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Evaluation for the Potential Use of Silicate Rocks from Four Volcanoes in Indonesia as Fertilizer and Soil Ameliorant Joko Priyono, Raden Sutriono, and Zaenal Arifin1 Received 10 January 2007 / accepted 11 August 2008 ABSTRACT Evaluation for the Potential Use of Silicate Rocks from

FourVolcanoes in Indonesia as Fertilizer and Soil Ameliorant (J. Priyono, R. Sutriono, and Z. Arifin): Silicate rocks, the abundant plant nutrient source in Indone- sia, have not been evaluated for use as a fertilizer/and soil ameliorant. This research was aimed to identify (1) mineral and elemental compositions of silicate rocks originated from Galunggung, Kelud, Tambora, and Rinjani Volcanoes and (2) soil properties determining dissolution rate of plant nutrients from the silicate rock fertilizers (SRFs). The rocks were ground with a ball mill for 10 min providing SRFs with medians of particle size of 30 – 50 ?m. Each SRF was added to 6 soils from West Java, East Java, and Lombok Island at a rate equivalent to 20 t ha-1, incubated for 28 days in a laboratory condition. Results indicate that adding SRFs clearly increased soil pH with negligible effect on soil salinity. Adding SRFs also increased quantity of citric-oxalic-extractable plant nutrients (Ca, K, Zn, and Cu) and activity of soil micro-organisms. Dissolution of plant nutrients from the SRFs in the soils was mainly determined by combination factors of C-organic content and pH of soils before application of the SRFs. It was concluded that SRFs originated from those volcanoes may be used as a plant-multi nutrient source and a reme- dial agent for acidic and biologically degraded soils. However, the true effectiveness of SRFs for those uses needs to be further tested under various soil-plant systems. Keywords: Ameliorant, basaltic, plant nutrients, silicate rock fertilizers, volcanic rocks INTRODUCTION During the last two decades, the possibility of using silicate rocks as fertilizers has received significant attention from agronomists and soil scientists, and some advantages over chemical fertilizers have been proposed by many researchers, such as Leonardos et al. (1987 and 2000), Coroneos et al. (1996), Hinsinger et al. (1996), Bolland and Baker (2000), Coventry et al. (2001), and Priyono (2005). In Indonesia, various silicate rocks are abundant, originated from about 130 active volcanoes. However, evaluation for the potential use of the materials as a plant-nutrient source/and soil ameliorant never been done. For many developing countries, including Indonesia that spends scarce dollars to import chemical fertilizers, locally produced silicate rock fertilizers (SRFs) may be an appropriate material for their farming systems. From an environmental point of view, applying SRF is non-polluting due to the slow release of nutrients to soil solution such that water pollution resulting from leaching or erosion of SRF from agricultural land will be least. Furthermore, SRF does not contain elevated levels of contaminants such as Cd, F, and U that occur in some chemical fertilizers and thus provide a more sustainable source of plant nutrients. The use of SRFs in broad scale agriculture has also been proposed for the utilization of quarry by-products in Western Australia (Coroneos et al., 1996; Hinsinger et al., 1996; Bolland and Baker, 2000), Queensland (Coventry et al., 2001), and Brazil (Leonardos et al., 1987), and the utilization of mine tailing (Bakken et al., 1997 and 200). Quarry industries have been operated in many places in Indonesia, mainly producing coarse-rock materials used for building and other constructions. But, no attempt has been made to use the materials for 1 Department of Soil Science, University of Mataram Jln. Pendidikan 37 Mataram, Lombok Island, NTB, Indonesia Corresponding author: Joko Priyono, Phone/Fax: +62 370 644793/+62 370 628143; e-mail: jokotanahunram@gmail.com J. Tanah Trop., Vol. 14, No. 1, 2009: 1-8 ISSN 0852-257X a.gricultural purposes. The rocks are most likely to be suitable fertilizers and soil ameliorant for farming systems in this country. This paper presents results of the first part of a multi year research relating to the evaluation for the possible use of silicate rocks, or in combination with organic materials and bio-fertilizer, as effective and environmentally sound fertilizer and soil ameliorant. The objectives of this research were to identify (1) the properties of silicate rocks originated from four volcanoes in Indonesia, associated to their potential use as fertilizer/and soil ameliorant and (2) soil properties determining dissolution rate of plant nutrients from the SRFs in soil. MATERIALS AND METHODS Rock and Soil Samples Silicate rocks were collected from the slope of Mt. Galunggung (in West Java), Mt. Kelud (in East Java), Mt. Rinjani in Lombok Island (which has been processed by a quarry industry in Mataram for road construction), and Mt. Tambora (in Sumbawa Island). The bulk samples of rocks were washed with water, air dried, and broken with a hammer to about 0.5-cm diameter. A 2kg of broken rock was ground for 10 minutes with a ball mill having capacity of 11.3L using 5 kg of ? 22mm-stainless steel balls. This milling time was presumed to be the optimum milling time based on result of Priyono (2005). Sub samples of ground rocks, termed as SRFs, were taken for mineralogical and total elemental analyses. The mineral composition of the SRFs was interpreted from their x-ray diffraction (XRD) patterns which were collected by using a Phillip Analytical X-ray B.V. with a PW1710 diffractometer using monochromatized Cu-Kα (λ = 1.54056 Å), generated at 40 kV and 30 mA. The diffraction intensity was recorded between 5 and 70° 2θ at a scanning rate of 0.02° per second. The XRD patterns of the ground rocks were presented in Figure 1. 3 .1 0 Å 3.75 Å 2.95 Å 2 .52 Å 1 .6 5 Å Relative Intencity of XRD 2.1 4 Å M t R inja ni 4 .04 Å 3 .0 1 Å M t. G alung g un g 1 .76 Å 1 .8 4 Å M t. K e lu d Mt . T am b o r a 5 15 25 35 2? (degree) 45 55 65 Figure 1. XRD patterns of the 10 min-ball milled rocks originated from Rinjani, Galunggung, Kelud, and Tambora volcanoes with d-spacing of several peaks Total elements composing the SRFs were identified using a wet digestion method with HF and H_3BO_4 (modified Jackson, 1958). Results of this analysis are presented in Table 1. Distribution of particle size was identified by using a pipette method (Gee and Bauder, 1986 with some modifications for sampling time and pipeting depth). Result of this measurement is presented in Figure 2.Soil samples of 20 cm-tops, excluding organic layers, were collected from six different places (from wet to dry areas), i.e., from Jasinga-Bogor, West Java (Oxisol), Darmaga-Bogor, West Java (Ultisol), Lamongan-East Java (Entisol), Batu-Malang, East Java (Inceptisol), Wonosalam-Mojokerto, East Java (Alfisol), and from Kayangan, West Lombok (Inceptisol). The samples were air-dried, lightly ground to break large aggregates, and screened to pass a 2mm-seiver. Soil pHH2O and EC (1 : 5) were measured consecutively Table 1. Mineral and total elemental (%) composition of SRF. N o. Ele me nt R1 (oxide) (Tambora) 1. 2. S iO2 51. 78 A l2 O3 26. 23 3. CaO 7. 12 4. MgO 3. 36 5. K 2O 0. 37 6. N a2O 2. 06 7. F eO 8. 56 8. MnO 0. 16 9. Z nO 0. 01 10. CuO 0. 34 11. Others < 0.01 Total * 100 R2 (Ke lud) 51.98 25.14 6.95 3.03 1.19 2.19 8.99 0.16 0.01 0.36 < 0.01 100 R3 (G alunggung) 54.73 24.36 7. 38 3. 30 0. 55 1. 88 7. 25 0. 16 0. 01 0. 38 < 0.01 100 R4 (Rinjani) 52.28 24.77 4.84 1.83 6.30 3.25 6.24 0.15 0.01 0.33 < 0.01 100 Augite Mg-hornblende Mineral Hyperstane composition** Albite Anothite Mica Muscovite Augite Fe-fargasite Tremolite Albite Anothite Mica Muscovite Augite Hyperstane Albite Anothite Gendrite Fargasite Albite Anorthite Muscovite * Normalized to 100 % ** Ranged to its relative abundance 100 90 Tambora 80 Kelud % (w/w) c k u u m m u u l l a a t v ie ve 70 Galunggung 60 Rinjani 50 40 30 20 10 0 0 20 40 60 80 100 120 Diameter (μm under) Figure 2. Particle size distribution of SRFs ball milled for 10 minutes. with pH- and EC- meter; CEC was identified by using 1N NH4Act pH 7 (Thomas, 1982), C-organic content was determined with the method of Wakley and Black (1934), the contents of exchangeable base cations were measured from the filtrates of CEC measurement using AAS, and soil texture was identified with a pipette method (Gee and Bauder, 1986). The results of soil analysis are presented in Table 2. Incubation Experiment A 5 g of SRF and a 250 g of air-dried soil were mixed in a 500mL-plastic bottle, moisten with H2O to about 125 % of its field capacity, and cupped. Triplicates and a control (soil without SRF) of the mixtures were prepared, then were incubated in laboratory condition at a temperature ambient of 22 – 25o C. Sub samples of incubated soils were taken after 28 days of incubation period for analyses of pH,EC (using above methods), and quantities of Ca, K, Zn, and Cu extractable in 0.01M citric-oxalic extracting solution. A 5g moist soil + 25mL citric- oxalic solution in a 50mL-plastic tube was shaken on a rotary shaker for 2 hours and the solution was filtered. The concentrations of Ca, K, Zn, and Cu in the filtrates were measured with AAS. The change of soil properties due to application of SRF (e.g., ‶pH, ‶EC, ‶Ca, ‶K, ‶Zn, and ‶Cu) were calculated from the corresponding values for treated soils minus that for the control. Another set of incubation experiment was prepared in duplicates for observation of soil biological activity, e.g., mixtures of SRF (from Mt. Tambora and Mt. Galunggung) + those 6 soils and controls (soils without SRF). The plastic bottles used for thisexperiment werefacilitated with linesfor CO2 outflow and atmosphere inflow (for supplying O2 to the soils). The CO2 produced by soil organism activity during incubation period was cached with 0.1N KOH solution. The total CO2 was measured weekly up to 3 weeks using a titration method with 0.01 NaOH. The value of ‶CO2 was calculated from total CO2 produced by treated soils minus that for untreated soil (control). Statistical Methods Analyses of variant were applied to identify the effects of SRF to each of the changes of dependent variables, i.e., ‶pH, ‶EC, ‶Ca, ‶K, ‶Zn, ‶Cu, and ‶CO2. Soil properties that significantly determine the values of these dependent variables were identified using linear-bivariate and multivariate (forward-step wise) analyses. These statistical analyses were done using STATISTICA 6 software. RERSULTS AND DISCUSSION General Characteristics of SRF and Soil As shown in Table 1, the mineral and chemical compositions of the 4 rocks are quite similar, which are dominated by ferromagnesian silicates such as augite, hornblend, and pyroxenes with some feldspars and micas. The rocks contain 51 – 55% SiO2, so they Table 2. Several properties of soils used in this experiment. No. Soil Properties 1. Sand 2. Silt 3. Clay 4. pHH2O (1:5) 5. EC (1:5) 6. C-organic 7. CEC 8. ECEC 9. Exch. Ca 10. Exch. Mg 11. Exch. K 12. Exch. Na 13. Exch. Acidity 14. Base Saturation Unit % % % - µS.cm- % cmolc.kg-1 cmolc kg-1 cmolc kg-1 cmolc kg-1 cmolc kg-1 cmolckg-1 cmolckg-1 % Soil Type* T1 34.43 26.29 39.28 4.30 56.60 0.59 50.58 27.68 10.90 3.56 0.41 0.34 22.90 30.05 T2 T3 T 4 T5 T6 24.24 51.12 22.24 44.29 80.61 59.04 27.07 21.34 37.17 13.80 16.72 21.81 56.42 18.54 5.59 4.88 5.40 4.99 7.54 6.53 48.40 31.10 35.80 59.70 54.60 1.68 0.87 1.22 2.77 0.27 20.32 26.24 26.40 48.66 5.33 19.57 25.84 25.85 48.41 4.93 4.62 4.62 12.34 43.62 3.11 0.66 2.38 0.39 0.13 0.30 0.69 0.86 1.41 0.45 0.70 0.45 0.28 0.49 0.20 0.34 0.75 0.40 0.55 0.25 0.40 31.52 31.01 55.43 91.24 83.57 * T1 = Oxisol – Jasinga; T2 = Ultisol – Darmaga; T3 = Inceptisol – Batu Malang; T4 = Alfisol – Wonosalam; T5 = Entisol – Lamongan; T6 = Inceptisol – Kayangan may be grouped as basaltic rocks (Deer et al., 1992). (Holdren and Berner, 1979; Gillman, 1980; Gillman These types of rocks are dissolved more quickly in et al., 2001 and 2002; Leonardos et al., 1987 and most soils than for felsic or silicious rocks (Aubert 2000; Wang et al., 2000; Coventry et al., 2001; Harley, and Pinta, 1977; Deer et al., 1992; Priyono, 2005). 2002; Priyono and Gilkes, 2004), indicating the Total content of aluminum is 24 – 26% Al2O3, calsium potential use of SRF as an ameliorating agent for and magnesium respectively are 5 – 7% CaO and 2 – acidic soils. The very low increase of soil EC in this 3% MgO. The total content of potassium for rock present research indicates the minimum negative from Rinjani is much higher (e.g., about 6% K2O) effect of SRF application to soil salinity hazard. than that for the other three rocks (0,3 – 1% K2O). Similar trends with those results were also shown by The total contents of other metal elements of the rocks Harley (2002) and Priyono (2005). are < 1%, except that for Fe (i.e., 6 – 8% FeO2). Based on their plant-nutrient composition, these volcanic Quantity of Nutrients Dissolved from SRFs rocks seem to be appropriate for a multi-nutrient fertilizer. The mean percentage of plant nutrients (“Ca, “K, The properties of soils used in this experiment “Cu, and “Zn) dissolved from applied SRFs relative (Table 2) vary widely. Soil texture or clay content is to total content of corresponding nutrient in SRF is ranged from coarse (6% clay) to fine (57% clay); soil presented in Figure 4. As shown in the figure, the pH is 4 – 7.5; C-organic content is 0.2 – 1.7 %; and quantity of most plant nutrients dissolved from SRFs CEC and base saturation (BS) are 5 - 51 cmolc kg-1 was quite different among soil types. The value of and 30 – 91%, respectively. For soil developed from “Ca for soils T5 (Entisol-Lamongan) and T2 (Ultisol K-rich chalk stones, soil T5 (Entisol-Lamongan), the – Darmaga) were similar, e.g., about 13 %, but that content of exchangeable Ca is 43.6 cmolc kg-1 which for the other soils were 2 – 7 fold lower. A note should is much higher than that for the other soils. be made that soil T5 already contained high Ca (e.g., 43.62 cmolc kg-1, see Table 2), so the addition of Ca Effects of SRF on Soil pH and EC from SRFs to this soil practically was meaningless. The highest values of “K, “Zn, and “Cu, were for soil The mean values of “pH and “EC are presented T1 (Oxisol-Jasinga) (e.g., about 25, 20, and 15 %, in Figure 3. As shown in the figure, the application respectively) which were 2-10 fold larger than those of the SRFs at a rate equivalent to 20 t ha-1 for the other soils. Based on the dissolution of these significantly increased soil pH and EC (“pH and “EC nutrients, it may be concluded that soil T2 was the were positive). The increases of pH were from 0.01 most responsive to the application of SRFs. to 0.3 units and those for EC were from 1 to 24 µS Results of simple bivariate and multivariate cm-1. analyses for the quantity of dissolved nutrients from The positive liming effects of adding SRF into SRFs are summarized in Tables 3 and 4. As shown in soils were also reported by many other researchers Table 3, soil properties individually determined less ΔpH (unit) ΔEC (µS cm-1) 0.25 30 ΔpH ΔEC 0.20 25 0.15 20 15 0.10 10 0.05 5 0.00 T1 T2 T3 T4 T5 T6 0 Soils Figure 3. Mean values of —pH and —EC for each type of soil. Notations for soil type (T1 – T6) refer to the explanation in Table 2. 30 T1 T2 T3 T4 T5 T6 25 % to total element in SRF 20 15 10 5 0 ΔC a ΔK ΔZn ΔC u Figure 4. Mean percentage of dissolved nutrients from SRFs (“Ca, “K, “Zn, and “Cu) in each soil (T1 – T6). Notations for soil type refer to the explanation in Table 2. than 50% to variation of the quantity of nutrients dissolved from SRFs (“Ca, “K, “Zn, and “Cu). However, further analysis (Table 4) indicates that soil C-organic content in association with soil pH (at initial condition) determined about 95% to variation of the values of “pH, “Ca, K, “Zn, and “Cu. Clearly, soil C-organic content together with soil pH were the main determinant factors for dissolution of plant nutrients from SRFs in soils. This finding was much different with that by other researchers. For examples, Hughes and Gilkes (1994) found that clay content in combination with exchangeable acidity of soils contributed only about 48% to the variation of dissolved rock phosphates in soils. Priyono and Gilkes (2004) found larger contribution of those soil properties to the variation of dissolution of ground- silicate rocks in soils from Western Australia (e.g., R2 was about 60 %). In both experiments, the activity of soil organism in incubated soils was eliminated by adding toluene, while in this present experiment, no biological suppressant was used. Therefore, there was an indication that soil organism activity had significant effects on dissolution of SRF in soil. Organic acids have important rule in dissolving rocks and minerals (Huang and Keller, 1970; Welch and Ullman, 1996; Blake and Walter, 1999; Zhang and Bloom 1999; Oelkers and Gislason, 2001). The Table 3. Coefficient determination (R2) for simple-linier relationship between quantities of nutrient dissolved from SRFs with soil properties. N o. Soil Quantity of Nutrient Released from SRFs Properties ?Ca ?K ?Cu ?Zn 1. Clay (%) 2. Sand (%) 3. C-organic (%) 4. pHH2O (1:5) 5. CEC (cmolc.kg-) 6. ECEC (cmolc.kg-) 7. Base Saturation (%) 8. Exch. Ca (cmolc.kg-) 9. Exch. K (cmolc.kg-) 10. Exch. (Al+3 + H+) (cmolc.kg-) 0.23 0.03 0.09 0.08 0.00 0.06 0.03 0.04 0.36 0.00 0.00 0.00 0.28 0.10 0.07 0.08 0.01 0.12 0.07 0.08 0.05 0.02 0.10 0.11 0.13 0.13 0.10 0.09 0.14 0.00 0.11 0.11 0.04 0.04 0.03 0.02 0.28 0.17 0.00 0.00 Table 4. Equations and coefficient of determination (R2) for multirelation- ships between quantities of nutrients released from SRFs with soil properties. No Equation R2 1. ?Ca (% total) = - 3.075 + 0.495 (C-org. %) + 0.472 (pH) 2. ?K (% total) = - 4.384 + 0.470 (C-org. %) + 0.475 (pH) 3. ?Cu (% total) = - 1.007 + 0.512 (C-org. %) + 0.449 (pH) 4. ?Zn (% total) = - 1.730 + 0.508 (C-org. %) + 0.461 (pH) 0.97 0.97 0.95 0.96 acids may act as cation exchangers and chelating agents, especially for polyvalent cations. The (Table 2) indicated that the value of •CO2 was significantly correlated only to soil base saturation involvement of soil organic in determining dissolution (with r = 0.91). Biological reactions in the soil are so of nutrients from SRFs (Table 4) was possibly complex that available data in the present research associable to the function of soil organic as the main are insufficient to provide further explanation. source of soil organic acid (John, 1998). The higher Practically, however, SRFs may be use as soil soil organic content for soils with high/neutral pH, biological ameliorant. the more active soil organisms decomposed soil organic matter, so the more organic acids were CONCLUSION produced in these soils. In other word, contribution of soil organic was parallel with that for quantity of Silicate rocks originated from Galunggung, soil organic acid in determining dissolution rate of Kelud, Rinjani, and Tambora volcanoes are nutrients from SRF in soil potentially appropriate materials for use as a Effect of SRFs to Soil Organism Activity multinutrient fertilizer/and soil ameliorant in general. Application of SRFs (e.g., finely ground silicate rocks The application of SRFs significantly increased originated from those volcanoes) clearly increased the activity of soil organism, as indicated by soil pH, so those were potentially used as liming increasing respiration rate (positive values of •CO2, materials with negligible effect on soil salinity. The Figure 5). The increase of respiration rate for soils application of the SRFs also increased the quantities T1, T2, and T3 was about 0.3 cmol kg-1, whereas that of plant nutrients (Ca, K, Zn, and Cu) extractable in for soils T4, T5, and T6 was about 3 fold higher (0.7 0.01M citric-acetic acids and activity of soil organism. – 1.0 cmol kg-1). Results of a simple bivariate analysis The dissolution of these nutrients from added SRFs for the relationships of •CO2 with soil properties in various soils was mainly determined by soil C- 1.2 ΔCO2 (cmol kg-1) 1.0 0.8 0.6 0.4 0.2 0.0 T1 T2 T3 T4 T5 T6 Soils Figure 5. The mean increase of respiration rates ("CO2) due to application of SRFs, incubated for 28 days. Notations for soil type (T1 – T6) refer to the explanation in Table 2. organic content in association with soil pH. Practically, SRFs may be used as a plant-nutrient source and soil ameliorant, especially applicable for organic-rich acidic/and biologically degraded soils. However, the true effectiveness of SRFs as fertilizers and soil ameliorant should be tested in soil-plant systems, observed in both short and long terms.

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