Available online at:
http://journal.unila.ac.id/index.php/tropicalsoil
DOI: 10.5400/jts.2016.21.1.49

Geochemical Investigation of Selected Elements in an Agricultural Soil: Case Study in Sumani Watershed West Sumatera in Indonesia

Aflizar[1], Muzakkir[1], Roni Afrizal[1], Muhammad Azadur Rahman[2]

[1]*State Polytechnic Payakumbuh for Agriculture (Politeknik Pertanian Negeri Payakumbuh), Indonesia 26271, e-mail:aflizar_melafu@yahoo.com.*
[2]*Department 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, 66-117 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 Barat-Indonesia. Penelitian ini menganalisi distribusi dan kelimpahan dari 16 unsur (Pb, Zn, Cu, Ni, Cr, 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 konsentrasi pada Sumatera BCSCST atau BCC di beberapa sampel. Nilai faktor pengayaan unsur menunjukkan pada kisaran rendah sampai moderat untuk unsur Pb, Zn, Cu, Rb, Ce dan Zr, sedangkan Th menunjukkan kontaminasi yang signifikan di tanah sayuran, berarti menunjukkan kontribusi dari sumber antropogenik. Kontribusi antropogenik dari logam terutama berasal dari proses alam. Namun, Pb, Ce, Th dan Zr dengan kisaran masing-masing yaitu 527-108, 41-89, 66-117 dan 35-100%, di tanah sayuran dan tanah sawah dan sedimen sungai mengkonfirmasi adanya 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 pada tanah sayuran dan tanah sawah dan sedimen sungai mungkin dikendalikan oleh logam non-ferrous (yaitu, aluminosilikat), ukuran butiran sedimen, atau komposisi batuan induk (andesit, kipas alluvial, *undifferentiated* material vulkanik , granit dan geneiss).

Kata Kunci : logam Trace, tanah pertanian, sedimen sungai, sumber Logam, kegiatan antropogenik, faktor Pengayaan, DAS

J Trop Soils, Vol. 21, No. 1, 2016: 49-66
ISSN 0852-257X

INTRODUCTION

Elemental distribution and accumulation in agricultural soil plays an important role in the existence of sustainable environments. Soil are the starting point of the food chain for some terrestrials life, because both organic and inorganic particles are food sources. Consequently, establishing the concentrations of metals, their probable sources, the factors that control metal deposition, and most importantly the thickness of any contaminated agricultural soil is important for treatment or dredging to restore the terrestrials environment (Azadur Rahman and Hiroaki Ishiga *et al*. 2012). Pollution by trace metals has become a serious concern worldwide because of their potential toxicity for humans, terrasterial life and aquatic life (Kumar *et al*. 2007; Hafizur *et al*. 2007). Heavy metals are persistent in the environment, and can easily bioaccumulate in soil over time (Anu *et al*. 2009). Toxic metals are a great threat to ecosystems, and may pose a continuing health risk for people living on terrestrialline and relying on farmers resources as food. Agricultural soil are important as sinks of essential nutrients, hence supporting soil organisms (Abdullah *et al*. 2007). Metals in agricultural soil are derived from several sources including terrigenous detritus (weathering and erosion), biogenic matter derived from decay of organisms, eolian or cosmogenic fallout, and anthropogenic inputs from human activity. Industrialization, urbanization, use of heavy metal-bearing fertilizers and pesticides in agriculture, and natural resource exploitation (mining and energy) are basic activities associated with modern living and a vibrant society (Nouri *et al*. 2008). However, as a result of these human activities, significant quantities of metals may be deposited in soils. These may have severe impacts, with likely loss of soil organism habitat, decrease in food production and terrasterial plant resources, and overall human health concern (Young 2007; Rahman *et al*. 2012).

The Sumani watershed in West Sumatra, Indonesia, presents a prime example of a setting where a potential threat for agricultural ecosystems and human health. Sources of heavy metal in Sumani watershed are irrigation water, volcanic ash, residue of fertilizer and pesticide since green revolution started in 1972 up till now also gas from vehicle as gasoline in Indonesia contain Pb. Soil pH, soil physicochemical and geological characteristic could control availability of heavy metal in an agricultural soil in Sumani watershed. Large parts of this agricultural area in Sumani watershed are irrigated with river water that is partly supplied by Lake 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 the area seems to have been polluted by anthropogenic metals, resulting in degradation of soil environment. Local farmers are at risk due to metal contamination from several anthropogenic activities. Agrochemical and urban wastes create frequent red tides and oxygen-deficient water masses, which in 2002 resulted in mass mortality of fish in Lake Dibawah and Lake Singkarak (Personal communication in 2010).

Several environmental studies have been conducted to determine trace metal concentrations in Indonesia and their rates of loading, pollution history, and the extent of contamination from trace metals in different areas of Sumatra and Java Island at river sediment and coastal sediment (van Rotterdam-Los *et al.* 2008). However, trace metal research of an Sumani watershed with various land use has received limited attention. In a previous study (Aflizar *et al*. 2012). We examined trace metal concentrations and sawah, vegetable soil and river sediment Sumani watershed (Figure 1). However the geochemical condition of sawah, vegetable soil and river sediment in Sumani watershed are not known. Data from these areas are also required to better evaluate the total environmental quality of the agricultural soil in Sumani watershed West Sumatra. Many people in these areas depend on agricultural soil for their livelihood, either by way of farmer worker, 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 elements in agricultural soil in Sumani watershed, to evaluate the factors that control their abundance, and to identify elements which may influence total environmental quality in this part of the agricultural watershed. 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-ray fluorescence (XRF) analysis. The results of this study combined with data from other studies of agricultural soil may establish baseline levels for this region. To identify agricultural soil quality, the data were compared with different agricultural soil, geochemical background standards, and toxicological references, and used for calculating enrichment factors (EF) and anthropogenic contributions (AC) by utilizing appropriate reference elements. Correlation matrices and principal component analysis were also applied to determine

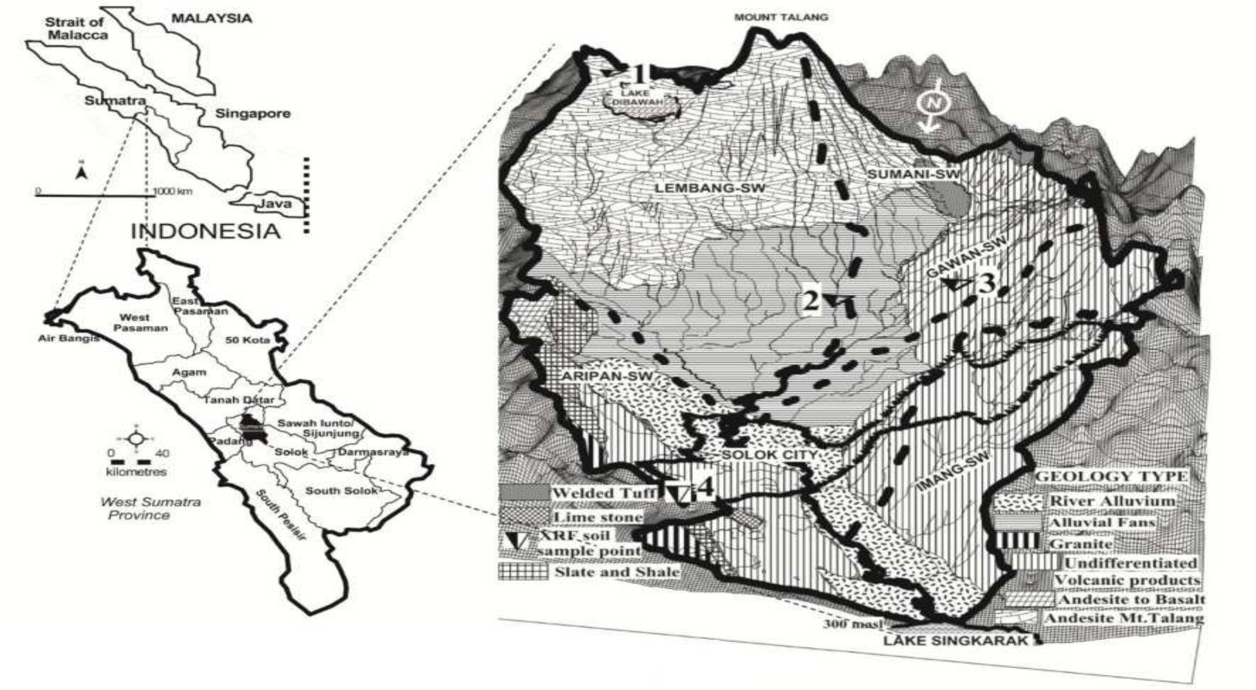

Figure 1. Study site and distribution of soil sampling points sites in Sumani watershed, West Sumatra, coordinates bases on UTM coordinate system WGS 84 Zone 47 Southern Hemispire.

the relations, origin, and factors that control elemental concentrations in Sumani watershed.

MATERIALS AND METHODS

Geological Outline of the Sumani Watershed

Geology of the Sumani watershed area is volcanic and intrusive rock which are mantled by Pleistocene (1,8 million years BP) that consist of Andesit mount Talang, undifferented 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 formation; surficial deposits consist of River alluvium and Alluvial fans (Indonesia Geological Research and Development Centre 1995; Fiantis *et al*. 2010) (Figure 1). The Sumani watershed is located in Solok regency (latitude 0^{o} 36’08" to 1^{o} 44’08" S, longitude 100^{o}24’11"- 101^{o}15’438" E) approximately 50 km east of Padang City in West Sumatra, Indonesia (Figure 1) and occupies 58330 ha. The watershed outlet is Lake Singkarak. Average annual precipitation ranges from 1669 to 3230 mm, and the watershed located on elevation between 300 m to 2500 m above sea level (asl) (Aflizar *et al*. 2010a; Aflizar *et al*. 2010b). It is situated in a humid tropical zone and a population of 500,000. The Sumani watershed consists of five sub-watersheds including Sumani , Lembang , Gawan , Aripan and Imang (Figure 1). Soil group distribution in sumani watershed was consist of six group such as Oxic Hapuldant, Andic Humitropept, Typic Kandiudult , Aeric Tropaquept ,Typic Distropept and Typic Eutropept. Lowland areas of Sumani watershed are both urban and agricultural and upland dominated by vegetables. The Upland River and tributaries and Lake Dibawah water run to the whole Sumani watershed and accumulate at Singkarak Lake, carrying municipal wastes and chemicals waste from agricultural land. Lowland areas thus receive wastewater from irrigation sourced from Lake Diatas in upland area. Their drainages at lowland are urbanized and housed industry such as *Tofu* and traditional food factory. The upland also serves as a recreational area for local residents. The lowland also housed car and motorcycle workshop for repairs and maintenance and gasoline sale stations.

Fields Survey and Data Processing for Mapping

Soil surveys were conducted at 4 sites occupying a variety of geomorphic positions and land use types (Figure 1) and this paper discuss about representative surface soil sample in 1 surface soil sample at vegetable (No. 1), 2 surface soil sample at sawah (No. 3 and No. 4) and surface sediment samples at river sediment(No. 4) that analyze using XRF. Soils were collected at depths of 0-20 cm and 20-40 cm. Soil samples were air dried and sieved through a 2 mm mesh for physico-chemical analyses.

Soil and Sediment samples weighing about 200 g were packed in ziplock bags and stored in a plastic box for transport to the Geoscience Laboratory and Phedosphere and Ecological Laboratory of Shimane University, 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 location in watershed was genereated by gridding topographic data using Surfer from Golden Software. Outline of the mapping procedure is explained as follows. In order to process mapping of soil properties and other data, regionalized variable theory, that has been successfully applied to soil property interpolation for nearly 30 years, was used in present study. Interpolation is the term a nearest neighboard gridding method in Surfer $^{(R)}$ 9 uses the optimal delaunay triagulation. The algorithm creates triangles by drawing lines between data point. The original points are connected in such a way that no triangle edges are intersected by other triangles. The result is a patchwork of triangular faces over the extent of the grid. This method is gridding nearest neighboard exact interpolator (Golden software 2010; Aflizar *et al.* 2013a; Aflizar *et al*. 2013b).

Analytical Procedures

Approximately 50 g of each sediment sample was dried in an oven at 110 ^{0}C for 24 h. The dried samples were then ground for 20 min in an automatic agate mortar and pestle. Selected major oxide [Ti, Fe , Ca, Si and P] and trace element (Pb, Zn, Cu, Ni, Cr, V, Sr, Zr, Th, and Sc) abundance in the soil and river sediments were determined by X-ray fluorescence (XRF) in the Department of Geoscience, Shimane University, using a RIX-2000 spectrometer (Rigaku Denki Co. Ltd.) equipped with Rh-anode X-ray tube. All samples were made on pressed powder disks, following Ogasawara (1987). Average errors for these elements are less than ±10%. Analytical results for USGS standard SCo-1 (Cody Shale) are acceptable, compared with the proposed values of Potts *et al*. (1992). Soil texture was determined by the pipette method (Gee and Bauder, 1986). Soil samples were analyzed for total carbon (TC) contents. Finely ground soil samples were oven dried at 80°C for approximately 24 h. Total carbon were determined by the dry combustion method (Nelson *et al*. 1982) using a Yanaco CN Corder Model MT-700 (Yanagimoto MFG. Co., Kyoto, Japan). Soil pH was measured using the glass electrode method with a soil : water ratio of 1:2.5 (IITA 1979). Exchangeable acidity was determined by first extracting with 1 mol L^{-1} KCl and titrating with NaOH (Mc Lennan 1963). Exchangeable base cations (Ca, Mg, K and Na) were extracted using 1 mol L^{-1} neutral ammonium acetate (Thomas 1982). Exchangeable Ca and Mg were determined using Inductively Coupled Plasma-Atomic Emission Spectroscopy (Shimadzu ICPS 2000, Kyoto, Japan) and exchangeable K and Na were determined using Atomic Absorption Spectrophotometer (Shimadzu AS 680). Effective Cation Exchange Capacity (eCEC) represents the sum of the exchangeable bases and the exchangeable acidity. For Mapping was conducted in Surfer® 9 (Golden software 2010) dealing with data from factors soil surveys, topographic maps and geology map

Calculation of Enrichment Factor and Anthropogenic Contribution

Trace metals in agricultural soil and river sediment mainly originate from natural sources (*e.g.*, weathering products) or anthropogenic processes. Anthropogenic processes comprise all processes connected with human activities and atmospheric deposition (*e.g*., erosion, leachates, run off, addition of volcanic ash and precipitation). Human activities responsible for heavy metal contamination in terrestrial environments include improper disposal of domestic wastes and effluents of diverse industries (*e.g*., gasoline pump, car and motor cycle repair, tool manufacturing, local food industries), construction, water drainage and indiscriminate use of heavy-metal-bearing fertilizer and pesticides in farming areas (Nouri *et al*. 2008; Rahman *et al.* 2012). Such activities are common in the Sumani watershed.

The EF concept developed by Chester and Stoner (1973) was originally applied to estimate anthropogenic contributions (AC) to the atmosphere and sea water, 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 2011) to evaluate the anthropogenic contribution and soil and sediment quality. The EF is calculated as the ratio of the concentration of an individual element to the concentration of a reference element in a given sample, divided by the same ratio in the local background or the upper crust (Chester and Stoner 1973).

$$EF = (M/TiO_2\ \text{sample}) / (M/TiO_2\ \text{background}) \qquad (1)$$

where (M/TiO_2) sample is the ratio of metal and TiO_2 concentrations of the sample and (M/TiO_2) background is the ratio of metal and TiO_2 concentrations of the background. As regional geochemical background values are not available,

Table 1. Elemental concentrations in in the surface soil sample in Sumani watershed West Sumatra Indonesia.

Area	code/	Lithology			Trace element (mg kg^{-1})											Major oxides (wt.%)				
(code)	Sample no.	Type	pH	CEC	Pb	Zn	Cu	Ni	Cr	V	Sr	Rb	Ce	Th	Zr	SiO_2	TiO_2	Fe_2O_3	CaO	P_2O_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

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; VAUT, Volcanic ash, leached from mount Talang from (Fiantis *et al.* 2010); na = not available average concentrations of Pb, Zn, Cu, Ni, Cr, V, Sr, Rb, Ce, Th and Zr in the BCC (Rudnick and Fountain 1995) were used in this study.

The anthropogenic contribution is thus calculated using the following equation (N'guessan *et al.* 2009):

$$\%\,\text{M Anthropogenic} = \frac{(\text{(M)sample} - (\text{TiO}_{2)}\,\text{sample} \times (\text{M/TiO}_2)\,\text{background}) \times 100}{\text{M sample}} \quad (2))$$

Statistical Analysis

Descriptive data analyses (range, mean, standard deviation) were carried out using Microsoft Office Excel 2007. Correlation coefficients and principal component analysis (PCA) were used to determine the relationships among different elements, and evaluate the factors that control their abundances and distributions in the agricultural soil and river sediment. The relationship among elements may help clarify the path by which individual metals are carried and deposited, and help resolve the processes involved. Metal oxides such as iron oxy-hydroxides usually act as scavengers for heavy metals (Tokalioglu *et al.* 2000; Rahman *et al.* 2012). Hence, correlations between any metal oxides and individual heavy metals may help to identify the processes involved in specific metal associations. In our data analysis, Pearson correlations were utilized to calculate the elemental interrelations, using PCA Minitab 14 software.

RESULTS AND DISCUSSION

Agricultural Soil and River Sediment Characteristics

General characteristics and elemental abundance in agricultural soil and river sediment are shown in Table 1. The Sumani watershed surface soils were mainly silty, loam and clay textural classes. The sub surface Sawah soil at middle and lower topography position were more silty clay than those of the upland areas, and the sawah sub surface color are soft, black, olive-black, or greenish-black in nature. Galasso *et al.* (2000) stated that the olive and black colors indicate less oxidizing or reducing conditions.

Average pH values of the surface soil at Sawah, vegetables and river sediment were 4.90-5.85, 4.96 and 5.34, respectively, indicating slight acid to acid soil characteristics. Upland area, dominantly cultivated by vegetables were enriched in organic matter due to andisol soil and farmers apply organic 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 according to criteria of Indonesia Soil Research Institute (1995). The term Sawah refer to a levelled and bounded rice field with inlet and outlet for irrigation and drainage (Wakatsuki *et al.* 1998)

Trace Element Distribution

Average abundance and range of geochemical composition of the major and trace elements in the top soil in Sumani Watershed are given in (Table 1), because there is no standard criteria for heavy metal in agricultural soil in Indonesia, we compare the XRF data to modern sediment data from Sumatra Bulk composition sediment solumns subdicting at trenches (BCSCST) from Plank and Lamuir (1998) and BCC (Bulk continental crust) from Rudnick and Fountain (1995).

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 BCSCST (Bulk composition sediment subdicting at trenches), but higher than BCC. Higher concentrations of Pb may derive from agrochemical residue, gas from car and motor cycle and addition of volcanic ash from mount Talang as active volcano. However concentration of Zn and Cu are lower than Sumatra, BCSCST (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 214.5 mg kg^{-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 vegetables, V and Zr at sawah soil and river sediment were mostly two time Sumatra BCSCST or BCC in several samples, which suggest recent enrichment may derive from agrochemical residue, gas from car and motor cycle and addition of volcanic ash from mount Talang as active volcano (Table 1). Average SiO_2, CaO and P_2O_5 abundance in Sumani watershed soil were lower than Sumatra BCSCST. In contrast, content of TiO_2, F_2O_3 were almost double compared to Sumatra BCSCST and BCC (Bulk continental crust), which suggested weathered parent rock of soil (Table 1). Average values of SiO_2, TiO_2, Fe_2O_3, CaO and P_2O_5 were 49.9%, 1%, 8.22%, 0.4% and 0.09%, respectively. They were mostly similar to Sumatra BCSCST and BCC (Table 1).

Lead (Pb) is considered to be a good indicator of pollution by urban runoff water. In Indonesia noted that addition of Pb to gasoline has been prohibited in since the 1990s, but fuel is still the main source of

Pb, even if other origins are taken into account. Furthermore, Pb concentrations in soil can be associated with Fe-bearing phases, most likely Fe oxides, oxy-hydroxides, and sulfides, depending on the existing oxidation–reduction conditions, as observed by Chandrajith *et al*. (1995). Overall, the maximum and minimum concentration of most metals and major elements in Sumani watershed showed wide variation, because of the diverse sampling points. Sampling sites located Upland, middle and lower topography or at vegetable, sawah areas and river sediment had showed high and low values (Table 1). This suggests that elements supplied by human activities and addition of volcanic ash from mount Talang.

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_2O_3	CaO	P_2O_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_2O_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_2O_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

Factors and Sources Controlling Metal Distribution

To identify possible associations existing among the elements, the data were subjected to simple correlation analysis and PCA. It then became possible to identify the factors controlling the spatial distribution of both major and trace elements (Rahman *et al.* 2012). Table 2 shows correlation matrices for elements in the vegetables, sawah and river sediment. Most metals in the agricultural soil and river sediment are well correlated. The most noticeable positive correlations were between P_2O_5 and Pb, Zn, Cu, Sr, Rb, Ce and Th. Also, The most noticeable positive correlations were between CaO and Zn, Sr, Rb and Th in Sumani watershed soil samples.These elements display the same affinity in the PCA analysis (Figure 2). This grouping of elements reflects clay mineral deposition, which may result from their similar behavior in redox conditions (Salomons and Forstner 1984), and suggests their possible association with P–Ca (oxy-) hydroxides. The presence of Zn in the same group with CaO and P_2O_5 in the PCA and strong correlation positive among these elements would suggest anthropogenic inputs (*i.e.*, Fertilizer and pesticide, home industrialization and public waste disposal) and reflect the complexing nature of organic matter (Ennouri *et al.* 2010; Rahman *et al.* 2012) that added by farmers in vegetables area and addition material volcanic ash from mount Talang. Strong association among Zn, Cu, Ni, Cr, Sr, Rb, Ce and Th and CaO, P_2O_5 might be due to common anthropogenic sources and similar properties in soil chemistry (Calace *et al.* 2005; Azadur Rahman *et al* . 2012).Cu with V, Rb, Ce, Th, SiO_2, Fe_2O_3 and CaO in Sumani watershed showed extensively poor correlation, which suggests that natural factors operated (*i.e.*, sorting, grain size, or carrying parent source rock type such as granite or gneiss). Strontium(Sr), V, Rb, Ce, Th and CaO show strong association in the correlation matrices Sumani watershed and show similar tendency in the PCA, reflecting their similar geochemical behavior and association with shell materials (Table 3; Figure 2). Their abundances are thus likely to be controlled by biogenic carbonates, which may also play an important role as a dilutant of heavy metals (Ahmed *et al*. 2010; Rahman and Ishiga 2012). Strong interrelation among Ti and Ni, Cr, V, and Zr in Sumani watershed suggests that the composition of the detrital component and grain size exert significant control on the bulk soil and river sediment chemistry.

The metal distributions in the soil and river sediment are generally linked to normal sub-aerial weathering, erosion and material of mount Talang after eruption, because most of the soil and river sediment would have been derived from sandstones, siltstones, and clays in the surrounding Sumani watershed. However, 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 atmospheric deposition and human activities, because the adjacent intensive agricultural activity and river basin are used for diverse irrigation activities and farming. These elements might be enriched in this area by the processes of leaching, emission, runoff, erosion and precipitation.

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_2O_3	-0.21	0.29	0.44
CaO	0.23	-0.26	0.01
P_2O_5	0.26	0.16	-0.19

Conversely, some samples reflect their origin from natural weathering processes or terrestrial

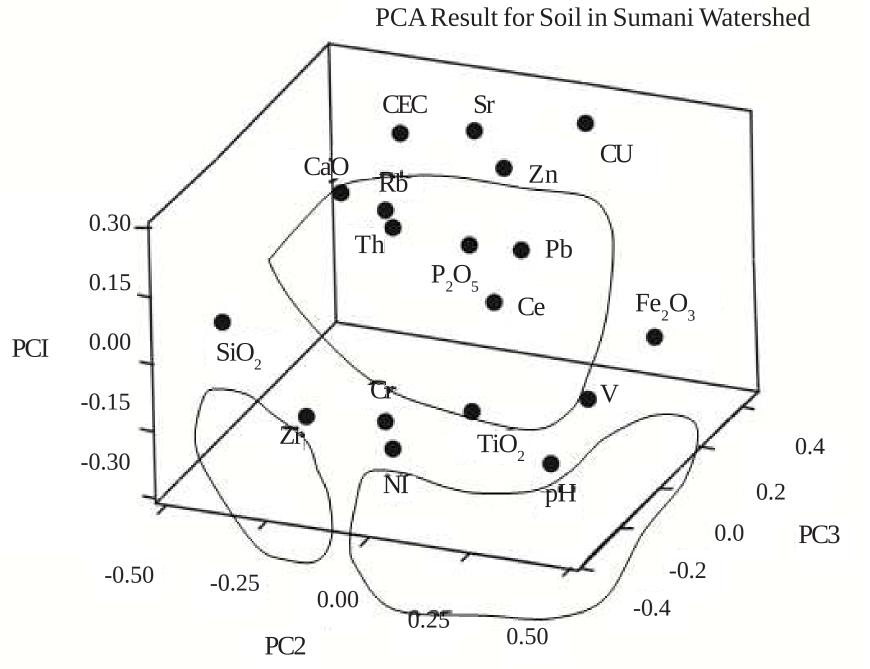

Figure 2. PCA results for agricultural soil in Sumani Watershed: plot of loadings of the three first components obtained in the analysis.

material, because their mean chemical compositions are similar to those in the Sumatra BCST and BCC. Provenance can also be evaluated using ratios formed between immobile minor or trace elements such as TiO_2, Th, Sc, Zr, and La. These elements have very low concentrations and low residence times in natural waters, and hence are transferred quantitatively from source to sediment (Taylor and McLennan 1985). Use of ratios of such elements overcomes any dilution effects from quartz concentration or diagenetic effects such as development of cements (Narantuya and Roser 2012).

A Th/Sc–Zr/Sc plot (McLennan *et al*. 1993) shows that the source rock characteristics for most samples are similar (Figure 3). Although the elements used in Figure 3 solely reflect similar composition, results for other elements when compared to BUC and UCC show enrichments at some sampling points, suggesting anthropogenic influence (Table 1 and Figure 4). Metal enrichments are seen in samples from vegetables, sawah and river sediment that are located in intensive agriculture area at upland, middle and lower topography position in Sumani watershed.

On a Zr/Sc–Th/Sc plot (McLennan *et al.* 1993) in Sumani watershed suite plots along a primary source evolution trend from average dacite to rhyolite, with samples concentrated at high ratios between average UCC, and rhyolite (Figure 3). This confirms the felsic source indicated by the major element data. Coherence to the primary source trend is characteristic of first-cycle volcaniclastic sediments (McLennan *et al*. 1993; Roser and Korsch 1999). The Sumani watershed suite also shows little tendency for the scatter to high Zr/Sc ratios caused by concentration of zircon from recycling, or by hydraulic sorting, as seen where abundant plutonic compositions, also near UCC. The combination of the modal compositions and the geochemical provenance indicators thus shows that the Sumani watershed soil and river sediment are first cycle, and were derived from an undissected to transitional arc source dominated (Nara and Roger 2012) by dacitic to rhyolite volcanic rocks.

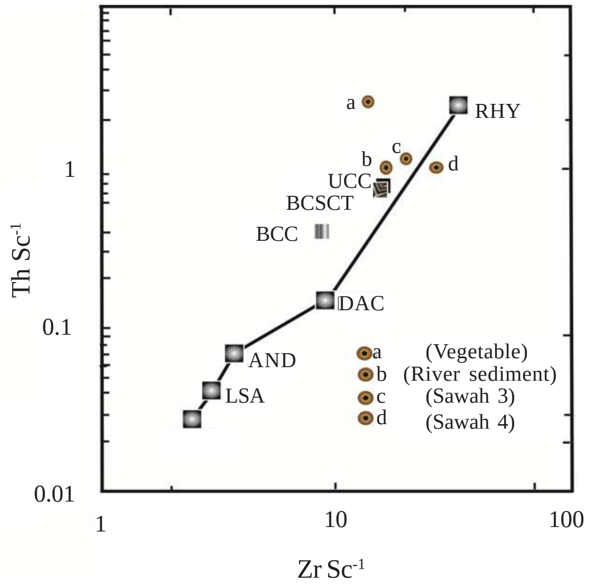

Figure 3. Th/Sc–Zr/Sc plot (McLennan et al. 1993) for agricultural soil at vegetable, river sediment and sawah in Sumani Watershed. BAS average basalt, LSA low-silica andesite, AND andesite, DAC dacite, RHY rhyolite, as plotted by Roser and Korsch (1999).

Comparative Study

In an attempt to evaluate the general condition of the sediments, the data were compared with other studies carried out in Sumani watershed and in other countries, and also with geochemical background standards and toxicological benchmarks (Table 4, 5, Figure 5). Pb, Zn and Cu at Sumani watershed Agricultural soil were comparable with Kirki region Agricultural soil in Greece. However, concentration Pb, Zn, Cu, Ni and Cr were lower compared than Mexico urban soil and Thailand urban soil. Comparison of average concentrations of Pb, Zn, Cu, Ni, Cr, V, Sr, Rb, Ce, Th, and Zr in Vegetables , Sawah and river sediment with UCC, BCC, BCSCST 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 Zn, Cu, Ni, Cr, 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 to or exceed, Canadian environmental Quality Guidelines (Canadian EQG-ISQG), US Environmental Protection Agency's (US EPA) toxicity reference values (TRV), 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 concentrations (PEC), high no effect concentrations (HNEC) defined by the US DOE, probable effect level classified by the Canadian EQG-IQG-PEL, and the severe effect level (SEL), LEL used by the Ontario MOE. However, the overall results show that the levels of Pb, Cu found in the vegetable soil and river sediments may have some adverse effect,

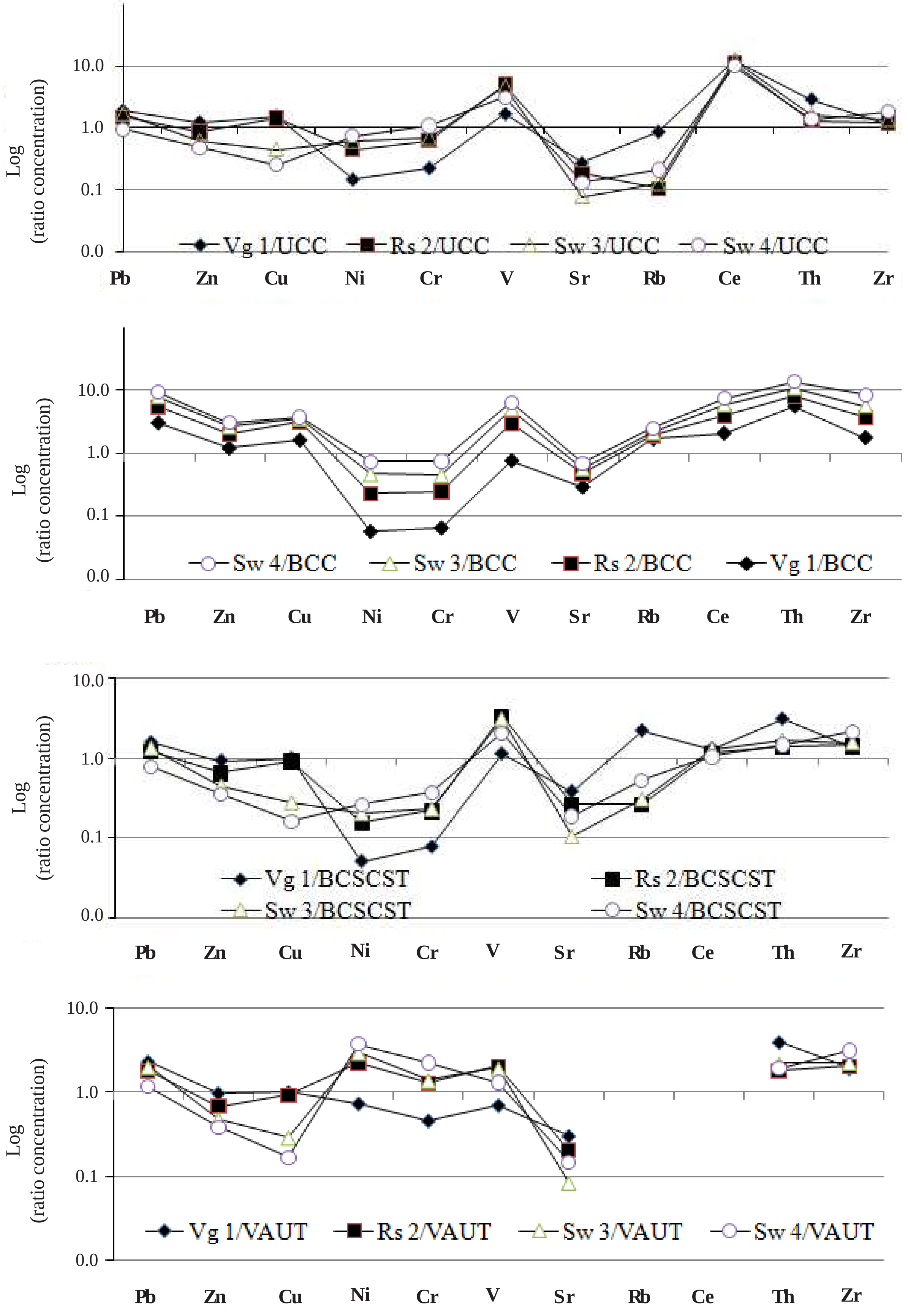

Figure 4. Comparison of trace metal concentrations in the Sumani watershed surface soil and river sediment normalized to UCC, BUC, BCSCST and VAUT (element/VAUT). UCC upper continental crust (Taylor and Mclennan 1985); BCC Bulk concinental crust, BCSCST Bulk composition sediment columns subdicting at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

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 (Cupper)	Ni (Nickel)	Cr (Chromium)	V (Vanadium)	Sr (Strontium)	Rb (Rubidium)	Ce (Cerium)	Th (Thorium)	Zr (Zirconium)	TiO_2	Fe_2O_3	P_2O_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 study
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)]

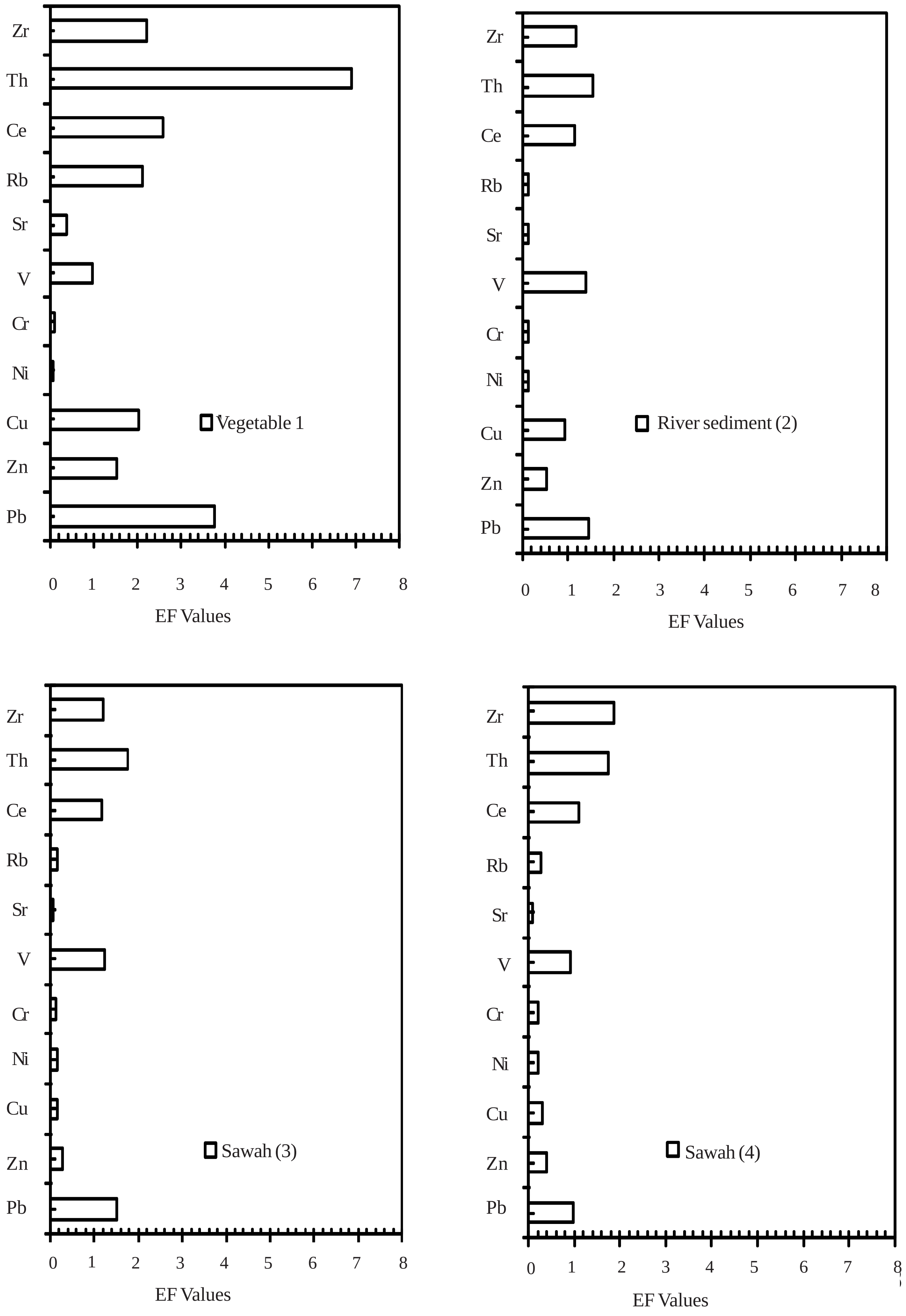

Figure 5. Bar plots showing EF values for Pb, Zn, Cu, Ni, Cr, V, Sr, Rb, Ce, Th, and Zr in surface soil and river sediment in the Sumani watershed.

Table 5 Comparison of average metal values in the Sumani watershed with geochemical background and toxicological reference values for Sediments.

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

UCC upper continental crust from Taylor and Mclennan (1985); JUC Japan upper crust from Togashi et al. 2000; US DOE United States Department of Energy; 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 guidelines and PEL probable effect level from CCME (2002); TRV toxicity reference value from the US Environmental Protection Agency (US EPA) (1999); Ontario MOE Ontario Ministry of Environment; LEL lowest effect level, SEL severe effect level from Persaud et al. 1993, na not available

Table 6 Anthropogenic contribution (% AC) values for the surface agricultural soil and river sediments in Sumani watershed.

Area	Anthropogenic contribution (% AC)										
	Pb (lead)	Zn (Zinc)	Cu (Cupper)	Ni (Nickel)	Cr (Chromium)	V (Vanadium)	Sr (Strontium)	Rb (Rubidium)	Ce (Cerium)	Th (Thorium)	Zr (Zirconium)
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

Bold text highlights anthropogenic contribution (% AC) whereas those from Sawah would have no harmful effect for Pb, Zn, Cu, Cr and Ni.

Enrichment Factor and Anthropogenic Contribution

It is well established that trace metals are introduced to coastal environments by both natural processes (*e.g.*, weathering and erosion) and anthropogenic activities within the catchment or neighboring shoreline (Nouri *et al.* 2008; Rahman and Ishiga 2012). Calculation of EF and AC is an important part of geochemical studies seeking to determine if heavy metals originate from human activities or natural processes (N'guessan *et al.* 2009; Rahman *et al.* 2011). Normalization of metal concentrations to a textural or compositional characteristic of the sediments is a commonly applied technique. However, selection of an appropriate reference element to evaluate EF is critical. The choice of reference element mostly depends on its correlation with other elements. It must be also stable, and not susceptible to redistribution by processes such as reduction/ oxidation and absorption/desorption, and be conservative during weathering (Luoma 1990). 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.* 2011) and Fe (Rezaee *et al.* 2011), have generally used as geochemical normalizers. The choice of reference material is quite complex, and there is no clear consensus.

To select the most suitable normalizer, most studies have applied step by step regression methods (Loring 1991; Tam and Yao 1998). In this work, Mn and Fe were tested as normalizers, using UCC for the reference values (Taylor and McLennan 1985) and BCC Rudnick and Fountain (1995). Fe shows strong correlation with most elements, and has a short residence time in sea water, it is not the best normalizer, because its deposition into soil and river sediment can be influenced by human activities (Santos *et al.* 2005). In addition, in this present study, the contents of Fe in some samples in Sumani watershed are very low (Table 1) compared to geochemical standards, and therefore would yield unrealistic EF values.

According to Sutherland (2000), EF values in the range 2–5 indicate moderate enrichment, between 5 and 20 significant enrichment, and greater than 40 extreme enrichment. However, Zenglu *et al.* (1987) stated that if EF exceeds 1 it means that the trace metal becomes a polluting element. Overall, EF values for the study areas here indicate no or only slight to moderate contamination, because most samples have EF values of less than 5. However, a few sampling sites show higher EF. At Vegetable soil, samples 1 have EF values of 7 for Th and EF values range 2–5 for Pb, Zn, Cu, Rb, Ce and Zr (Figure 5). Elevated Th, Pb, Zn, Cu, Rb, Ce and Zr EF values at vegetable soil in upland Sumani watershed are located in and close to mount Talang as active volcano (Table 1) where erupted in year 2000 and soil covered by volcanic ash about 5-15 cm (Fiantis *et al.* 2010) possibly suggest that there is a local point source input of these metals (Table 1).

These Upland Sumani watershed are under intensive vegetable cultivation, so application of pesticides in agricultural activities could be a source of Pb enrichment (personal communication 2012). Furthermore, EF might be increased owing to the fine-grained nature of the Andisol soil, and high organic matter contents in upland Sumani watershed (Aflizar *et al.* 2013 a, b). Conversely, low EF values at most sampling sites at sawah and river sediment suggest their natural origin (*i.e.*, natural weathering processes) and primary control by source rock composition. The sawah soil and river sediment are dominated by alluvial fan, granite, undifferentiated volcanic product, and river alluvium, which might have influenced the distribution patterns of the elements. Consequently, source lithology can also be considered as a dominant factor influencing low elemental abundances. Figure 6 depicts the distribution of EF values of Zr, Th, Ce, Rb, V, Cu, Zn, Pb in the watershed. The values ranged from 0.1 to 6,8. Upper topographical areas showed moderate level EF values of Zr, Th, Ce, Rb, Cu, Pb.

Average AC values in the soil and river sediments of the study areas calculated using Eq (2) show that the anthropogenic contribution of Pb is 53.47% at vegetable; 94.46% at river sawah (3); 107.74% at sawah (4) and 51.97% at river sediment, respectively (Table 6), indicating that these metals have an anthropogenic proportion around 77 % and natural proportion about 23%. This means that the study areas are highly enriched in Pb as a result of anthropogenic influence. Anthropogenic contribution of Zn is 13.86 % at vegetable (1). The anthropogenic contribution of Cu is 30.39% at vegetable; 53.37% at sawah (3). Thus, this metal has a natural proportion higher than 86% at vegetable(1), 69% at vegetable, and approximately 46 % at sawah(3). Anthropogenic contribution of Ce, Th and Zr is 41.38, 65.55 and 34.86% at vegetable(1); 75.16, 97.71 and 97.71% at sawah(3); 89.17, 116.87 and 90.55% at sawah (4); 61.71, 96.69 and 100.22, respectively. Indicating that these metals have an anthropogenic proportion around 44-100% and natural proportion

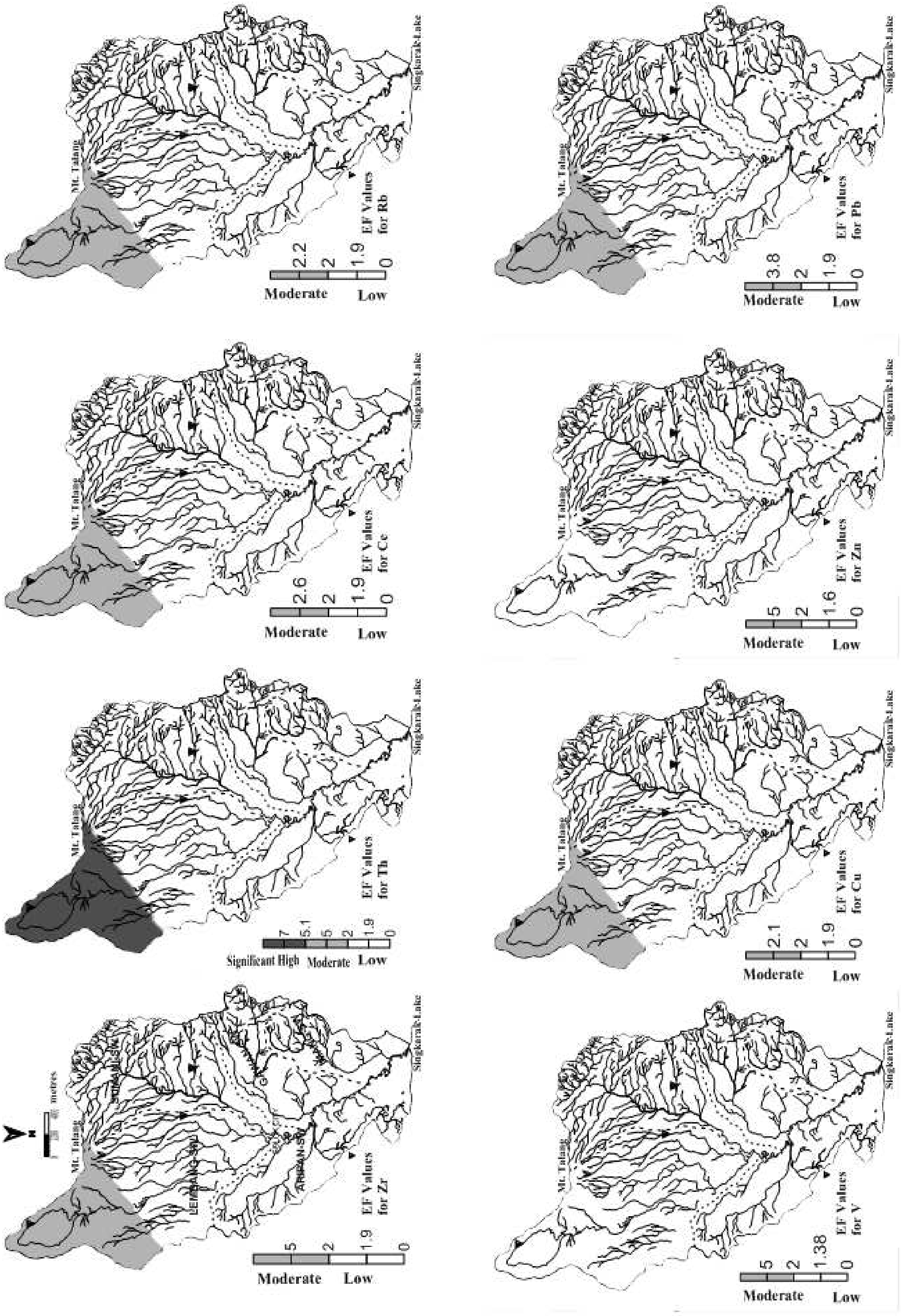

Figure 6. Spatial Distribution of EF values in Sumani Watershed. a: Zr, b: Th, c: Ce, d: Rb, e: V, f: Cu, g: Zn, h: Pb.

about 0-56%. This means that the study areas are highly enriched in Ce, Th and Zr as a result of anthropogenic influence where sources from volcanic ash from mount 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 sediment (2). Thus, this metal has a natural proportion higher than 9% at sawah (3), 8% at sawah (4), and approximately 54% at river sediment (2). Other metals like Zn, Cu, Ni, Cr, Sr and Rb exhibit a negative contribution at most study sites, indicating that these metals arise mostly from natural processes, such as weathering of granitic, andesite, alluvial fan, river alluvium and undifferentiated volcanic material source rocks.

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 transported material by erosion). Although AC values for most sampling sites reflect only natural weathering processes, the elevated levels of Pb, Cu, V, Ce, Th and Zr confirm that some anthropogenic contamination has occurred.

CONCLUSIONS

Trace metal concentrations in Sumani watershed at vegetable, sawah and river sediments were characterized as reference values for environmental monitoring in this region. Calculated EF and AC values confirm that spatial distributions of Pb, Cu, V, Ce, Th and Zr are directly related to both anthropogenic and natural sources, depending on the sampling location. Statistical procedures indicated that pH, CEC, iron (Fe), titanium(TiO_2) and calcium (CaO) are the main geochemical scavengers in soil and river sediment in Sumani watershed, and these elements and chemical properties influence the abundance and distribution of most trace metals in study area. Deposition of metals at Sumani watershed may also be influenced by non-ferrous metal (*i.e.*, aluminosilicates), sample grain size, and source rock (*i.e.*, granite, volcanic rock and gneiss) composition. Strong correlation between titanium and other elements suggests that the composition of the detrital component and grain size are also significant controls of soil and river sediment chemistry. The findings in this study are significant, because they provide the first information about soil and river sediments in this area, which will be helpful for further research in the near future. Continuous monitoring, determination of elemental baselines in soil and river sediments and historical changes, the effect of intensive agriculture, and water quality studies are essential for achieving clear views of the total environmental condition of the Sumani Watershed, West Sumatra Indonesia.

ACKNOWLEDGEMENTS

The authors deeply acknowledged The Ministries of Research and Technology and Higher education, Republic of Indonesia, for supporting this research under the Stranas, IbM and Ristek RT programe granted to the first author. We thank Professor Tsugiyuki Masunaga and Hiroaki Ishiga of Shimane University, Japan, for their invaluable help during soil analysis, and many helpful suggestions.

REFERENCES

Abdullah MH, J Sidi and AZ Aris. 2007. Heavy metals (Cd, Cu, Cr, Pb and Zn) in Meretrix meretrix roding, water and sediments from estuaries in Sabah, North Borneo. *Int J Environ Sci Edu* 2: 69-74.

Aflizar, A Roni and T Masunaga. 2013a. Assessment Erosion 3D hazard with USLE and Surfer Tool: A Case study of Sumani Watershed in West Sumatra Indonesia. *J Trop Soils* 18: 81-92.

Aflizar, AC Idowu, R Afrizal, Jamaluddin, H Muzakir and T Masunaga. 2013b. 3D Agro-ecological Land Use Planning Using Surfer Tool for Sustainable Land Management in Sumani Watershed, West SumatraIndonesia. *J Trop Soils*18: 241-254.

Aflizar, A Saidi, Husnain, Ismawardi, B Istijono, Harmailis, H Somura, T Wakatsuki and T Masunaga. 2010a. A land use planning recommendation for the Sumani watershed, West Sumatera, Indonesia. *Tropics* 19: 43-51.

Aflizar, A Saidi, Husnain, R Indra, Darmawan, Harmailis, H Somura, T Wakatsuki and T Masunaga. 2010b. Soil erosion characterization in an agricultural watershed in West Sumatra, Indonesia.*Tropics* 19: 29-42.

Ahmed F, MH Bibi, T Fukushima, K Seto, H Ishiga and T Fukushima. 2010. Abundances, distribution, and sources of trace metals in Nakaumi-Honjo coastal lagoon sediments, Japan. *Environ Monit Assess* 167: 473-491.

Anu G, SM Nair, NC Kumar, KV Jayalakshmi and D Pamalal. 2009. A baseline study of trace etals in a coral reef sedimentary environment, Lakshadweep Archipelago. *Environ Earth Sci* 52: 1245-1266. doi:10.1007/s12665-009-0113-6.

MA Rahman and H Ishiga. 2012. Trace metal concentrations in tidal flat coastal sediments,Yamaguchi Prefecture, southwest Japan. *Environ Monit Assess* 184: 5755-5771.

Chandrajith RLR, M Okumura and H Hashitani. 1995. Human influence on the Hg pollution in Lake Jinzai, Japan. *Appl Geochem* 10: 229-235.

Chester R and JH Stoner. 1973. Pb in particulates from the lower atmosphere of the eastern Atlantic. *Nature* 245: 27-28.

Calace N, S Ciardullo, BM Petronio, M Pietrantonio, F Abbondanzi, T Campisi and N Cardellicchio. 2005. Influence of chemical parameters (heavy metals, organic matter, sulphur and nitrogen) on toxicity of sediments from the Mar Piccolo (Taranto, Ionian Sea, Italy). *Microchem J* 79: 243-248.

Ennouri R, L Chouba, P Magni and MM Kraiem. 2010. Spatial distribution of trace metals (Cd, Pb, Hg, Cu, Zn, Fe and Mn) and oligo-elements (Mg, Ca, Na and K) in surface sediments of the Gulf of Tunis (Northern Tunisia). *Environ Monit Assess* 163: 229-239.

Fernando M, JL Pinedo, JL Davilla, JE Oliva, RJ Speakman and MD Glascock. 2011. Assessing sediment pollution from the Julian Adame-Alatorre dam by instrumental neutron activation analysis. *Microchem J* 99: 20-25.

Fiantis D, M Nelson, J Shamsuddin, TB Goh and EV Ranst. 2010. Determination of the Geochemical Weathering Indices and Trace Element Content of new Volcanic Ash deposits from mt. Talang west Sumatra) Indonesia. *Eurosian Soil Sci* 43: 1477-1485.

Galasso JL, FR Siegel and JH Kravitz. 2000. Heavy metals in eight 1965 cores from the Novaya Zemlya Trough, Kara Sea, Russian Arctic. *Mar Pollut Bull* 40: 839-852. doi:10.1016/S0025-326X(00)00080-1.

Gee GW and JW Bauder. 1986. Particle-size Analysis. In: Methods of Soil Analysis, Part 1. Physical and Mineralogical Methods, (eds. Klute, A.), American Society of Agronomy and Soil Science Society of America, Madison, Wisconsin, p. 399-404.

Golden Software. 2010. Surfer® 9 for windows. Golden,Colorado. Available online http://www.goldensoftware.com/products/surfer/surfer.shtml.

Hissler C and JL Probst. 2005. Impact of mercury atmospheric deposition on soils and streams in a mountainous catchment (Vosges, France) polluted by chlor-alkali industrial activity: the important trapping role of the organic matter. *Sci Total Environ* 361.163-178.

IITA (International Institute of Tropical Agriculture). 1979. Selected Methods for Soils and Plant Analysis, Manual Series No. 5, IITA, Ibadan, Nigeria, pp. 70.

Indonesia Geological Research and Development Centre. 1995. Systematic Geological map of the Solok, quadrangle Sumatra.0815. scale: 1:250000 edition 2 by PH silitonga and Kastowo. Base map by U.S. Army Map service, series T-503 (index number, SA 47-4). Index showing quadrangle names and number according to national coordination agency for surveys and mapping (NCSAM), 1975.

Indonesia Soil Research Institute. 2005. Chemical analyses for soil, plant, water and fertilizer. Indonesia soil research institute. http://balittanah.litbang.deptan.go.id. pp. 118-136.

Jones DS, GW Suter II and RN Hull. 1997. Toxicological benchmarks for screening potential contaminants of concern for effects on sediment-associated biota: 1997 revision. ES/ER/TM-95/R4, Oak Ridge National Laboratory, Oak Ridge, Tenn

Luoma SN. 1990. Processes affecting metal concentrations in estuarine and coastal marine sediments. In: R Furness and P Rainbow (eds) Heavy metals in marine environment. CRC, Boca Raton, pp 51-66.

Loring DH. 1991. Normalisation of heavy metal data from estuarine and coastal sediments. *ICES J Mar Sci* 48: 101-115.

Loring DH and RTT Rantala. 1990. Sediments and suspended particulate matter: total and partial methods of digestion. *ICES Tech Mar Environ Sci* 9: 1-14.

McLennan SM, S Hemming, DK Mc Daniel and GN Hanson. 1993. Geochemical approaches to sedimentation, provenance and tectonics. In: MJ Johnson and A Basu (eds) Processes controlling the composition of clastic sediments. Geo Soc Am Spec Paper, USA, pp. 21-40.

Matthai C, GF Birch and GP Bickford. 2002. Anthropogenic trace metals in sediment and settling particulate matter on a high energy continental shelf (Sydney, Australia). *Mar Environ Res* 54: 99-127.

Narantuya P and B Roser. 2012. Geochemistry of Devonian–Carboniferous clastic sediments of the Tsetserleg terrane, Hangay Basin, Central Mongolia: Provenance, source weathering, and tectonic setting.. Island Arc. Wiley Publishing Asia Pty Ltd.

Nelson WD and LE Sommers. 1982. Total carbon, organic carbon and organic matter. In: methods of soil analyses, No.9, Part 2. L Page, DE Baker, R Ellis Jr (eds) . *Am Soc Agron Inc Soil Sci Am* Inc Publisher, Madison. pp. 552-553.

Nouri J, AH Mahvi, GR Jahed and AA Babaei. 2008. Regional distribution pattern of groundwater heavy metals resulting from agricultural activities. *Environ Geol* 55: 1337-1343.

N'guessan YM, JL Probst, T Bur and A Probst. 2009. Trace elements in stream bed sediments from agricultural catchments (Gascogne region, S-W France): where do they come from? *Sci Total Environ* 407: 2939-52. doi:10.1016/JSCITOTENV.2008.12.047.

Nirmal Kumar JI, H Soni and RN Kumar. 2007 Evalution of biomonitoring approach to study lake contamination by accumulation of trace elements in selected aquatic macrophytes: a case study of Kanewal Community Reserve, Gujarat, India. *Appl Eco Environ Res* 6: 65-76

Ogasawara M. 1987 Trace element analysis of rock samples by X-ray fluorescence spectrometry, using Rh anode tube. Bull Geol Sur Jpn 38: 57-68

Ozbas EE. 2011. Heavy metals in Surface soils of groves: A study from Istambul, Turkey. *Sci Res Essays* 6:1667-1672.

Persaud D, A Jaagumagi and A Hayton. 1993. Guidelines for the protection and management of aquatic sediment quality in Ontario. Ontario Ministry of the Environment. Queen's Printer of Ontario. http://www.ene.gov.on.ca/envision/gp/B1-3.pdf .

Plank T and CH Langmuir. 1998. The chemical composition of subducting sediment and its consequences for the crust and mantle. *Chem Geol* 145: 325-394.

Potts PJ, AG Tindle and PC Webb. 1992. Geochemical reference material compositions. Whittles, Caithness.

Rezaee K, MR Abdi, EB Saion, K Naghavi and MA Shafaei. 2011. Distribution of trace elements in the marine sediments along the South China Sea, Malaysia. *J Radio Anal Nucl Chem* 287: 733-740. doi:10.1007/s10967-010-0950-5.

Roser BP and RJ Korsch. 1999. Geochemical characterisation, evolution and source of a Mesozoic accretionary wedge: the Torlesse terrane, New Zealand. *Geol Manag*e136: 493-512.

Roussiez V, JC Aloisi, A Monaco and W Ludwig. 2005. Early muddy deposits along the Gulf of Lions shoreline: a key for a better understanding of land-to-sea transfer of sediments and associated pollutant fluxes. *Mar Geol* 222-223: 345-358.

Rudnick RL and DM Fountain. 1995. Nature and composition of the continental crust: a lower crustal perspective. *Rev Geophys* 33: 267-309.

Santos IR, EV Silva-Filho, CEGR Schaefer, MR Albuquerque-Filho and LS Campos. 2005. Heavy metal contamination in coastal sediments and soils near the Brazilian Antarctic Station, King George Island. *Mar Pollut Bull* 50: 185-195.

Salomons W and U Forstner. 1984. Metals in hydrocycle. Berlin: Springer. pp.63-98.

Sutherland R. 2000. Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. *Environ Geol* 39: 611-627.

Syed Hafizur R, K Dilara, M. Ad Tanveer, SI Mohammad, AA Mohammad and AA Mohammad. 2012. Assessment of Heavy Metal Contamination of Agricultural Soil around Dhaka Export Processing Zone (DEPZ), Bangladesh: Implication of Seasonal Variation and Indices *Appl Sci* 2: 584-601; doi:10.3390/app2030584.

Technical Secretariat of the CCME Task Group on Water Quality Guidelines. 2002. Canadian sediment quality guidelines for the protection of aquatic life. CCME (Canadian Council of Ministers of the Environment), Ottawa.

Tam NFY and MWY Yao. 1998. Normalization and heavy metal contamination in mangrove sediments. *Sci Total Environ* 216: 33-39.

Taylor SR and SM McLennan. 1985. The continental crust: Its composition and evolution. Oxford: Blackwell.

Togashi S, N Imai, Y Okuyama-Kusunose, T Tanaka, T Okai, T Koma and Y Murata. 2000. Young upper crustal chemical composition of the orogenic Japan Arc. *Geochem Geophys Geosyst* 1 (paper number 2000GC000083).

Tokalioglu S, S Kartal and L Elci. 2000. Determination of heavy metals and their speciation in lake sediments by flame atomic absorption spectrometry after a four-stage sequential extraction procedure. *Anal Chim Acta* 413: 33-40.

US EPA. 1999. U.S. Environmental Protection Agency. Screening level ecological risk assessment protocol for hazardous waste combustion facilities. vol 3, Appendix E: Toxicity reference values, EPA530-D99-001C. http://www.epa.gov/epaoswer/hazwaste/combust/eco-risk/voume3/appx-e.pdf.

Van Rotterdam-Los AMD, Heikens A, Vriend SP, van Bergen MJ and van Gaans RFM. 2008a. Impact of acid effluent from Kawah Ijen crater lake on irrigated agricultural soils: soil chemical processes and plant uptake. *J Volcanol Geotherm Res* 178: 287-296.

Wakatsuki T, Y Shinmura, E Otoo and GO Olaniyan. 1998. African-based sawah system for the integrated watershed management of the small in land valley of West Africa. *FAO Water* Report no. 17, pp. 5-79.

Windom HL, SJ Schropp, FD Calder, JD Ryan, RG Jr Smith, LC Burney, FG Lewis and H Rawlin-Son. 1989. Natural trace metal concentrations in estuarine and coastal marine sediments of the southeastern United States. *Environ Sci Technol* 23: 314-320.

Yanguo T, Shijun N, Xianguo T, Chengjiang Z and Yuxiao M. 2002. Geochemical baseline and trace metal pollution of soil in Panzhihua mining area. *Chin J Geochem* 21: 213-245.

Young E. 2007. Can ‘fertilizing’ the ocean combat climate change? Companies are planning to boost the ocean’s plankton, hoping they will harvest more CO2 from the air. But will it work? *New Sci* 15: 42-45.

Zenglu X, Li S and Li T. 1987. Soil element background and study method [M]. Meteor Press, Beijing, pp 9294 (in Chinese with English abstract).