithionite-citrate solution dissolves the metals Al, Fe, Si, and other cations from crystalline, amorphous, and complex humus mineral components while ammonium-oxalate solutions can dissolve Al, Fe, and Si in the form of amorphous fractions and complex humus forms, while sodium pyrophosphate solution dissolves the Al and Fe metal bonds in the bond of the humus complex. By using these selective solutions, we can determine the form of oxide, crystalline form, and index of Fe crystallinity has used this selective solution for the determination of amorphous and crystalline fractions on Andisols from Merbabu mountain of Central Java [29] and Ultisols from Jasinga, West Java [8]. Based on the results of the analysis of Al, Fe, and Si by using extraction of dithionite-citrate and ammonium-oxalate, the results obtained varied between the crystalline oxide fractions and the Fe crystallinity index on the three soil orders in dryland of Aceh Besar District.

4. Conclusions

(1) The content and distribution of Al, Fe, and Si oxides of soil in the dryland of Aceh Besar (Indonesia) varied between soil orders and also differed between horizons because of different in parent material and process of soil genesis.
(2) The dithionite-extractable Al in three soil orders (Inceptisols, Ultisols, and Oxisols) ranged from 0.18% to 13.14% (very low to high), the dithionite-extractable Fe ranged from 1.01% to 4.08% (low), while the dithionite-extractable Si ranged from 0.62% to 4.29% (very low to low). The oxalate-extractable Al ranged from 2.47% to 6.44% (low to medium), the oxalate-extractable Fe ranged from 0.23% to 1.62% (very low to low), while the oxalate-extractable Si ranged from 1.37% to 18.5% (low to very high).

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