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49 J Trop Soils, Vol. 21, No. 1, 2016: 49-66 Available online at: http://journal.unila.ac.id/index.php/tropicalsoil DOI: 10.5400/jts.2016.21.1.49 J Trop Soils, Vol. 21, No. 1, 2016: 49-66 ISSN 0852-257X Geochemical Investigation of Selected Elements in an Agricultural Soil: Case S tudy in Sumani Watershed West Sumatera in Indonesia Aflizar1, Muzakkir1, Roni Afrizal1, Muhammad Azadur Rahman2 1State Polytechnic Payakumbuh for Agriculture (Politeknik Pertanian Negeri Payakumbuh), Indonesia 26271, e-mail:aflizar_melafu@yahoo.com.

2Department of Geoscience, Graduate School of Science and Engineering, Shimane University , 1060 Nishikawatsu-Cho, Matsue 690-8504, Japan, e-mail: muhammad_azadur@yahoo.com Received 17 September/ accepted 20 December 2015 ABSTRACT This paper presents the geochemical study of agricultural soil and river sediments along Sumani watershed, West Sumatra in Indonesia.

We examined the distribution and abundances of 16 elements (Pb, Zn, Cu, Ni, Cr ,V , Sr, Rb, Ce, Th, Zr, Si, Ti, Fe Ca, and P) in vegetable soil, sawah soil =and river sediment sample, to evaluate the factors controlling their abundances, possible sources, and environmental implications. Average concentrations of Pb, Zn, Cu, Ni, Cr ,V , Sr , Rb, Ce, Th, Zr at vegetable (1) soil were 38, 88.3, 38.7, 3, 8, 101, 96, 98, 87, 31 and 218 mg kg -1 , 26, 39.05, 8.8, 13.5, 31, 231.5, 37, 19, 78, 16 and 303.5 mg kg -1 at sawah soil (3, 4) and 30, 61.6, 35.7, 9, 22, 294, 65, 12, 78, 14 and 232 mg kg -1 at river sediment (2), respectively .

The concentration of Pb, Rb, Th and Zr at upland vegetables, V and Zr at sawah soil and river sediment were mostly two time Sumatra BCSCST or BCC in several samples. Enrichment factor values showed low to moderate enrichment of Pb, Zn, Cu, Rb, Ce and

Zr , whereas Th showed significant contamination at vegetables soil, suggesting contributions from anthropogenic sources. Anthropogenic contributions of most metals mainly originate from natural processes.

However , Pb, Ce, Th and Zr ranges of 527–108, 41-89, 66-1 17 and 35-100%, respectively , at Vegetable and sawah soil and river sediment confirm their anthropogenic contribution. Factor analysis and correlation matrices suggested that elevated metal concentrations at agricultural soil in Sumani watershed might be controlled by pH, CEC, Fe-oxy-hydroxides.

Deposition of metals at vegetable and sawah soil and river sediment might be controlled by non-ferrous metal (i.e., aluminosilicates), sediment grain size, or source rock composition (andesite, alluvial fan, undifferentiated volcanic material, granite and gneiss). Keyword: Agricultural soil, anthropogenic activities, enrichment factor , metals source, river sediment, watershed trace ABSTRAK Penelitian ini menyampaikan studi geokimia tanah pertanian dan sedimen sungai di sekeliling DAS Sumani, Sumatra , V , Sr, Rb, Ce, Th, Zr, Si, Ti, Fe Ca, dan P) di sampel tanah sayuran, tanah sawah dan sedimen sungai untuk mengevaluasi faktor yang mengendalikan kelimpahan atau paparan unsur , sumber, dan implikasi terhadap lingkungan.

Konsentrasi rata- rata Pb, Zn, Cu, Ni, Cr , V , Sr , Rb, Ce, Th, Zr di sampel tanah sayuran (1) masing-masingnya yaitu 38, 88,3, 38,7, 3, 8, 101, 96, 98, 87, 31 dan di tanah sawah yaitu 218 mg kg -1, 26, 39,05, 8,8, 13,5, 31, 231,5, 37, 19, 78, 16 dan 303,5 mg kg -1 (3, 4) dan pada sedimen sungai (2) yaitu 30, 61,6, 35,7, 9, 22, 294 , 65, 12, 78, 14 dan 232 mg kg -1.

Konsentrasi Pb, Rb, Th dan Zr pada tanah sayuran di dataran tinggi, V dan Zr di tanah sawah dan pada sedimen sungai sebagian besar dua kali , sedangkan Th menunjukkan kontaminasi yang signifikan di tanah sayuran, berarti menunjukkan kontribusi dari sumber antropogenik. Kontribusi antropogenik Analisis faktor dan korelasi matrik menunjukkan bahwa konsentrasi logam yang tinggi pada tanah pertanian di DAS Sumani dapat dikendalikan oleh pH, KTK, Feroxy-hidroksida. Penumpukan logam undifferentiated material vulkanik , granit dan geneiss).

Kata Kunci : logam Trace, tanah pertanian, sedimen sungai, sumber Logam, kegiatan antropogenik, faktor Pengayaan, DAS 50 Aflizar et al.: Geochemical Investigation of Selected Elements in an Agricultural Soil INTRODUCTION Elemental distribution and accumulation in agricultural soil plays an important role in the , establishing the concentrations of metals, their probable sources, the et al. 2012). Pollution by trace metals has become a serious .

2007; Hafizur et al. 2007). Heavy metals are persistent in the environment, and can easily et al. 2009). Toxic metals are a great threat to ecosystems, and may pose a continuing health risk for people living Agricultural soil are important as sinks of essential nutrients, hence supporting soil organisms et al. 2007). Metals in agricultural soil are derived from several sources including .

Industrialization, urbanization, use of heavy metal-bearing fertilizers et al. 2008). However, as a result of these human activities, significant quantities of metals may terrasterial plant resources, and overall human health concern (Y oung 2007; Rahman et al. 2012).

The Sumani watershed in West Sumatra, Indonesia, presents a prime example of a setting , volcanic ash, residue of fertilizer and pesticide since green revolution Large parts of this agricultural area in Sumani watershed are irrigated Dibawah on the west of Mount Talang as active volcano (2500 m asl). Our study area lies Upland and lowland areas in Solok district.

The Upland and lowland part of Several environmental studies have been conducted to determine trace metal concentrations , and the extent of contamination from trace metals in different areas of Sumatra and Java Island et al. 2008). However, trace metal research of an Sumani watershed with various land et al . 2012). We examined trace metal concentrations and sawah, vegetable soil and river 1). However the geochemical condition of sawah, vegetable soil and West Sumatra.

Many people in these areas depend on agricultural , trade, fishing, tourism, or home industrial activity. Degradation of the soil environment could thus impact severely on their life and property. With the above issues in mind, we examined the spatial distribution of selected major and trace Trace and major element (As, Pb, Zn, Cu, Ni, Cr, V , Sr, Rb, Ce, Th, Zr, Si, Ti, Fe, P, and Ca) concentrations were determined by routine X-To identify agricultural soil quality , the data were compared with different agricultural soil, 51 J Trop Soils, Vol. 21, No.

1, 2016: 49-66 the relations, origin, and factors that control MATERIALS AND METHODS Geological Outline of the Sumani Watershed Geology of the Sumani watershed area is volcanic and intrusive rock which are mantled by Talang, undif ferented volcanic product and Andesite to basalt; metamorphic rock which are mantled by Triasic (251 million years BP) that consist of slate and shale member of Tuhur formation and Limestone member of kuantan Alluvial fans (Indonesia Geological Research and Development Centre 1995; Fiantis et al. 2010) (Figure 1).

The Sumani watershed is located in Solok o 36’08" to 1 o 44’08" S, longitude 100o24’11"- 101o15’438" E) approximately 50 km east of Padang City in West Sumatra, Indonesia (Figure 1) and occupies 58330 ha. The watershed Average annual precipitation ranges from 1669 to 3230 mm, and the et al. 2010a; Aflizar et al. 2010b). It is situated in a humid tropical zone and a population of 500,000. The Sumani Aripan and Imang (Figure 1).

Soil group distribution in sumani Andic Humitropept, Typic Kandiudult , Aeric Tropaquept ,T ypic Distropept and Typic Eutropept. Lowland areas of Sumani watershed are Tofu and traditional food factory . The upland also serves as a recreational area for local residents. The lowland Soil surveys were conducted at 4 sites occupying a variety of geomorphic positions and land . Soils were collected at depths of 0-20 cm and 20-40 cm.

Soil samples were air dried and sieved Figure 1. S tudy site and distribution of soil sampling points sites in Sumani watershed, West Sumatra, coordinates bases on UTM coordinate system WGS 84 Zone 47 Southern Hemispire. 52 Aflizar et al.: Geochemical Investigation of Selected Elements in an Agricultural Soil Soil and Sediment samples weighing about 200 g , Japan.

Data selected element from four soil sampling location in Sumani Watershed and Distribution polygon map was generated using Surfer . A block diagram showing geomorphic feature and sampling , that has been successfully applied to soil property interpolation for nearly 30 years, was . Interpolation is the term a nearest neighboard gridding method in Surfer (R) 9 uses the optimal delaunay triagulation. The algorithm Aflizar et al.

2013a; Aflizar et al. 2013b). Analytical Procedures Approximately 50 g of each sediment sample was dried in an oven at 110 0C for 24 h. The dried samples were then ground for 20 min in an automatic i, Fe , Ca, Si and P] and trace element (Pb, Zn, Cu, , V, Sr, Zr, Th, and Sc) abundance in the soil and river sediments were determined by X-ray , using a RIX-2000 spectrometer (Rigaku Denki Co. Ltd.)

equipped with All samples were made on pressed powder disks, following Ogasawara (1987). verage errors for these elements are less than ±10%. Analytical results for USGS standard SCo-1 (Cody Shale) are acceptable, compared with the et al. (1992). Soil texture was determined by the pipette method (Gee and , 1986). Soil samples were analyzed for total carbon (TC) contents.

Finely ground soil samples otal carbon were determined by the dry combustion method (Nelson et al . 1982) using a Yanaco CN Corder Model MT -700 (Y anagimoto MFG . Co., Kyoto, Japan). Soil pH was measured using the glass A 1979). Exchangeable acidity was determined by first extracting with 1 mol L ″1 KCl and titrating with NaOH (Mc Lennan 1963).

Exchangeable base ″1 neutral ammonium acetate (Thomas 1982). Exchangeable Ca and Mg were determined using Absorption Spectrophotometer (Shimadzu AS 680). Effective Cation Exchange Capacity . For Mapping was conducted in Surfer® 9 (Golden software 2010) Trace metals in agricultural soil and river sediment mainly originate from natural sources (e.g.,

weathering products) or anthropogenic processes. e.g., erosion, leachates, run off, addition of volcanic ash and precipitation). Human activities e.g., gasoline pump, car and motor cycle repair, tool manufacturing, local food industries), construction, water drainage and indiscriminate use et al . 2008; Rahman et al. 2012).

Such activities are common in the Sumani The EF concept developed by Chester and Stoner (1973) was originally applied to estimate , and was then employed in studies of rivers (Tam and Yao 1998), dams (Fernando et al. 2011), soils (N'guessan et al . 2009), and coastal sediments (Rahman et al. 2012) and agricultural soil (Ozbas 201 1) to evaluate the anthropogenic contribution and soil and sediment quality.

The EF is calculated as the ratio of the concentration of an iO 2 sample)/ (M/T iO2 background) (1) where (M/TiO2) sample is the ratio of metal and TiO2 concentrations of the sample and (M/T iO2) background is the ratio of metal and TiO 2 concentrations of the background. As regional geochemical background values are not available, 53 J Trop Soils, Vol. 21, No. 1, 2016: 49-66 Table 1.

Elemental concentrations in in the surface soil sample in Sumani watershed West Sumatra Indonesia. BCSCST, Bulk composition sediment columns subdicting at trenches Plank and Lamuir (1998), BCC, Bulk continental crust from Rudnick and Fountain (1995), na not available, nd not detected, SC silty clay , FMS fine to medium sand; Si, Silty; C, Clay , L, Loam, SL, Silty loam; V AUT, Volcanic ash, leached from mount Talang from (Fiantis et al. 2010); na = not available Area (code) code/ Sample no. Lithology Trace element (mg kg - 1) Major oxides (wt.%) Type pH CEC Pb Zn Cu Ni Cr V Sr Rb Ce Th Zr SiO 2 TiO 2 Fe 2 O 3 CaO P 2 O 5 Upland (1) Vegetable (1) Si 4.96 17.83 38 88.3 38.7 3 8 101 96 98 87 31 218 52.84 0.56 1.94 0.66 0.16 Middle (2) River Sediment L 5.34 13.99 30 61.6 35.7 9 22 294 65 12 78 14 232 40.07 1.14 15.33 0.27 0.07 Side (3) Sawah (3) C 5.85 9.17 33 43.7 11.2

12 24 277 27 14 86 17 256 42.33 1.08 10.14 0.18 0.10 Lower (4) Sawah (14) L 4.90 15.32 19 34.4 6.4 15 38 186 47 24 70 15 351 64.54 1.22 5.49 0.47 0.02 Range 4.90- 5.85 9.17- 17.83 19- 38 34.4- 88.3 6.4- 38.7 3- 15 8- 38 101- 294 27- 96 12- 98 70- 87 15- 31 218- 351 40.07- 64.54 0.56- 1.22 5.49- 15.33 0.18- 0.66 0.02- 0.16 Mean 5.26 14.08 30 55.75 23 9.75 23 214.5 58.8 37 80.25 19.3 264.3 49.95 1.00 8.22 0.40 0.09 S.D. 0.44 3.64 8.04 23.72 16.56 5.12 12.27 89.30 29.28 41.00 7.93 7.93 59.92 11.21 0.30 5.81 0.21 0.06 Sumatra BCSCST 24.5 95.7 39.4 57.5 101.5 90 251 45.1 67 10.23 165 62.94 0.69 4.95 3.16 0.15 UCC 20 71 25 20 35 60 350 112 7.1 10.7

190 65.89 0.50 5.00 4.2 0.16 BCC 12.6 73 24 51 119 131 325 58 42 5.60 123 59.10 0.7 6.60 6.40 0.20 VAUT 16.50 90.60 38.50 4.10 17.40 144.66 318.40 na na 7.90 114.43 57.61 0.49 5.39 4.79 0.18 54 Aflizar et al.: Geochemical Investigation of Selected Elements in an Agricultural Soil average concentrations of Pb, Zn, Cu, Ni, Cr , V , Sr, Rb, Ce, Th and Zr in the BCC (Rudnick and Fountain . The anthropogenic contribution is thus calculated using the following equation (N'guessan et al.

2009): % M Anthropogenic = ((M) sample – (TiO_2) sample × (M/TiO_2) background) × 100 (2)) M sample tatistical Analysis Descriptive data analyses (range, mean, standard deviation) were carried out using Microsoft okalioglu et al. 2000; Rahman et al. 2012). Hence, correlations between any metal oxides and RESULTS AND DISCUSSION Agricultural Soil and River Sediment General characteristics and elemental abundance in agricultural soil and river sediment are Table 1. The Sumani watershed surface soils were mainly silty , loam and clay textural classes.

The sub surface Sawah soil at middle and et al. (2000) stated that the olive and black colors indicate less oxidizing or reducing Average pH values of the surface soil at Sawah, vegetables and river sediment were 4.90- , indicating slight acid to acid soil characteristics. Upland area, ganic fertilizer. The CEC ranges between 9.17 to 15.32 cmol kg -1 in Sawah; 17.83 cmol kg -1 in vegetable garden and 13.99 cmol kg -1 in river sediment ranging from low to very high soil fertility conditions in agricultural land in Sumani watershed akatsuki et al.

1998) Trace Element Distribution Average abundance and range of geochemical composition of the major and trace elements in the Watershed are given in (T able 1), because there is no standard criteria for heavy metal modern sediment data from Sumatra Bulk composition sediment solumns subdicting at trenches from Plank and Lamuir (1998) and BCC (Bulk continental crust) from Rudnick and Fountain The result of XRF showed that the Sumani watershed contained 30 mg kg -1 Pb, 55.75 mg kg -1 Zn and 23 mg kg -1 Cu. The Pb content of Sumani watershed soils was mostly similar to

Sumatra Talang as active volcano.

However concentration of Zn and Cu are lower than (Table 1). Ni and Cr abundance range from 3 to 15 mg kg -1 and 8 to 38 mg kg -1, while Sr and Ce ranged from 27 to 96 mg kg -1 and 70 to 87 mg kg -1, respectively , indicating a depletion based on Sumatra BCSCST.

However on average V and Pb concentration at Sumani watershed were -1 and 37 mg kg -1, respectively , while Zr concentration averaged 264.3 mg kg -1. The concentration of Pb, Rb, Th and Zr at upland Talang as active volcano (T able 1). Average SiO 2, CaO and P 2O5 abundance in Sumani watershed soil were lower than Sumatra BCSCST.

In contrast, content of TiO2, F 2O3 were almost double compared to Sumatra BCSCST and BCC able 1). Average values of SiO 2, TiO2, Fe 2O3, CaO and P 2O5 were 49.9%, 1%, 8.22%, 0.4% and 0.09%, respectively . They were mostly similar to Sumatra BCSCST and BCC (T able 1). Lead (Pb) is considered to be a good indicator of pollution by urban runof f water .

In Indonesia noted that addition of Pb to gasoline has been prohibited 55 J Trop Soils, Vol. 21, No. 1, 2016: 49-66 Table 2. Correlation matrices for the Sawah, Vegetables soil and River sediment in Sumani watershed west sumatra. pH CEC Pb Zn Cu Ni Cr V Sr Rb Ce Th Zr SiO 2 TiO 2 Fe 2 O 3 CaO P 2 O 5 pH 1 CEC -0.94** 1 Pb 0.32 0.02 1 Zn - 0.28 0.60 * 0.80 ** 1 Cu -0.22 0.53 0.68* 0.92** 1 Ni 0.21 -0.53 -0.85** -1.00** -0.90** 1 Cr - 0.02 - 0.32 - 0.95 ** - 0.95 ** - 0.83 ** 0.97 ** 1 V 0.75** -0.80** -0.19 -0.53 -0.23 0.51 0.38 1 Sr -0.66* 0.88** 0.47 0.90** 0.85** -0.86** -0.72** -0.69* 1 Rb -0.54 0.73** 0.57 0.82** 0.55 -0.81** -0.73** -0.91** 0.83** 1 Ce 0.47 -0.18 0.96** 0.63* 0.46 -0.70* -0.85** -0.14 0.25 0.48 1 Th -0.36 0.58* 0.70* 0.83** 0.55 -0.84** -0.81** -0.83** 0.76** 0.98** 0.65* 1 Zr -0.32 -0.03 -0.93** -0.81** -0.83** 0.84** 0.91** -0.02 -0.51 -0.40 -0.82** -0.51 1 SiO 2 -0.78** 0.55 -0.59* -0.23 -0.42 0.27 0.43 -0.67* 0.12 0.30 -0.57 0.15 0.75** 1 TiO 2 0.28 -0.55 -0.79** -0.90** -0.66* 0.91** 0.89** 0.75** -0.79** -0.95** -0.71** -0.99** 0.64* -0.01 1 Fe 2 O 3 0.60 * - 0.58 * - 0.10 - 0.31 0.05 0.30 0.22 0.95 ** - 0.43 - 0.80 ** - 0.14 - 0.75 ** - 0.18 - 0.73 ** 0.64 * 1 CaO -0.87** 0.92** 0.13 0.58* 0.36 -0.54 -0.37 -0.97** 0.80** 0.88** 0.01 0.77** 0.00 0.66* -0.70* -0.85** 1 P 2 O 5 0.11 0.20 0.96** 0.85** 0.65* -0.89** -0.96** -0.44 0.58* 0.76** 0.93** 0.86** -0.83** -0.35 -0.92** -0.36 0.36 1 **, P value <0.01 and *, P value < 0.05 Pb, even if other origins are taken into account.

et al. (1995). Overall, the maximum and minimum concentration of most able 1). This suggests that elements supplied by human activities and addition of volcanic Talang. Factors and Sources Controlling Metal To identify possible associations existing among the elements, the data were subjected to simple et al . 2012).

Table 2 shows correlation matrices for elements in the vegetables, sawah and 2O5 and Pb, Zn, Cu, Sr, Rb, Ce and Th. Also, The most noticeable positive correlations were between CaO , Rb and Th in Sumani watershed soil samples.These elements display the same affinity conditions (Salomons and Forstner 1984), and suggests their) hydroxides.

The presence of Zn in the same group with CaO 2O5 in the PCA and strong correlation positive among these elements would suggest anthropogenic i.e ., Fertilizer and pesticide, home industrialization and public waste disposal) and et al. 2010; Rahman et al. 2012) that added by farmers in vegetables area and addition material Talang.

Strong association among Zn, Cu, Ni, Cr, Sr, Rb, Ce and Th and CaO, P 2O5 might be due to common anthropogenic sources and similar properties in soil chemistry et al . 2005; Azadur Rahman et al . 2012).Cu with V , Rb, Ce, Th, SiO 2, Fe2O3 and CaO in Sumani watershed showed extensively poor i.e., sorting, grain size, or carrying parent 56 Aflizar et al.:

Geochemical Investigation of Selected Elements in an Agricultural Soil source rock type such as granite or gneiss). trontium(Sr), V , Rb, Ce, Th and CaO show strong association in the correlation matrices Sumani able 3; Figure 2). Their abundances are thus likely to be controlled by . 2010; Rahman and Ishiga 2012).

Strong interrelation among Ti and Ni, Cr , V, and Zr in Sumani watershed suggests that the composition of . The metal distributions in the soil and river sediment are generally linked to normal sub-aerial Talang after eruption, because most of the soil and river , the enrichment of Pb, Zn, Cu, V, Rb, Ce, Th and Zr in vegetable sample and the enrichment of Pb, Cu, V , Ce and Zr in sawah sample also the enrichment of Pb, Cu, V, Ce, Th and Zr in river sediment sample may have arisen from enriched in this area by the processes of leaching, Conversely, some samples reflect their origin from natural weathering processes or terrestrial Table 3. Principal component analysis (PCA) values of the agricultural soil in Sumani watershed.

Variabels PCA values of Agricultural soil in Sumani Watershed PCA1 PCA2 PCA3 Eigenvalues 13.24 4.40 0.37 pH -0.14 0.40 -0.30 CEC 0.22 -0.27 0.32 Pb 0.23 0.25 -0.13 Zn 0.27 0.07 0.15 Cu 0.25 0.13 0.43 Ni -0.27 -0.09 -0.10 Cr -0.26 -0.16 -0.01 V -0.23 0.25 0.18 Sr 0.27 -0.07 0.29 Rb 0.27 -0.09 -0.11 Ce 0.22 0.28 -0.33 Th 0.27 -0.03 -0.19 Zr -0.21 -0.30 -0.13 SiO 2 -0.01 -0.47 -0.18 TiO 2 -0.27 -0.02 0.13 Fe 2O3 -0.21 0.29 0.44 CaO 0.23 -0.26 0.01 2O5 0.26 0.16 -0.19 Figure 2.

PCA results for agricultural soil in Sumani Watershed: plot of loadings of the three first components obtained in the analysis. 1234567890123456789012 0.30 -0.15 PCI 123456789 1234567890 123456789 123456789 123456789 -0.50 PC2 -0.25 0.00 0.25 123456789 0.50 12345678 -0.4 123456789 -0.2 123456789 0.0 12345678901 0.2 0.4 12345678 PC3 123456 NI 1234567 pH 1234567 V 12345 1234567 TiO 2 12345 12345 1234 Zr 12345678901 SiO 2 1234567 12345 CaO 123456789 CEC 1234567 Sr 123456789 Zn 12345678 CU 1234567890123 Fe2O3 12345678901 P2O5 123456789 Ce 123456789 Pb 12345 Th 123456 Rb 123456 12345 Cr 1234567890123456789012345678901212345678901234 5 PCA Result for Soil in Sumani Watershed 57 J Trop Soils, Vol. 21, No. 1, 2016: 49-66 material, because their mean chemical compositions TiO 2, Th, Sc, Zr , and La.

These elements have very low concentrations and low residence aylor and McLennan 1985). Use of ratios of such elements A Th/Sc–Zr/Sc plot (McLennan et al. 1993) shows that the source rock characteristics for most Although the elements used in Figure 3 solely reflect similar able 1 and Figure 4). Metal enrichments are seen in samples from vegetables, sawah and On a Zr/Sc–Th/Sc plot (McLennan et al.

1993) in Sumani watershed suite plots along a primary between average UCC, and rhyolite (Figure 3). This et al . 1993; Roser and Korsch 1999). The Sumani watershed suite also shows little tendency for the scatter to high Zr/Sc tudy In an attempt to evaluate the general condition of the sediments, the data were compared with other able 4, 5, Figure 5).

Pb, Zn and Cu at Sumani watershed Agricultural soil were comparable with Kirki region , concentration Pb, Zn, Cu, Ni and Cr were lower compared than , V , Sr, Rb, Ce, Th, and Zr in Vegetables , Sawah and river sediment with UCC, BCC, and VAULT shows marked enrichments or anomalous levels for Pb, V, Ce and Th except Zn, Cu, Ni, Cr, Sr, Rb, and Zr, whereas Vegetables soil sample show Pb, Zn, Cu, V , Ce and Th high enrichment but Sawah soil and river sediment show , Sr, Rb, and Zr are actually depleted relative to UCC and BCC standards (Figure 5).

The mean total concentrations of Pb and Cu at vegetables soil and river sediment are comparable o or exceed, Canadian environmental Quality Guidelines (Canadian EQG-ISQG), US Environmental Protection Agency's (US EP A) toxicity reference values (TR V), and the Ontario Ministry of Environment's (Ontario MOE) lowest effect levels (LEL) and TEC (Table 5).

Pb, Zn, Cu, Ni and Cr at sawah sites have values below TEC, probable effect , the overall results show that the levels of Pb, Cu found in the vegetable soil Figure 3. Th/Sc–Zr/Sc plot (McLennan et al. 1993) for agricultural soil at vegetable, river Watershed. BAS average basalt, LSA low-silica AND andesite, DAC dacite, RHY rhyolite, as plotted by Roser and 123456 Th Sc-1 123456 1 0.1 123456 0.01 123456789012345678901234567890121234567890123456789012345 1 10 100 Zr Sc -1 123456789 BAS 1234567 123456 LSA AND 1234567 DAC 12345678901 BCC 123456 UCC 12345678901 BCSCT b 12345678 1234 c 1234 a 123 d RHY 12345 a b 123456789012345678 (Vegetable) (River sediment) (Sawah 3) 58 Aflizar et al.:

Geochemical Investigation of Selected Elements in an Agricultural Soil Figure 4. Comparison of trace metal concentrations in the Sumani watershed surface soil and river sediment normalized to UCC, BUC, BCSCST and VAUT (element/VAUT). UCC upper continental crust (Taylor and Mclennan 1985); BCC Bulk concinental crust, BCSCST Bulk composition sediment columns subdicting at trenches Plank and Lamuir (1998), V AUT, V olcanic ash, leached from mount Talang from (Fiantis et al. 2010).

1234567890123456789012345678901212345678901234567890123456789012123456789012345678901234567890121234567890123456789012 Pb Zn Cu Ni Cr V Sr Rb Ce Th Zr 12345678901234567 10.0 1.0 Log (ratio concentration) 1234567890123456 10.0 1.0 Log (ratio concentration) 1234567890123456789012345678901212345678901234567890123456789012123456789012345678901234567890121234567890123456789012 Pb Zn Cu Ni Cr V Sr Rb Ce Th Zr 123456789012345 10.0 1.0

Log (ratio concentration) 1234567890123456789012345678901212345678901234567890123456789012123456789012345678901234567890121234567890123456789012 Pb Zn Cu Ni Cr V Sr Rb Ce Th Zr 12345678901234567 10.0 1.0 Log (ratio concentration) 1234567890123456789012345678901212345678901234567890123456789012123456789012345678901234567890121234567890123456789012 Pb Zn Cu Ni Cr V Sr Rb Ce Th Zr 59 J Trop Soils, Vol. 21, No. 1, 2016: 49-66 Table 4.

Comparison of average major and trace element concentrations in the study areas with other agricultural soil and rivers sediment in Sumani watershed Indonesia and Other country. Type Area Trace element (mg/kg) major oxides (wt.%) Reference Pb (lead) Zn (Zinc) Cu (Cup- per) Ni (Nick el) Cr (Chromi- um) V (Vanadi- um) Sr (Stronti- um) Rb (Rubi dium) Ce (Ceri- um) Th (Thori- um) Zr (Zirco- nium) TiO 2 Fe 2 O 3 P 2 O 5 Agricultural soil Vegetable (d19) Upland (1) 38 88.3 38.7 3 8 101 96 98 87 31 218 0.56 1.94 0.16 This study Sawah (47) Side (3) 33 43.7 11.2

12 24 277 27 14 86 17 256 1.08 10.14 0.10 This study Sawah (100) Lower (4) 19 34.4 6.4 15 38 186 47 24 70 15 351 1.22 5.49 0.02 This stu dy Local river study area River

Sediment Middle (2) 30 61.6 35.7 9 22 294 65 12 78 14 232 1.14 15.33 0.07 This study Local rivers, in Japan R. Asa, Ube 45 458 63 40 59 na na na na na na 0.60 4.79 0.22 GSJ, AIST Rahman et al. 2012 R. Ariho, Ube 25 117 18 19 60 na na na na na na 2.22 4.66 0.06 GSJ, AIST Rahman et al. 2012 R. Kotou, Ube 45 117 27 36 55 na na na na na na 0.58 3.78 0.10 GSJ, AIST Rahman et al. 2012 Greece, River sediment Kirki Region 110.4

2,750 26.7 na na na na na na na na na 2.2 na Christos Nikolaidis et al. 2010 Greece, Agricultural soil Kirki Region 28.5 103.6 12.8 na na na na na na na na na 2.63 na Christos Nikolaidis et al. 2010 Mexico, urban soil Mexico City 140.5 306.7 100.8 39.8 117 na na na na na na na na na O. Morton-Bermea et al. 2009 Thailand, urban soil Bangkok 47.8 118 41.7 24.8 26.4 na na na na na na na na na Wilcke et al. (1998). GSJ, AIST [Geological Survey of Japan, AIST (http://riodb02.ibase.aist.go.jp/geochemmap/index_e.htm)] 60 Aflizar et al.:

Geochemical Investigation of Selected Elements in an Agricultural Soil 0 1 2 3 4 5 6 7 8 Pb Zn Cu Ni Cr V Sr Rb Ce Th Zr Vegetable(1) EF Values 0 1 2 3 4 5 6 7 8 Pb Zn Cu Ni Cr V Sr Rb Ce Th Zr Sawah(3) EF Values 0 1 2 3 4 5 6 7 8 Pb Zn Cu Ni Cr V Sr Rb Ce Th Zr River sediment(2) EF Values 0 1 2 3 4 5 6 7 8 Pb Zn Cu Ni Cr V Sr Rb Ce Th Zr Sawah(4) EF Values Figure 5.

Bar plots showing EF values for Pb, Zn, Cu, Ni, Cr, V, Sr, Rb, Ce, Th, and Zr in surface soil and river sediment in the Sumani watershed. 123456789 Zr Th Sr V Cr Cu 12345678901234567890123456789012123456789012345678901234567 0 1 2 3 4 5 6 7 8 EF Values 123456789012345678901 Vegetable 1 123456789 Zr Th Rb Sr V Cr Cu 12345678901234567890123456789012123456789012345678901234567 0 1 2 3 4 5 6 7 8 EF Values 1234567890123456789012345678 River sediment (2) 123456789 Zr Sr V Cr Cu 12345678901234567890123456789012123456789012345678901234567 0 1 2 3 4 5 6 7 8 EF Values 12345678901234 Sawah (3) 1234567890 Zr Sr V Cr Ni Cu 12345678901234567890123456789012123456789012345678901234567890123456 0 1 2 3 4 5 6 7 8 EF Values 12345678901234 Sawah (4) 61 J Trop Soils, Vol. 21, No.

1, 2016: 49-66 Table 5 Comparison of average metal values in the Sumani watershed with geochemical background and toxicological reference values for Sediments. UCC upper continental crust from Taylor and Mclennan (1985); JUC Japan upper crust from Togashi et al. 2000; US DOE United S tates Department of Ener gy; TEC threshold effect contamination, PEC probable effect contamination and HNEC high no effect contamination from Jones et al.

(1997); Canadian EQG Canadian Environmental Quality Guidelines; ISQG interim sediment quality probable ef fect level from CCME (2002); TRV toxicity reference value from the US Environmental Protection Agency (US EP A) (1999); Ontario MOE Ontario Ministry of Environment; LEL lowest effect level, SEL severe effect level from Persaud et al.

1993, na not available Trace Metal Geochemical standard US DOE Canadian EQG US EPA TRV Ontario MOE This Study UCC BCC Sumatra BCSCST TEC PEC HNEC ISQG PEL LEL SEL Mean Vegetble Sawah River Sediment Pb 20 12.6 24.5 34.2 396 68.7 35 91.3 31 31 250 30 38 26 30 Zn 71 73 95.7 159 1,532 541 123 315 110 120 820 55.75 88.3 39.05 61.6 Cu 25 24 39.4 28 77.7 54.8 35.7 197 16 16 110 23 38.7 8.8 35.7 Ni 20 51 57.5 39.6 38.5 37.9 - - 16 16 75 9.75 3 13.5 9 Cr 35 119 101.5 56 159 312 37.3

90 26 26 110 23 8 31 22 V 60 131 90 - - - - - - - - - - - 214.5 101 231.5 294 Sr 350 325 251 - - - - - - - - - - - 58.8 96 37 65 Rb 112 58 45.1 - - - - - - - - - - - 37 98 19 12 Ce 7.1 42 67 - - - - - - - - - - - 80.25 87 78 78 Th 10.7 5.60 10.23 - - - - - - - - - - - 19.3 31 16 14 Zr 190 123 165 - - - - - - - - - - - 264.3 218 303.5

232 Table 6 Anthropogenic contribution (% AC) values for the surface agricultural soil and river sediments in Sumani watershed. Bold text highlights anthropogenic contribution (% AC) Area Anthropogenic contribution (% AC) Pb (lead) Zn (Zinc) Cu (Cup- per) Ni (Nickel) Cr (Chro- mium) V (Vana- dium) Sr (Stron- tium) Rb (Rubi- dium) Ce (Ceri- um) Th (Tho- rium) Zr (Zirco- nium) Vegetable (1) 53.47 13.86 30.39 -1280.00 -1110.00 -23.76 -190.83 32.65 41.38 65.55 34.86 Sawah (3) 94.46 - 30.14 53.37 - 760.00 - 718.05 90.29 - 651.43 - 624.29 75.16 97.71 76.51 Sawah (4) 107.74 -195.56 -479.29 -566.43 -689.88 91.86 -1923.60 -547.76 89.17 116.87 90.55 River Sediment (2) 51.97 -103.45 -176.33 -370.29 -328.87 45.62 -912.58 -218.57 61.71 96.69 100.22 Mean 76.91 -78.82 -142.96 -744.18 -711.70 51.00 -919.61 -339.49 66.86 94.21 75.54 62 Aflizar et al.:

Geochemical Investigation of Selected Elements in an Agricultural Soil whereas those from Sawah would have no harmful and Anthr opogenic Contribution It is well established that trace metals are introduced to coastal environments by both natural e.g ., weathering and erosion) and anthropogenic activities within the catchment or et al. 2008; Rahman and Ishiga 2012).

Calculation of EF and AC is an important part of geochemical studies seeking to et al . 2009; Rahman et al. 2011). Normalization of metal concentrations to a textural or compositional , selection of an appropriate reference element to evaluate EF is To date, Cs (Roussiez et al. 2005), Sc (Yanguo et al. 2002), Al (Windom et al . 1989), Li (Loring and Rantala 1990) Mn (Matthai et al .

2002), organic matter (Hissler and Probst 2005), Ti (Rahman et al. 201 1) and Fe (Rezaee et al. 201 1), have generally used as geochemical normalizers. The choice of To select the most suitable normalizer , most studies have applied step by step regression methods Tam and Yao 1998). In this work, Mn and Fe were tested as normalizers, using UCC for aylor and McLennan 1985) and BCC Rudnick and Fountain (1995).

Fe shows , it is not the best normalizer, because its deposition into soil and river sediment can be influenced by human activities et al. 2005). In addition, in this present study , the contents of Fe in some samples in Sumani able 1) compared to geochemical standards, and therefore would yield According to Sutherland (2000), EF values in the range 2–5 indicate moderate enrichment, , Zenglu et al.

(1987) stated that if EF exceeds 1 it means that the trace metal becomes a polluting element. Overall, only slight to moderate contamination, because most , a few sampling sites show higher EF . At Vegetable soil, samples 1 have EF values of 7 for Th and EF Talang as active volcano (T able 1) where erupted in year 2000 and soil covered by volcanic ash about 5-15 et al. 2010) possibly suggest that there is a local point source input of these metals (T able 1).

These Upland Sumani watershed are under intensive vegetable cultivation, so application of Andisol soil, and high organic matter contents in upland Sumani watershed et al. 2013 a, b). Conversely , low EF values at most sampling sites at sawah and river sediment i.e., natural weathering processes) and primary control by source rock , source lithology can also be considered as a dominant factor influencing , Th, Ce, Rb, V , Cu, Zn, Pb in the watershed. The values ranged from , Th, Ce, Rb, Cu, Pb.

Average AC values in the soil and river sediments of the study areas calculated using Eq able 6), indicating that these metals have an anthropogenic proportion around 77 % and Anthropogenic contribution of Zn is 13.86 % at vegetable (1). The anthropogenic 16.87 and 90.55% at sawah (4); 61.71, 96.69 and 100.22, respectively . Indicating that these metals have an anthropogenic 63 J Trop Soils, Vol. 21, No. 1, 2016: 49-66 Figure 6. Spatial Distribution of EF values in Sumani Watershed.

a: Zr, b: Th, c: Ce, d: Rb, e: V , f: Cu, g: Zn, h: Pb. 64 Aflizar et al.: Geochemical Investigation of Selected Elements in an Agricultural Soil about 0-56%. This means that the study areas are Talang eruption, pesticide and fertilizer . The anthropogenic contribution of V is 90.29% at sawah (3); 91.86% at sawah (4); 45.62 at river , Sr and Rb exhibit a negative contribution at most study sites, indicating AC values for Zr , Th, Ce, Rb, V , Cu, Zn, Pb are depicted in Figure 7.

% AC values are greater than 50% were detected in areas at upper , middle and lower topography . These areas exhibited the highest % AC values in the watershed, indicating the strong of antropogenic input (i.e. Fertilizer and pesticide, volcanic ash from Mt. Talang, home industrialization, public waste disposal and Although AC values for most sampling sites reflect only natural , Ce, Th and Zr confirm that some anthropogenic contamination has occurred.

CONCLUSIONS Trace metal concentrations in Sumani watershed at vegetable, sawah and river sediments AC values confirm that spatial distributions of Pb, Cu, V , Ce, Th and Zr are directly related to both anthropogenic and natural sources, depending iO 2) and calcium (CaO) are the main geochemical i.e., aluminosilicates), sample grain size, and source rock (i.e., granite, volcanic rock and gneiss) composition. Strong correlation .

The findings in this study are significant, because they provide the first information about soil and river sediments in this area, which Watershed, West Sumatra Indonesia.
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