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A Case Study in Cianjur West Java, Indonesia: A Correlation Humic and Fulvic Acids with Mineralogical Composition and Physico-Chemical Analysis Using Partial Least Square

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ABSTRACT

Humic and fulvic acids are important materials for the health of the soil. This is related to the capability of humic and fulvic acids as chelating agent for pollutant in soil. The relationship between humic and fulvic acids with that of the soil properties is an important aspect to determine the characteristics of soil. Furthermore, production of humic and fulvic acids is a time-consuming process with several stages. Regarding this problem, the selection of sample size to study humic and fulvic acids is important. The relationship between the soil properties was analysed using the Partial Least Square (PLS) analysis, which is regarded as a solution to solve the analysis of complicated problems by offering a powerful approach. This study aimed to analyse the relationship between humic and fulvic acids, in terms of their mineral and physicochemical properties using the PLS method. The study was carried out in West Java, Indonesia. The results showed that the relationship between the chemical, physical, mineral contents with humic and fulvic acids, affected the negative and positive aspects of the relationship. Humic acids had a weak to good model category (0.269–0.940) with regards to the soil properties, and fulvic acids had a moderate model category (0.495–0.603) against all soil properties. Thus, the PLS method can solve a problem in study relationship between the soil properties with small sample and can help in understanding the soil characteristics in general.

Keywords: soils properties, humic acids, fulvic acids, partial least square

INTRODUCTION

Soil is an accumulation of mineral matter, which covers the land surface as a result of weathering processes. Soil can be defined based on specific terms across several fields of study (Nortcliff et al., 2012). Furthermore, soil is an important aspect of life, because it is supports living beings, such as plants. Organic matter has a large influence toward the health of the soil. Mineralisation and secondary humification processes from organic matter can influence the growth of plants, as well as affect their properties (Boguta & Sokołowska, 2014; Mulyani et al. 2019). The relationship between soil properties have been studied by several researchers, for example, soil properties and electrical resistivity, the correlation between soil properties and pedogenic processes, as well as soil micronutrients and chemical content (Haque et al. 2000; Neely, Morgan et al. 2016; Siddiqui & Osman, 2013; Verdoodt et al. 2009). The relationship between organic matter in the soil and its properties is important. Researchers have tried to find the correlation between soil properties and organic matter (Christensen, 1992; Kome et al. 2019). Several studies found that the relationship between organic matter and soil properties had specific correlation. In (Ristori et al. 1992) it was stated that strong hydrogen bonds resulted between organic matter and soil minerals.

The clay mineral content in soils also has a strong influence on macro elements, such as carbon and nitrogen. In another relationship it was shown that the soils with a small fraction usually have a lower C/N ratio, although the soil organic matter content is much higher (Christensen, 1992).

Further decomposition of organic matter produces humic substances such as humic acids, fulvic acids, and humin (Purmalis et al. 2013). Humic substances have a good effect toward soil properties, including its physical and chemical properties (Boguta & Sokołowska, 2014). Humic acids have many benefits, such as decrease of the heavy metals content as a result of complex formations with other metals, amino acids, peptides, and carbohydrates (Tserenpilet et al. 2010). The ability of this material to modify the characteristics of the soil needs to be studied to understand the relationship between humic and fulvic acids with that to the mineral and physico-chemical properties of the soil. The relationship between humic and fulvic acids can be studied using the regression or correlation methods. However, the availability of an insufficient number of samples can be a problem. In order to produce humic acid and fulvic acid, a lot of time is required as well as a process analysis. (Ahmed et al. 2004), state that the purification process of humic material takes from two days up to one week. This process is time consuming, and can be a limit in determining the number of samples to be taken in a study. For that reason, the Partial Least Square (PLS) method is proposed.

PLS is a multivariate statistical technique which can handle many response variables, as well as explanatory variables, all at once. This analysis is a good alternative for multiple regression analysis methods and principal component regression, because it is more robust. PLS is a powerful analytical method which is not based on a multitude of assumptions or conditions, such as normality and multicollinearity tests. This method has its advantages, for example, the data does not have to have a normal multivariate distribution with categorical indicators. It can be categorical, ordinal, or simply exist as interval to ratio data scales. Another advantage is the analysis fit for the small sample size for small data observations. The relationship between variables can be very complex for a small sample size. PLS is a solution to solve the analysis of complicated problems by offering a powerful approach (Wold et al. 2001). The main objective of this study was to validate the relationship between humic and fulvic acids with small sample of soil, which can be expressed in terms of its mineral and physico-chemical properties. This information lends meaning to the behaviour of the soil properties, as a function of the soil quality, using the PLS method analysis.

MATERIALS AND METHODS

Study Area

The study was conducted in the Bojongpicung District, Cianjur, which is located in West Java, Indonesia (Fig. 1). Surveys, comparative and descriptive methods were used. Surveys were conducted to obtain the primary data using a free physiographic survey method, which categorized the land according to land units. This was created by analysing the formed landscape from maps of slopes, land used, soil types, and rainfall. The results of the land unit analysis resulted in five land units. From each land unit, two samples were selected, i.e., the topsoil (0–30 cm) and subsoil (30–60 cm), for physical and chemical analysis. For a large area, 2 points were taken for comparative purposes. The coordinates of each location point were recorded using a GPS unit (Garmin 585), and then plotted against the map using an ArcGIS desktop 10.2 software. The samples were collected by purposive random sampling.

Sample Collection

The soil samples were taken at the 0–30 cm and 30–60 cm depth from each point, with a weight of ± 2 kilograms across 14 points in the area (Figure 1) above. The soil was passed through

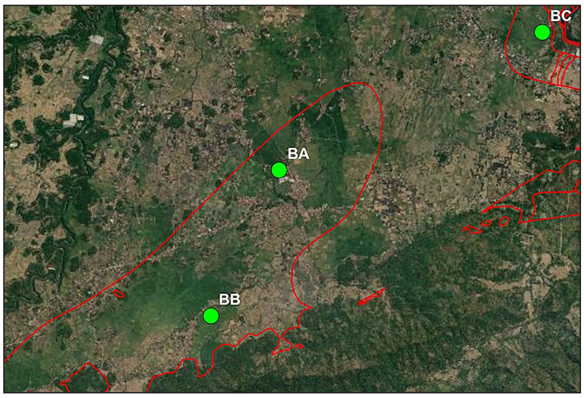


Figure 1. Location of samples point

a 2 mm sieve. Repeated powdering and sieving resulted in particles which were >2 mm in size. The material was collected and stored in a plastic container or polythene bag, with proper labelling for laboratory analysis.

Analysis Procedures

Chemical Analysis

The total N was determined using the Kjeldahl method as an index for the N value (Bremner, 1965). Organic analysis for the C content used the Walkley and Black Method (Yeomans & Bremner, 1989). This method is commonly used for the analysis of the total N in the soil. The measurement of the pH is expressed as an inverse log of the hydrogen ion concentration. The pH of the soil solution controls the form and solubility of many plant nutrients. The soil pH was measured using a soil-water suspension ratio of 1:2.5 (Okalebo et al. 2002). The available phosphorus was determined colorimetry using a spectrophotometer after the extraction of the soil samples, using 0.5 M sodium bicarbonate ($NaHCO_3$) at a pH value of 8.5, according to the Olsen extraction method (Kovar & Pierzynski, 2009).

The exchangeable basic cations (Ca, Mg, K and Na) were extracted using 1 N ammonium acetate at a pH value of 7 (Okalebo et al., 2002). The exchangeable Ca and Mg were determined from this extraction using an atomic absorption spectrophotometer, while the exchangeable K and Na were determined from the same extract with a flame photometer. The cation exchange capacity (CEC) of the soil was determined from ammonium acetate saturated samples, which were subsequently replaced by sodium from a percolated sodium chloride solution, after removal of the excess ammonium through repeated washing with alcohol (Okalebo et al., 2002). The exchangeable acidity was determined by saturating the soil sample with a 1 M KCl solution and titrating it with 0.05 N NaOH, as described by (Okalebo et al., 2002). The exchangeable capacity was extracted using a NH_4OAc (ammonium acetate) solution, such that the maximum exchange occurred between NH_4 and the cations which originally occupied the exchange sites on the soil surface (Okalebo et al., 2002). The percent base saturation was computed as the ratio of the sum of exchangeable bases to the number of CEC. Soil micronutrient cations (Fe, Mn, Cu and Zn) were extracted using the ethylene diamine tetraacetic acid (EDTA) method (Okalebo et al., 2002). The extraction of humic acids from the soil was done using the NaOH ratio of 1:10 (soil:extractor) (De Souza & Bragança, 2018) according to the extraction of fulvic acids (Saputro & Karmanto, 2020).

Physical Analysis

The soil texture was determined by a pipette method which used H_2O_2 as an organic matter digester. The method was a direct sampling of soil particles from the suspension using a pipette, at a fixed depth, h, and time, t (BBLSLP, 2006). The water content was expressed as a gravimetric comparison between the mass / weight of the water in the sample before drying at 105°C, and the sample mass / weight after drying, until it reached a fixed mass / weight (BBLSLP, 2006).

Mineral Analysis

The analysis of soil minerals was determined by the X-ray diffraction (XRD) method, used tool of Rigaku Smartlab, with the Cu Kα radiation (1.5418 Å). The data collection was carried out across 2θ, with a step of 0.01°. The X-ray diffraction data was analysed to result an information of qualitative and quantitative evaluation.

Statistical Analysis

The data obtained from the laboratory was analysed using Partial Least Square (PLS) to examine the relationship between the mineral and physico-chemical parameters of soil with the humic and fulvic acid content. The Partial Least Square (PLS) tool is a Structural Equation Modelling (SEM) technique, which is able to analyse the latent variables, indicator variables, and direct measurement errors. PLS is an alternative method for analysis with weak supporting theories, indicators which do not meet the reflective measurement models, or for data which is not normally distributed. There are three model analysis for the relationship between variables from the indicators, namely the outer model, inner model, and the weight relation. The explanation of the three relationship models is as follows (Wiyono, 2011, Ghozali, 2016):

1. The outer model or measurement model, is a specification of the relationship between latent variables and their indicators, also known as outer relations or measurement models, which

explains the characteristics of latent variables with indicators. The reflective model equation can be written as follows:

$$x = \lambda_x \xi + \varepsilon_X$$
$$y = \lambda_y \eta + \varepsilon_y$$

where: x and y are indicators for exogenous (ξ) and endogenous (η) latent variables, while λ_x and λ_y is the loading matrix that describes the simple regression coefficients which connect the latent variables with their indicators. Residuals are measured using ε_x and ε_y, which are interpreted as measurement errors.

2. The inner model shows the existence of a relationship between latent variables (structural model), which is often referred to as inner relation. This model shows a relationship between the latent variables based on the substantive theory. The formative model equation can be written as follows:

$$\eta_j = \Sigma_i \beta_{ji} \eta_i + \Sigma_i \gamma_{jb} \xi_b + \xi_j$$

3. The weight relation is an estimate of the case value of the latent variables. The value of the case for each latent variable can be estimated as follows:

$$\xi_b = \Sigma_{kb} W_{kb} X_{kb}$$
$$\eta_i = \Sigma_{ki} W_{ki} Y_{ki}$$

where: W_{kb} and X_{kb} are the k weight factors used to form an estimate of the latent variables, ξ_b and η_i. The estimation of the latent variables is linear aggregate of the indicators, which weight values are obtained using the estimation procedure of the PLS.

RESULTS AND DISCUSSION

The soil samples came from the Neglasari Village, located in Cianjur, West Java. It has the characteristics of a volcanic area, which is 294 m above sea level. Its parent material is andesite and basalt; it has a flat relief (1%), an effective depth of 180 cm, slow drainage, and is used as a rice field. The soil profile is shown in Figure 2.

Chemical parameters

In general, the chemical characteristics of soil can be seen in Table 1 and Table 2. The CEC of soil for all the samples were in the range of 12.78–44.64 Cmol/Kg, with the Ca content in the range of 21.95–30.06 Cmol/Kg. The Mg content ranged between 14.11–22.12 Cmol/Kg, while the K and Na content ranged between 0.08–0.64 Cmol/Kg and 0.28–0.68 Cmol/Kg, respectively. The total base cations ranged between 36.60–50.43 Cmol/Kg. In general, the CEC, cations, and the total base in the soil samples varied from low to very high criteria.

In Table 2 above, the pH value for all the given samples ranged between 6.72–7.89. The rice field conditions of the soil affected the chemical characteristics of the soil, such as its pH value. In (Morales, Paz-Ferreiro, Vieira, & Vázquez, 2010) it was stated that during the rice growth period, the pH value can increase up to two units. This shows that the pH value in the rice fields can range from neutral to slightly alkaline conditions. The further decomposition of organic matters such as humic acid can affect the pH of soil due to the soil acidity value which acts as a buffer (Stevenson, 1994). The organic C gave a range value of 0.77–1.92% and a N range of 0.05–0.21%. The humic acid from the humification process of organic matter gave a range value of 0.07–2.61%, while the fulvic acid had a range value of 2.41–3.89%. The C and N chemical content ranged from very low to low, this condition

Figure 2. Soil profile in the area of research

Table 1. The CEC, cations and total base cations

Code	CEC (Cmol/Kg)	Cations (Cmol/Kg)				Total Base Cations (Cmol/Kg)
		Ca	Mg	K	Na	
BAP I (0–30)	31.31	21.95	14.11	0.16	0.39	36.60
BAP II (30–60)	37.89	23.29	15.69	0.10	0.35	39.43
BAV I (0–30)	29.34	22.77	14.02	0.11	0.28	37.17
BAV II (30–60)	37.91	23.90	16.01	0.08	0.27	40.27
BA I (0–30)	44.21	26.03	15.65	0.81	0.48	42.97
BA II (30–60)	12.78	30.06	14.64	0.21	0.60	45.51
BB I (0–30)	22.43	26.08	16.83	0.64	0.47	44.01
BB II (30–60)	34.85	28.48	16.50	0.22	0.66	45.86
BC I (0–30)	41.92	28.88	16.25	0.67	0.66	46.47
BC II (30–60)	42.26	27.57	19.18	0.50	0.58	47.83
BD I (0–30)	44.64	28.92	16.58	0.41	0.57	46.48
BD II (30–60)	38.83	27.44	22.12	0.19	0.68	50.43
BE I (0–30)	40.01	29.41	14.48	0.61	0.63	45.13
BE II (30–60)	27.28	27.97	17.91	0.49	0.59	46.96

Table 2. The pH, organic C, total N, humic and fulvic acids

Code	pH	Organic C (%)	Total N (%)	Humic Acids (%)	Fulvic Acids (%)
BAP I (0–30)	6.72	1.92	0.21	2.61	2.41
BAP II (30–60)	7.06	1.10	0.09	0.21	2.66
BAV I (0–30)	6.80	1.87	0.15	1.34	2.72
BAV II (30–60)	7.21	0.84	0.05	0.10	2.75
BA I (0–30)	6.96	1.43	0.17	0.79	3.76
BA II (30–60)	7.64	0.77	0.09	0.11	3.89
BB I (0–30)	6.98	1.61	0.20	1.89	2.99
BB II (30–60)	7.59	0.79	0.09	0.07	3.35
BC I (0–30)	7.73	1.49	0.17	0.33	2.64
BC II (30–60)	7.89	1.22	0.09	0.11	2.74
BD I (0–30)	7.84	1.05	0.09	0.12	2.79
BD II (30–60)	7.65	0.87	0.06	0.06	2.66
BE I (0–30)	7.40	1.52	0.13	0.46	2.68
BE II (30–60)	7.59	0.87	0.09	0.07	2.69

can influence the humic materials content in soil (Mulyani et al. 2019). In the top soil, the organic carbon and total N content was larger, compared to that of the subsoil. A similar pattern was shown in a study by (Andersson, et al. 2013). The use of the soil as a rice field land can affect the availability of nutrients in the soil. This correlates with the decomposition process of organic matter from root exudates and root debris, which can add N toward the soil (Inubushi, Watanabe, & Inubushi, 1986). The Cations Exchange Capacity (CEC) parameter also has an important influence toward the characteristics of the soil, especially for holding or storing the cations. Anions, such as nitrates, sulphates and chlorides can reduce the concentration, if the negative charge in the soil increases. The measurement of the CEC can determine the mobility of elements in the soil (Saidi, 2012). On the basis of the relationship between the chemical parameters, it was shown that each parameter has a connecting effect with one another, with regards to the specific soil characteristics.

Physical Parameters

The physical parameters showed that the variation in the data resulted from soil samples (Table 3). The bulk density ranged between 1.05–1.18. The bulk density ranged between 1.05–1.18, particle density ranged between

2.11–2.66 and the porosity ranged between 49.22–56.69. In terms of soil characteristics, the sand ranged between 3.67–13.69%, the dust ranged between 22.56–82.68%, and the clay ranged between 9.07–68.12%.

In general, the physical characteristics had a correlation with other soil parameters. The behaviour of these parameters had a strong or weak relationship, depending on the characteristics of the soil itself. within terms of the chemical characteristics, the correlation was related to the availability of nutrients in the media, as a direct and indirect mechanism. Apart from that, the chemical properties had a correlation with the physical properties of the organic matter. It is an important agent which can influence the physical properties of the soil, such as the aggregate stability (Xing et al. 2004). The porosity value in the soil can affect the other aspects of the soil parameters, such its root density. When the soil was porous, the root system could work well as a necessary function, to support the plant growth. In general, the soil physical characteristics can affect the root density, especially in the subsoil levels (Yu et al., 2018). For other functions, the organic matter can decrease the concentration of pollutants in the soil through adsorption processes which result from human activities, chemicals, or fertilizers. The humic and fulvic acids further decompose organic matter, which will give the same advantage toward the soil characteristics. (Ye et al. 1999) showed that the physical characteristics could also be improved through the addition of manure in mine tailings. The soil texture has an important effect in terms of physical properties, especially for fine clay fractions. It has an important function toward the bioavailability of important nutrients, and also for water retention and for maintaining the soil structure (Saidi, 2012). On the other hand, related to bulk density parameter, Foth (1992) states that the soil with high organic matter can causes the behaviour of soil to change. The soil becomes loose and forms clumps which makes the weight of the soil volume low.

Mineral Parameters

XRD was used to determine the crystal structure and lattice parameters formed in the sampled soil. The data obtained from the XRD analysis showed the relationship between the intensity (I) at the peak of the spectrum, and the diffraction angle (2θ). The Miller Index was determined from the formation of the diffraction peaks. The results of the XRD characteristics from the top soil (0–30 cm) can be seen in Figure (3–9) and sub soil (10–16).

The quantitative analysis from the diffractogram showed the characteristics of the minerals from the soil samples which primarily comprised quartz, cristobalite, labradorite, anorthite, stilbite and kaolinite. For the soils with higher concentrations of quartz, it was indicated that the land had further development, low soil nutrient reserves, and was mostly acidic (BPPP, 2004). For the minerals from the soil samples with high contents of quartz and cristobalite, it contained SiO_2, as well

Table 3. Physical parameters of soil samples

Code	Bulk Density (BD)	Particle Density	Porosity	Texture		
				Sand (%)	Dust (%)	Clay (%)
BAP I (0–30)	1.15	2.66	56.69	4.19	45.36	50.45
BAP II (30–60)	1.11	2.14	47.92	3.67	40.06	56.27
BAV I (0–30)	1.14	2.18	47.57	5.84	31.05	63.11
BAV II (30–60)	1.18	2.69	56.06	6.06	31.67	62.27
BA I (0–30)	1.12	2.24	50.22	13.69	49.97	36.34
BA II (30–60)	1.10	2.18	49.50	7.86	40.50	51.64
BB I (0–30)	1.05	2.16	51.64	13.16	40.42	46.41
BB II (30–60)	1.08	2.19	50.84	9.19	25.34	65.47
BC I (0–30)	1.07	2.11	49.22	7.80	30.21	61.99
BC II (30–60)	1.11	2.18	49.43	8.26	82.68	9.07
BD I (0–30)	1.08	2.13	49.56	7.89	29.01	63.10
BD II (30–60)	1.11	2.19	49.05	5.50	28.25	66.26
BE I (0–30)	1.08	2.17	50.16	9.25	22.56	68.18
BE II (30–60)	1.05	2.15	51.08	6.90	36.18	56.92

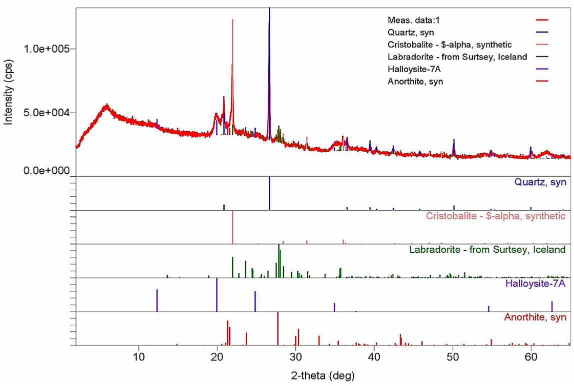


Figure 3. BAP I Sample

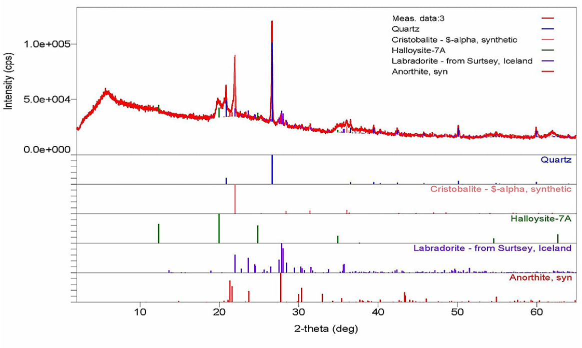


Figure 4. BAV I Sample

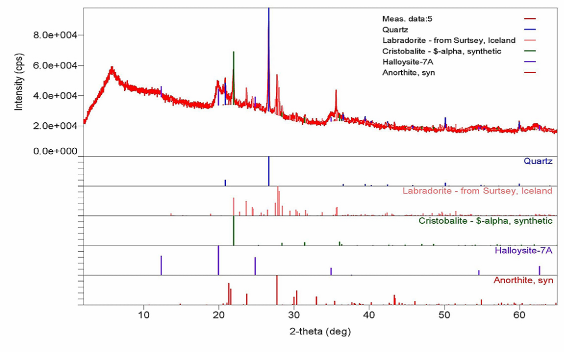


Figure 5. BA I Sample

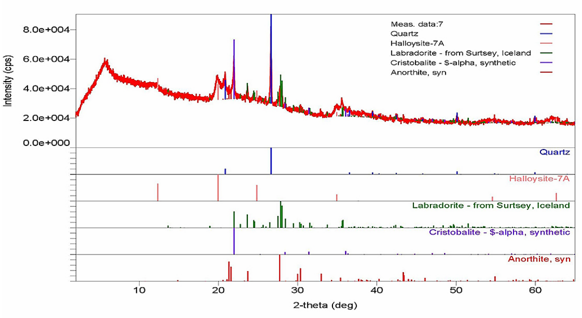
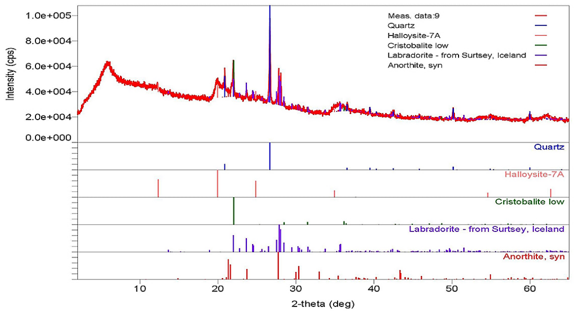


Figure 6. BB I Sample



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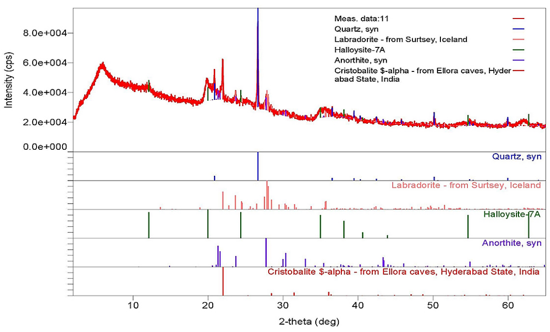

Figure 8. BD I Sample

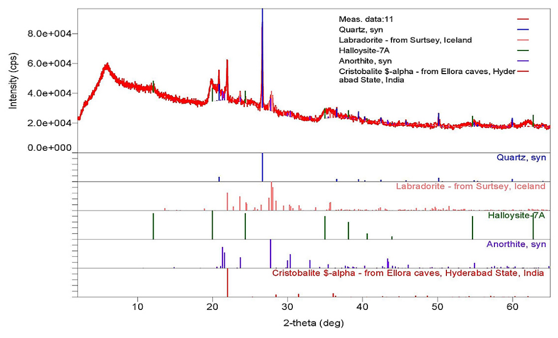

Figure 9. BE I Sample

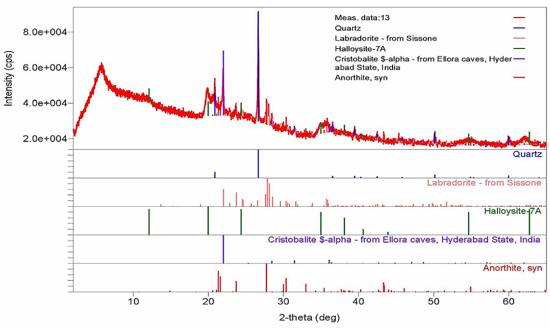

Figure 10. BAP II

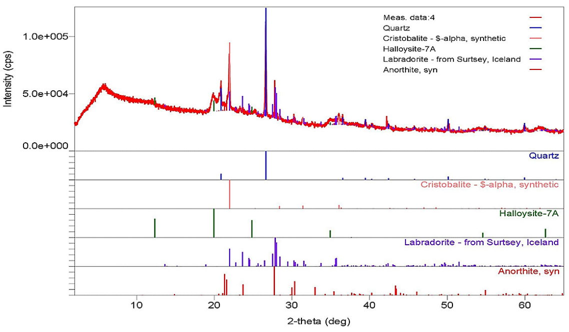

Figure 11. BAV II

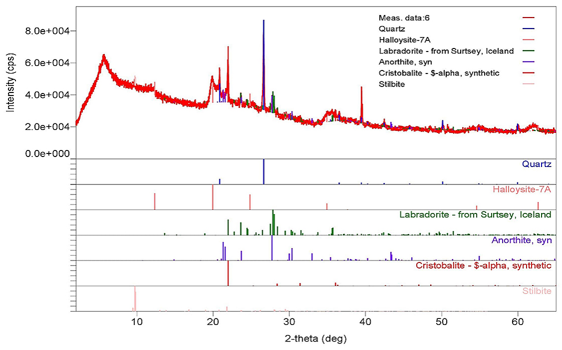

Figure 12. BA II

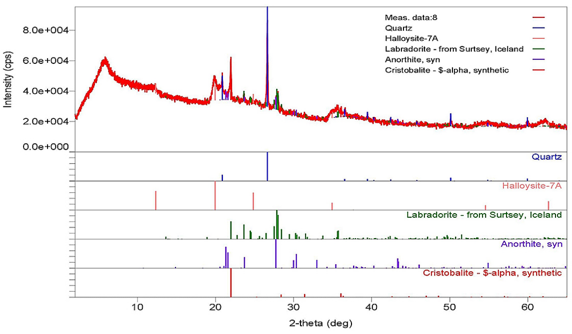

Figure 13. BB II

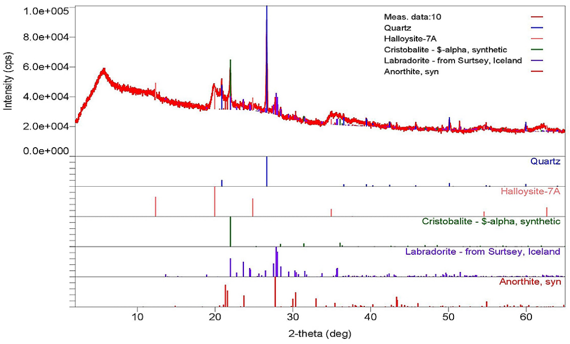

Figure 14. BC II

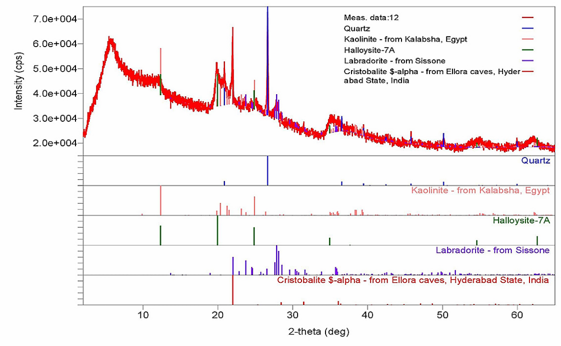

Figure 15. BD II

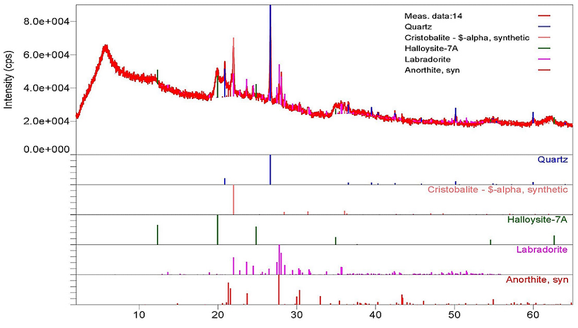

Figure 16. BE II

as labradorite which contained $CaNaAl_2Si_2O_8$, halloysite which contained $Al_2Si_2O_5(OH)_4$, and anorthite which contained Ca $(Al_2Si_2O_8)$. In general, soil minerals are a main ingredient of soil compounds (Brady, 1990). The minerals in soils come from the physical and chemical weathering of rocks, which are the soil parent material. The process of forming soil minerals comes from recrystallization of other weathering compounds, or weathering of the existing primary and secondary minerals. The mineral content in the soil can be an important factor to identify the potential nutrients in the soil. The chemical compounds which form the minerals in the soil can be categorized as macro and micro nutrients, which are needed by the plants. Thus, to determine the level of nutrient reserves in a soil type, it is necessary to analyse the composition of the primary minerals of the soil. A soil with a higher mineral content of feldspar has micro elements such as Na^+, Ca^+, K^+ and Ba^{2+} (Huang, 1989). The further weathering of feldspar can result in clay minerals such as kaolinite (Rice et al. 1985). Clay minerals such as illite and kaolinite are mostly found in rice fields. Kaolinite can be formed as a result of smectite weathering in an acidic environment, and can also be present in the soil as a result of weathering in the upstream area, which is deposited in

Table 4. Quantitative characteristics

Code	Quartz	Cristobalite	Labradorite	Anorthite	Stilbite	Kaolinite
BAP I (0–30)	43.90	26.45	22.46	7.19	0	0
BAP II (30–60)	47.33	30.21	21.15	1.31	0	0
BAV I (0–30)	24.71	6.20	61.67	7.42	0	0
BAV II (30–60)	55.84	29.91	8.87	5.38	0	0
BA I (0–30)	57.00	16.00	8.00	19.00	0	0
BA II (30–60)	35.86	8.07	37.84	13.15	5.08	0
BB I (0–30)	9.15	58.48	28.98	3.39	0	0
BB II (30–60)	7.58	7.09	18.94	66.39	0	0
BC I (0–30)	20.91	10.78	52.01	16.30	0	0
BC II (30–60)	0.04	0.03	99.89	0.03	0	0
BD I (0–30)	8.60	2.40	22.97	66.03	0	0
BD II (30–60)	14.85	6.47	23.90	0	0	54.78
BE I (0–30)	10.09	2.40	20.10	67.41	0	0
BE II (30–60)	16.32	19.95	48.05	15.68	0	0

the alluvial material deposition system (BPPP, 2004). Generally, natural clay soils contain more than one type of mineral, i.e., either clay minerals, non-clay minerals, or other organic and inorganic materials. To date, there have not been any studies which clearly explain the influence and interaction of each individual mineral type on the soil behaviour. However, the information on the composition and proportion of these minerals is important to provide a comprehensive understanding, which can be used as a reference for describing the soil behaviour, be it qualitatively, quantitatively or empirically.

Relationship Model between Humic and Fulvic Acids with the Chemical Properties of Soil

The relationship model between humic and fulvic acids with chemical properties of the soil can be seen in Table 5 below.

From Table 5 above, the value of each chemical parameter gave a variant for the relationship between the humic acid parameter. For K, organic C and the total N, the relationship was negative against humic acid. The discriminant validity from the humic acid and the chemical parameters in general, gave a value of X = -0.972 Y, with a $R^2 = 0.940$. This means that the relationship between chemical parameters and humic acid had a negative relationship and included in a good model category. The R^2 value in this analysis reflects the parameters which simultaneously affect the variations of the humic acid by almost 97.2%, and 2.8% of which is influenced by other variables. Based on the p values, humic acid was not affected significantly by CEC, Ca, Mg, K, Na and total base cations parameters, but only pH, organic C and total N affected the humic acid significantly at 5% critical level. The fulvic

Table 5. Relationship model between humic and fulvic acids on chemical properties

Parameters	Humic Acids		Fulvic Acids	
	Standardize Coefficient	p -Value	Standardize Coefficient	p-Value
CEC	0.285	0.361	-0.429	0.175
Ca	0.621	0.052	0.474	0.135
Mg	0.439	0.166	-0.223	0.473
K	-0.025	0.936	0.262	0.400
Na	0.460	0.147	0.246	0.429
Total Base Cations	0.650	0.042	0.213	0.491
pH	0.796	0.010	0.083	0.788
Organic C	-0.853	0.005	-0.415	0.189
Total N	-0.875	0.003	-0.048	0.877

acid showcased a close correlation with that of the humic acid.

The CEC, Mg, organic C, and the total N gave a negative relationship, but for the other parameters was positive. The discriminant validity from the fulvic acid and the chemical parameters as a group, gave a X = 0.796 Y, with a R^2 = 0.603. This means that the chemicals parameters and fulvic acids had a positive relationship and included in a moderate model category. The R^2 value in this analysis reflects the parameters which affect the fulvic acid by almost 60.3%, 39.7% of which is influenced by other variables. Based on the p values, all the parameters did not affect the fulvic acid significantly at 5% critical level. In Table 5 above, the humic and fulvic acid had the same connection path with some of the chemical properties. Mindari et al. (2014) showed that the addition of humic acid and cations can significantly affect the cation exchange (Ca, Mg. K, Na) and pH of soil. The humic materials contributed to the complex ion exchange properties. It was related to the capability of the humic acid in binding processes of soil mineral surfaces, which are influenced by the hydrophobic and hydrophilic characteristics (Mikkelsen, 2005). This mechanism was also applied to fulvic acids, which can be seen from the capability of the humic and fulvic acids in its interaction processes with compounds of transition elements (Klučáková et al., 2000). The other mechanism is the availability of micronutrients, caused by adsorption processes which were affected by the humic and fulvic acid content in the soil. Thus, in general, it is related to the adsorption mechanism, and fulvic acid has a strong influence toward the physical and chemical properties of the soil (Da Costa Saab et al., 2010).

Relationship Model between Humic Fulvic Acids with the Physical Properties of Soil

From Table 6, the value of each physical parameters provided a variant in the relationship of the humic acids parameters. In terms of the parameters which reflected on the texture of the soil (clay), this was negatively correlated toward the humic acids and positive for others. The discriminant validity from the humic acids and physical parameters in general gave a value of X = 0.645 Y, with a R^2 = 0.367. This means the relationship was a positive relationship and included in a good model category. The R^2 value in this analysis represents the parameters which simultaneously affect the variables of the humic acid by 36.7%, 63.3% of which is influenced by other variables. Based on the p values, humic acid was not affected significantly by bulk density and texture parameters. Only particle density and porosity affected the humic acid significantly at 5% critical level. The p value of humic acid was not a significant effect toward the parameters all the physical parameters, because it was more than 0.05. The relationship between the fulvic acids and the physical parameters such as sand and dust itself, gave a negative relationship but not for others.

The discriminant validity from the fulvic acids and the physical parameters in general gave a value of X = -0.677 Y, with a R^2 = 0.413. It means that the relationship was a negative relationship and included in moderate model category. The R^2 value in this analysis showed that the physical parameters simultaneously affected the variables of the fulvic acid by 41,3% and 58,7% of which is influenced by other variables. Based on the p values, fulvic acid was not affected significantly by almost all parameters except for sand that was significant at 5%

Table 6. Relationship Model Between Humic and Fulvic Acids on Physical Properties

Parameters	Humic Acids		Fulvic Acids	
	Standardize Coefficient	p -Value	Standardize Coefficient	p-Value
Bulk Density	0.290	0.328	0.150	0.616
Porosity	0.673	0.016	0.270	0.364
Particle Density	0.613	0.031	0.311	0.294
Sand	0.117	0.696	-0.877	0.000
Dust	0.157	0.600	-0.126	0.673
Clay	-0.172	0.564	0.284	0.339

critical level. In general, from Table 6 above, it was shown that the relationship between these materials with the physical properties varied across the behaviour of the soil. The physical, chemical and biological properties can be influenced by fulvic acid, which can also improve the nutrients availability in the soil (Sootahar et al., 2019). In (Sootahar et al., 2020) it was shown showed that the fulvic acid played an important role in the plant's growth, which can also improve the structure and fertility of the soil across varying textures. The influence of humic substances in the soil properties connected it to the important function of increasing some of the soil properties, as a direct or indirect mechanism. Thus, this was related to the availability of nutrients in the soil. (Sharif et al. 2002) showed that the further decomposition of humic substances such as fulvic, humic, and humin, provided a much more effective impact across various soil properties such as its water holding capacity, through increased soil aggregation and soil aeration.

Relationship between Humic and Fulvic Acids on Mineral Contents

In Table 7 above, the relationship between humic acids and mineral parameters such as quartz and cristobalite resulted in a negative relationship but not for others. In general, a model for mineral parameters and humic and fulvic acids gave a value of X = -0.570 Y, with a $R^2 = 0.269$. It means that the relationship is negative and included in a weak category. The R^2 value in this analysis represents the parameters which affected the variability of the humic acid by 27% and 73% of which is influenced by other variables. Based on the p values, humic acid was not affected significantly by almost all parameters except for Cristobalite that was significant at 5% critical level. The value of each mineral parameter provides variants toward the relationship on of the fulvic acid parameters. For cristobalite, labradorite and kaolinite gave a negative relationship against the fulvic acids, but not for the other factors. The discriminant validity from the fulvic acids and mineral parameters in general gave a value of X = 0.731 Y, with a $R^2 = 0.495$. This means that the relationship was positive and included in a weak model category. The R^2 value in this analysis means that the parameters simultaneously affect the variables of the fulvic acid by 49.5% and 50.5% of which is influenced by other variables. Based on the p values, fulvic acid was not affected significantly by almost all parameters except for Stilbite that was significant at 5% critical level. Minerals are the main components of soils, which are very important.

The larger percentage of the soil, which is about 45%, is made up of components of minerals, and the rest is organic matter, water and gas (Foth, 1992). The role of minerals in the soil is quite important, also as an indicator of the nutrient reserves in the soil, and an indicator of soil content and its evolution in its environment. Clay minerals are important materials in the soil, which can influence the soil quality in general. The composition of minerals in the soil will affect the soil quality, because the content of the mineral usually differs between types of minerals, especially between primary minerals and secondary minerals. Primary minerals such as olivine, feldspar, apatite, mica, and so on, contain a number of nutrients such as Ca, Mg, Fe, and K. These elements are important components which act as quality indicators. For this reason, the application of techniques to measure soil mineralogy is needed (Kome et al., 2019).

Table 7. Relationship Model Between Humic and Fulvic Acids with Mineral Contents

Parameters	Humic Acids		Fulvic Acids	
	Standardize Coefficient	p -Value	Standardize Coefficient	p-Value
Quartz	-0.320	0.280	0.300	0.313
Cristobalite	-0.902	0.000	-0.105	0.725
Labradorite	0.153	0.609	-0.287	0.334
Anorthite	0.447	0.127	0.197	0.508
Stilbite	0.303	0.307	0.874	0.000
Kaolinit	0.334	0.259	-0.222	0.456

CONCLUSIONS

In general, the relationship for the soil properties is an important factor to understand the characteristics of the soil. The PLS method is a powerful analysis tool for specific cases, especially for humic and fulvic study. This is a solution to solve problematic data sets which have many assumptions or conditions, such as normality and multicollinearity test issues. The chemical, physical and mineral contents in the soil samples provided a variation of the data across the top soil and subsoil samples. Moreover, the humic and fulvic acids content of this soil correlation across one to the other element depended on the characteristics of the elements in the soil. The humic acid has a varied model category from weak to good across some of the soil properties, and fulvic acid had the same relationship for all soil properties, which was included in moderate model category. Thus, this study can help understand the further decomposition of organic matter such as humic and fulvic acids, which can affect the soil properties in general.

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