ASSESSMENT OF TOXICITY LEVEL IN SELECTED HEAVY METAL IN VOLCANIC SOILS FROM TAWAU, SABAH.

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ABSTRACT. *Heavy metals are one of the serious pollutants in environment because its toxicity. Severe concentration of heavy metals can harm the plants, animals and even human. During the pedogenesis process, heavy metals from the parent rock are mobilized in soils and redistribute in to the environment. The objective of this paper is to study the concentration and toxicity level of selected heavy metals in volcanic soils around Tawau, Sabah. In this study 10 soil samples were collected from different sampling stations. The selection of soil samples were based on the different type of volcanic rocks in the study area. The determination of concentration of heavy metals in soil samples were carried out using X-Ray Fluorescence (XRF) analysis. The result shows, the highest concentration is chromium with the average of 141 ppm followed by zinc with 112 ppm. The concentration of copper is 49 ppm, nickel 15 ppm, lead 8 ppm and arsenic 7 ppm. The soil samples is identified as polluted due to the elevated concentration of certain heavy metals when compared with the Sediment Quality Guidelines of US EPA. Chromium is regarded as heavily polluted agent while zinc, copper and arsenic indicated that the area is moderately polluted. Nickel and lead average concentration show no indication of pollution in the area. It is concluded that the combined source of heavy metals in the study area would be the parent materials of the soils and other anthropogenic effluent. From the study also, it is found out that pH value, organic matter and clay percentage has influenced the heavy metal concentration in volcanic soil in the study area.*

Key Words. Heavy Metals, Tawau, Volcanic Soils, XRF.

INTRODUCTION

Mason (1958) defined geochemistry as a study to determine the abundances of elements in earth. It also relates to the principles which control the elements distribution and mobility to the various parts of earth. Heavy metal is defined as trace elements that possess a density more than 5 g/cm3. Heavy metals are one of the serious pollutants in our natural environment because of its toxicity (Pekey, 2006). Metal elements existence has importance in the industrial arena and also in our daily life; a trace amount of common metals are found in the environment and in our daily consumption does give benefits to humans. However, severe concentration of a certain metals can harm plants, animals and even human. Examples of heavy metals are Arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb), selenium (Se) dan zinc (Zn). The abundance of heavy metal is influenced by several factors such as parent rock, clay existence, pH value and organic matter content in soil. Metal concentration levels vary from one place with one another, depending on natural geological factors of the area (Sabri *et al*., 1993).

Weathering is the breakdown and alteration of rocks and minerals at or near the earth's surface into products that are more in equilibrium with conditions found in the environment (Yalcin, 2007). Weathering can be divided into mechanical, chemical and biological activity (Jenny, 1994). Tropical rainforest climate which is intense sun and rainfall all year round contribute to the active weathering process. Chemical weathering is a major process affecting rocks mineral composition and is controlled by many variables such as parent rock type, topography, climate and biological activity (Islam *et al*, 2001). During pedogenesis process, heavy metals are mobilized in soils and redistribute among soil components (Sipos, 2004). Due to high temperatures and heavy rainfall, the predominant soils of humid tropical regions are oxisols (Young, 1976). The high ratio of precipitation to evaporation generally favours downward percolations; due to very high rainfalls the humid tropical environment provides the optimum conditions for metal dispersion (Olade, 1987). To investigate such occurrence, a study is carried out to assess the distribution of selected heavy metal and its toxicity level in volcanic soils from Tawau, Sabah.

DESCRIPTION OF STUDY AREA

The research area is located in Tawau, Sabah. The area is bounded by the latitude 4° 15' N to 4° 30' N and the longitude 117° 30' E to 118° 15' E, as shown in Figure 1. Tawau area is underlain by volcanic rocks aged Pliocene to Quartenary (Kirk, 1968; Tjia *et al.,* 1992). Volcanic activities in Tawau involved lava flows and pyroclastics, The type of rocks that was produced by lava flows are basalt, andesite and dacite, while pyroclastics deposits are scoria, lapilli, ashes, breccia, and tuff (Baba *et al*, 2008). Volcanic activities during Pliocene was attributed to the pyroclastic and lava eruption which then transported, faulted and eroded during Late Pliocene and Early Quartenary producing similar volcanic facies morphology (Sanudin & Baba, 2007).

MATERIALS AND METHODOLOGY

In this study 10 soil samples were taken from different sampling stations in Tawau area. The selection soil samples were based on the different type of volcanic rocks in the study area, noted as C1 until C10. The soil pH value was taken insitu during sampling. Samples were carefully secured in a clean polyethylene bag to avoid any contamination and taken to the lab for further analysis. Samples then undergone test for determination of organic matter content, where samples were dried in a furnace with temperature 400°C overnight. The remaining samples were air dried for the next analysis. Particle size distribution was carried out to identify the percentage of silt, clay and sand fraction, dry sieving and pipette method were employed to analyse the soil sample (BS1377-1990). For determination of selected heavy metal concentration, samples are tested using X-Ray Fluorescence method. Samples were grinded and sieved to obtain grain sized less than 50 µm (Schlotz & Uhlig, 2006) and pressed pellets are used for trace elements determination (Norrish & Hutton, 1969).

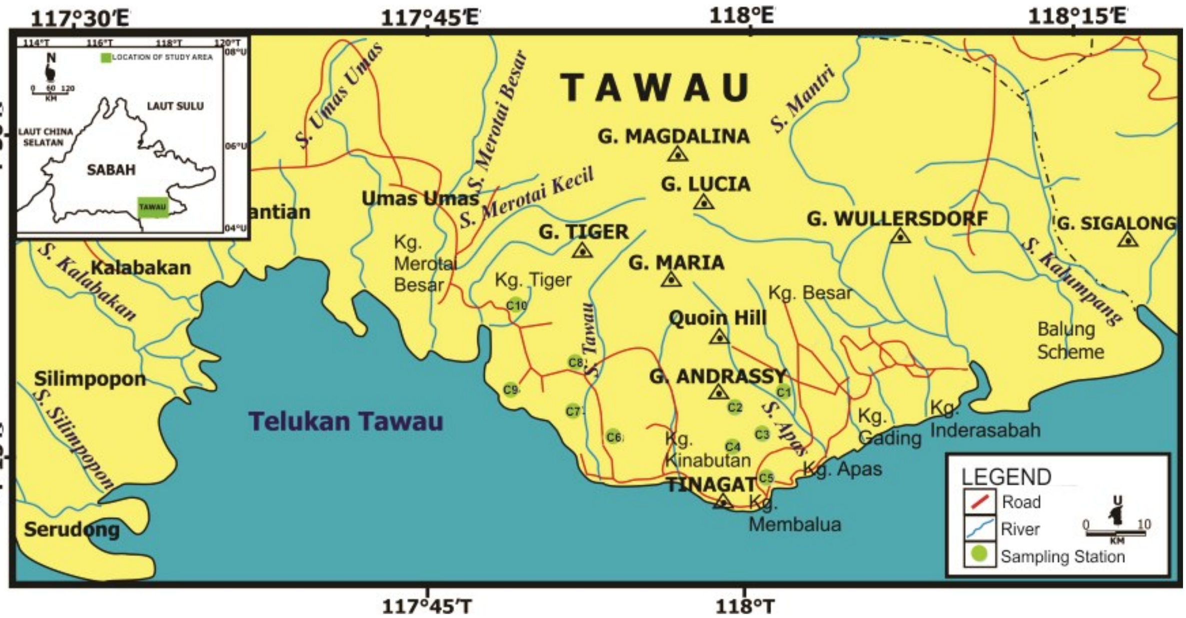

Figure 1: Location of study area and sampling station.

RESULTS AND DISCUSSION

Heavy Metal Concentration in Soil

Ten samples (C1 until C10) represent different types of volcanic rocks. Each sampling station corresponds with different types of volcanic rocks; sample C1 to C5 made up by hypersthene andesite, C6 to C9 is taken from dacite and C10 consists of olivine basalts, which reflects the possible source of heavy metal to soil. Seven types of heavy metals are chosen in terms of concentration in the soils, the heavy metals are arsenic (As), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn). A summary of heavy metal concentration of each sampling area and its average against Sediment Quality Guidelines (SQG) of US EPA (Pekey, 2006 after Perin *et al*., 1997) are shown in Table 1.

Table 1: Heavy metal concentration of each sampling area and its average against Sediment Quality Guidelines (SQG) of US EPA.

Element (ppm)	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	Avg	SQG of US EPA (ppm)		
												Non-Polluted	**Moderately Polluted**	**Heavily Polluted**
As	8	5	5	8	10	7	7	7	5	6	**7**	<3	3~8	>8
Cr	154	108	139	220	93	125	134	134	118	182	**141**	<25	25~75	>75
Cu	40	43	55	10	59	42	28	69	88	57	**49**	<25	25~50	>50
Ni	19	10	9	11	10	19	17	17	23	17	**15**	<20	20~50	>50
Pb	*bdl	3	3	*bdl	2	17	19	3	24	4	**8**	<40	40~60	>60
Zn	112	92	132	74	122	117	112	128	114	120	**112**	<90	90~200	>200

*bdl – below detection limit.

Table 2: Mean heavy metal contents of igneous rock (mg/kg) reported in literature.

Parent Material	As	Cr	Cu	Ni	Pb	Zn
Igneous rock (Adapted from Alloway, 1995)	1.5	200	90	150	3	58

From Table 1, chromium shows the highest concentration average of 141 ppm, followed by zinc with 112 ppm, copper with 49 ppm, nickel with 15 ppm, lead with 8 ppm and arsenic with 7 ppm. These elements will undergo leaching process and dispersed through weathering agents. Sediments can be classified as: non-polluted, moderately polluted and heavily polluted based on the Sediment Quality Guidelines of US EPA (Perin *et al.*, 1997). Based on this guideline, the average concentration of chromium is regarded as a heavily polluted agent while zinc, copper and arsenic indicated that the area is moderately polluted. Nickel and lead average concentration shows no indication of pollution in the area while cobalt is not measured in this guideline. Parent materials of the study area is mainly igneous rocks, the concentrations of heavy metals in volcanic soils from Tawau (Table 1) were lower compared to the heavy metals concentration of igneous rock by Alloway (1995) with the exception of arsenic, lead and zinc. The elevation concentration of As, Pb and Zn may derived as a result of cycling through vegetation, atmospheric deposition and adsorption by the soil organic matter (Alloway, 1995). Based on a report by Shan *et al.* (2010), concentration of heavy metals in soils originating from different parent materials were close to each other for there were no differences among different parent materials, which may relate to the development history of soils. The reports also mentioned that on the early stages, pedogenesis is mainly controlled by parent material, but in subsequent long term evolution of soil, the effect of other factors on soil forming processes may exceed that of parent material.

The Relationship Between Heavy Metal Concentration to pH Value, Organic Content and Clay Percentage.

Factors such as pH value, the presence of organic matter and clays are seen to have association with heavy metal concentration in soil samples. Table 3 shows a summary of pH value, organic content, clay percentage and heavy metal concentration in soil samples. The relationship between the heavy metal concentrations versus pH value of soil samples are shown in Figure 2, based on the graph he abundance of metals are found in the acidic soil pH ranging from pH 3.60 to 4.29. This shows that acidic pH is able to control the abundance concentration of heavy metals, similar findings by Lara *et al*. (2006) in which stated that based on the results, it was found that high mobilization of heavy metals (Cr, Cu, Zn, Cd and Pb) takes place under strong acidic conditions (pH $\cong$ 2). A study by Myung (2008) indicates the factors influencing the bioavailability of metals are controlled by soil pH among other factors, surface soil from mine dump have an average pH of 4.1 (acid) in which possesses the highest amount of heavy metals compared to the other sample.

Table 3: pH value, organic content, clay percentage and heavy metal concentration in soil samples.

Sample	pH	Organic content (%)	Clay (%)	Heavy Metal Concentration (ppm)					
				As	Cr	Cu	Ni	Pb	Zn
C1	3.88	8.49	44.11	8	154	40	19	bdl	112
C2	3.60	7.94	61.32	5	108	43	10	3	92
C3	3.90	7.08	68.48	5	139	55	9	3	132
C4	3.69	7.25	55.59	8	220	10	11	*bdl	74
C5	4.29	6.80	69.64	10	93	59	10	2	122
C6	3.91	3.91	71.39	7	125	42	19	17	117
C7	3.85	5.09	67.04	7	134	28	17	19	112
C8	4.15	5.51	64.41	7	134	69	17	3	128
C9	3.99	3.71	60.42	5	118	88	23	24	114
C10	3.67	2.23	63.71	6	182	57	17	4	120

*bdl – below detection limit

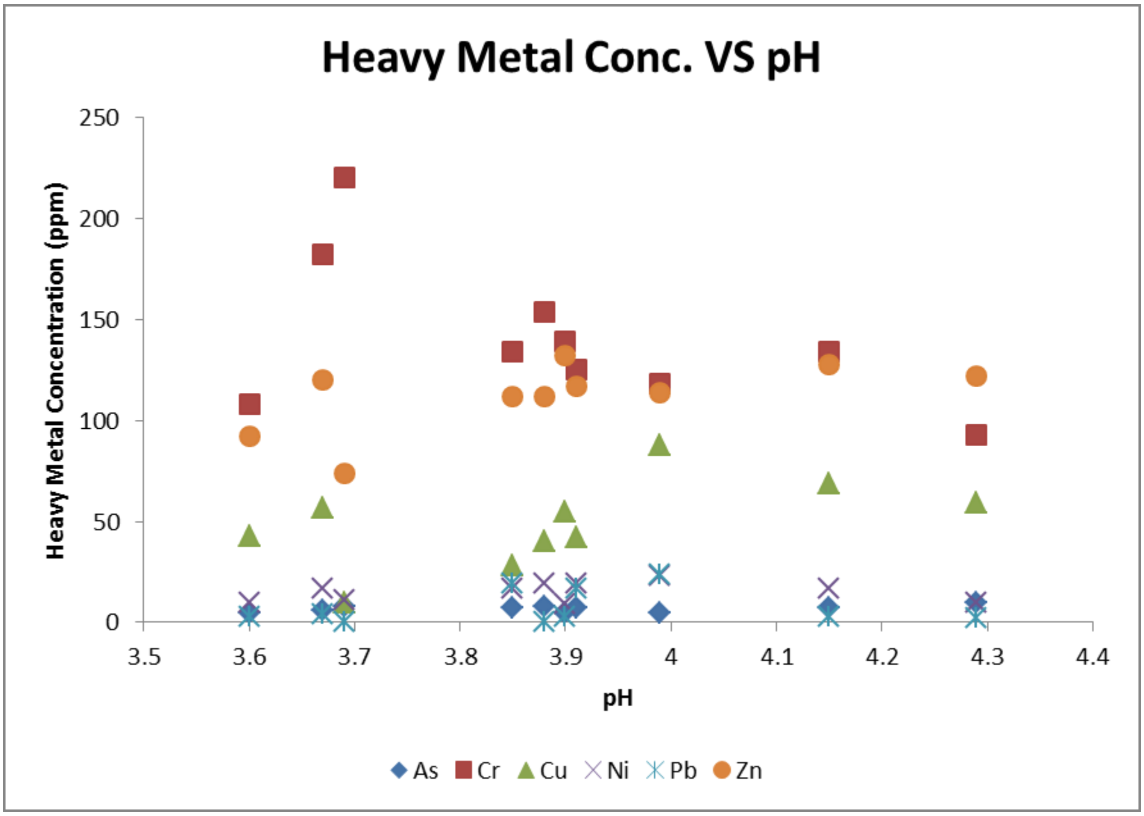

Figure 2: The relationship between the heavy metal concentrations versus pH value of soil samples.

The relationship between the heavy metal concentrations versus of organic matter in soil samples is shown in Figure 3. The graph shows that the abundance and concentration of heavy metals is controlled by organic matter. The higher organic matter content the higher the abundance and concentration of heavy metals. Sipos (2004) mentioned in his findings that among the studied samples organic matter has the most important role in binding heavy metals. However, the degree of trace element re-distribution is usually dependent on the mobility characteristics and the effects of other environmental parameters such as organic matter content (Olade, 1987).

The relationship between the heavy metal concentrations versus with clay content soil samples is shown in Figure 4. It shows that the higher the percentage of clay in a sample, the higher the abundance and concentration of heavy metals. According to Villaescuasa-Celaya *et al*. (2000), the accumulation of heavy metals is abundance in the silt and clay particles. It is generally accepted that most transition elements are enriched more in the fine fraction than in the coarse fraction of sediments (Terashima, 1993). A similar finding was reported by Prego & Cobelo Garcia (2003), which mentioned that sediment fraction <0.063mm shows a strong chemical potential absorption of heavy metals.

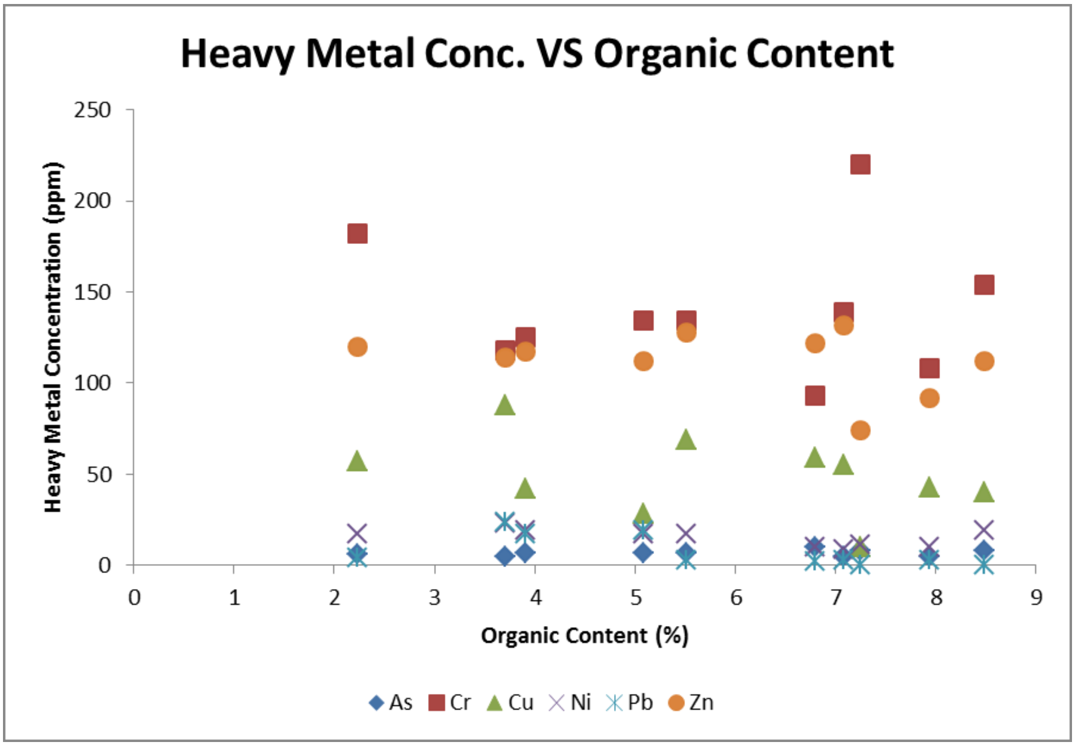

Figure 3: The relationship between the heavy metal concentrations versus of organic matter in soil samples.

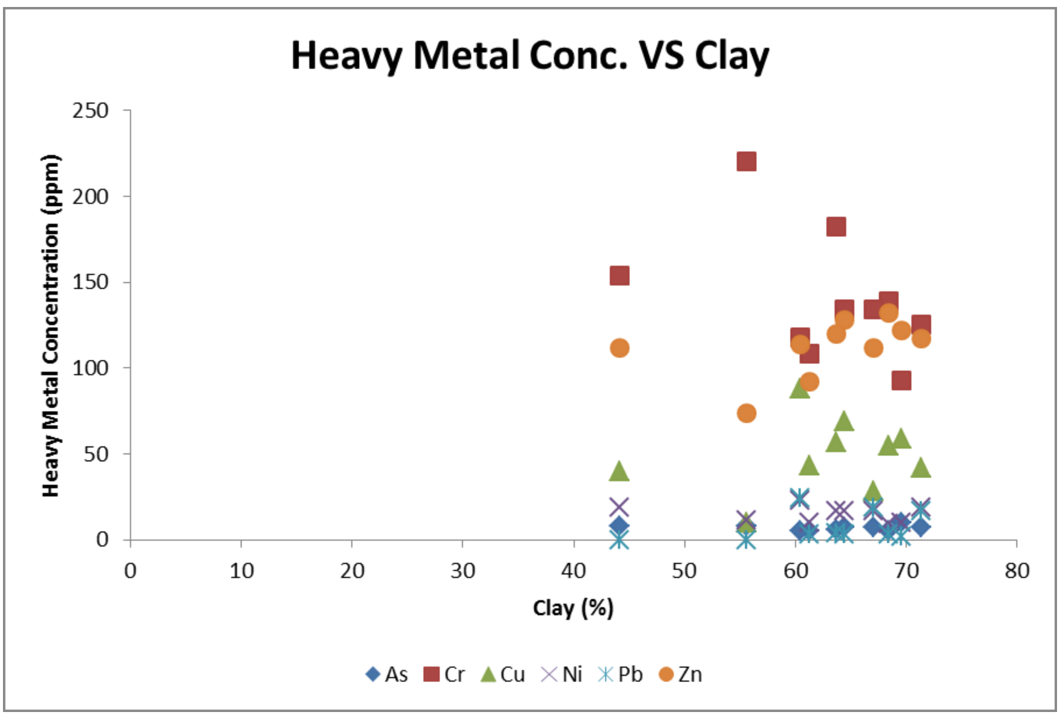

Figure 4: The relationship between the heavy metal concentrations versus with clay content soil samples.

Source of Heavy Metals

Heavy metal contamination is present in the environment as a result of both natural and human activities (Chen *et al*., 2012). With the exception of soils derived from physical and chemical weathering of parent materials containing elevated levels of trace elements (e.g. black shales and basic igneous rocks), the presence of elevated metal concentrations is related to man's activities (Myung, 2008). Distributions of heavy metals amounts are determined mostly by the parent material, which may be modified by eventual anthropogenic effects, while the partition of heavy metals among the soils components is mostly regulated by the pedogenic effects (Sipos, 2004). Figure 5 shows the geological map of the study area, consisting different types of volcanic rocks.

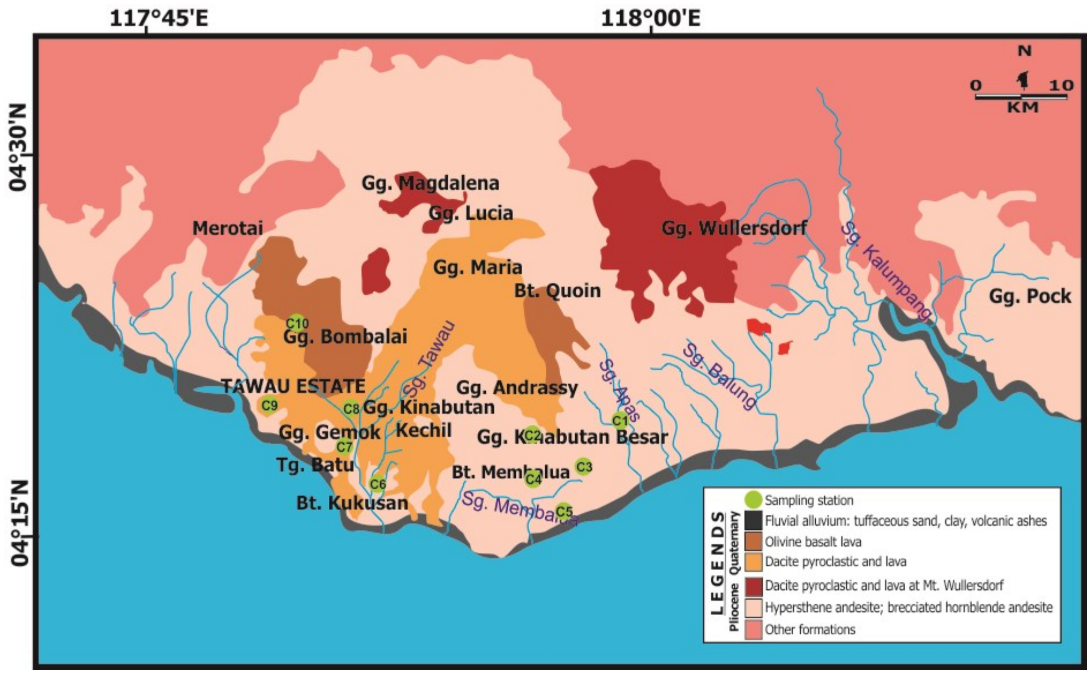

Figure 5: Geological map of the study area (modified after Kirk, 1962)

As shown in Figure 5, each sampling station corresponds with different types of volcanic rocks; sample C1 to C5 made up by hypersthene andesite, C6 to C9 is taken from dacite and C10 consists of olivine basalts. Chromium, zinc, copper and arsenic are classified as pollutants as the concentration exceeds the permissible value of Sediment Quality Guidelines of US EPA. Mafic and ultramafic rocks are richest in chromium and also found in igneous basaltic with the average of 200 mg/kg and range of 40-600 mg/kg, where it readily substitutes for Fe which has an ionic radius of 0.067nm (McGarth, 1995). The volcanic rocks of the area occur as igneous basaltic where the source of high concentration of chromium may originate. Higher concentrations of zinc exhibit by basic igneous rocks, such as basalts with the average of 100 mg/kg. This is due to zinc occurrence in ferromagnesian minerals including augite, hornblende and biotite, where it has been isomorphously substitute for Fe2+ or Mg2+ which are the principal components of the crystal lattice, along with silicon, aluminium and oxygen (Alloway, 2008).

The abundance of copper is highest in basic igneous rocks with the average of 90 mg/kg and range of 30-160 mg/kg, the abundance of copper in basaltic rocks is greater than for granitic rocks; it is partly controlled by the process of differentiation during crystallization (Baker & Senft, 1995). The average natural content of arsenic in soils is 5 mg/kg (Backer & Chesnin, 1975). In rocks, arsenic is concentrated in magmatic suphides and iron ores, the most important iron ores are pyrite, realgar and orpiment (Matera *et al.,* 2003). As for the source of arsenic in the study area, pyrite has been seen to be associated with andesite in Balung area. The source of heavy metals in the study area can be regarded by the parent material of the underlying different rocks, which mainly consists of igneous body and are rich with heavy metal components in the minerals, but effluent from other anthropogenic effects is also undeniable. Based on the field observation, other potential sources of metals to soils in the study area are mining activities, agricultural activities and fossil fuel combustion.

CONCLUSION

The heavy metal concentrations in soils taken from Tawau were determined using the XRF technique. The soils samples are identified as polluted due to the concentration of heavy metals when measured using Sediment Quality Guidelines of US EPA. Chromium with an average concentration of 141 ppm is regarded as a heavily polluted agent while zinc, copper and arsenic with an average concentration of 112 ppm, 49 ppm and 7 ppm respectively, indicated that the area is moderately polluted. Nickel and lead average concentration of 15 ppm and 8 ppm shows no indication of pollution in the area. It is concluded that the combined source of heavy metals in the study area would be the parent materials of the soils and other anthropogenic effluent. From the study also, it is found out that pH value, organic matter and clay percentage serves factors influencing the heavy metal concentration of a particular soil in the study area.

REFERENCES

Alloway, B.J. 1995. Heavy Metals in Soils 2nd Edition. Chapman and Hall.

Alloway, B.J. 2008. *Zinc in Soils and Crop Nutrition*. International Zinc Association (IZA) & International Fertilizer Industry Association (IFA).

BS 1377-1990. *Methods of Test for Soils for Civil Engineering Purposes*. London : British Standard Institution.

Baba, M., Hennie F.W.S.E. & Sanudin, T. 2008. Geochemical Characterization of Volcanic Soils From Tawau, Sabah. *Geological Society of Malaysia*, Bulletin **54**.

Backer, D.E. & Chesnin, L. 1975. Chemical Monitoring of Soils For Environment Quality and Animal and Human Health. Adv. Agron. **27**, 305–374.

Baker, D.E. & Senft, J.P. 1995. Copper. *In* Alloway B.J. (ed.) Heavy Metals in Soils 2nd Edition, pp. 179-205. Glasgow: Chapman and Hall.

Chen, Y.Y., Wang, J., Gao, W., Sun X.J. & Xu, S.Y. 2012. Comprehensive Analysis of Heavy Metals in Soils From Boashan District, Shanghai: a heavily industrialized area in China. *Environmental Earth Science*, Springer-Verlag.

Islam, M.R., Stuart, R., Risto, A.,Vesa, P. 2001. Mineralogical changes during intense chemical weathering of sedimentary rocks in Bangladesh. *Journal of Earth Sciences* 20 (2002) 889-901.

Jenny, H. 1994. *Factors of Soil Formation: A System of Quantitative Pedology*. Dovers Publication, Inc.

Kirk, H.J.C. 1962. *The Geology and Mineral Resources of Semporna Peninsula. North Borneo* Geology Survey Department British Territories in Borneo 14. Sarawak Government Printing Office.

Kirk, H.J.C. 1968. The Igneous Rocks of Sarawak and Sabah. *Geological Survey of Malaysia*, Bulletin 5.

McGarth, S.P. 1995. Chromium and Nickel. *In* Alloway B.J. (ed.) Heavy Metals in Soils 2nd Edition, pp. 152-178. Glasgow: Chapman and Hall.

Matera, V., Le Hécho, I., Laboudigue, A., Thomas, P., Tellier, S. & Astruc, M. 2003. A Methodological Approach for The Identification of Arsenic Bearing Phases in Polluted Soils. *Environmental Pollution* 126 (2003) 51-64.

Mason, B. 1958. *Principles of Geochemistry*, 2nd Edition. Wiley.

Myung, C.J. 2008. Heavy Metal Concentrations in Soils and Factors Affecting Metal Uptake by Plants in The Vicinity of A Korean Cu-W Mine. *Sensors 2008*, 8, 2413-2423.

Norrish, K. & Hutton, J.T. 1969. An Accurate X-Ray Spectographic Method For The Analysis of A Wide Range of Geological Samples. *Geochem. Et Cosmochim*. Acta, 33, 431-453.

Olade, M.A. 1987. Dispersion of Cadmium, Lead and Zinc in Soils and Sediments of a Humid Tropical Ecosystem in Nigeria. *Lead, Mercury, Cadmium and Arsenic in The Environment, Scope*. John Wiley & Sons Ltd.

Pekey, H. 2006. Heavy Metal Pollution Assessment in Sediments of The Izmit Bay, Turkey. *Environmental Monitoring and Assessment, Springer* **123**:219-231.

Perin, G., Bonardi, M., Fabris, R., Simoncini, B., Manente, S., Tosi, L. & Scotto, S. 1997. Heavy Metal Pollution in Central Venice Lagoon Bottom Sediments: Evaluation of Metal Bioavailability by Geochemical Speciation Procedure. *Environmental Technology* **18** 593-604.

Prego, R. & Cobelo-Garcia, A. 2003. Twientieth Century Overview of Heavy Metals in The Galician Rias (NW Iberian Peninsular). Environmental Pollution, 121:425-425.

Sabri, A.W., Rasheed, K.A. & Kassim, T.I. 1993. Heavy Metal in The Water, Suspended Solids and Sediment of The River Tigris Impoundment At Samarra. *Journal of Water Research,* **27**:1099-1103.

Saria, L., Takayuki, S. & Kentaro, M. 2006. Leaching of Heavy Metals in Acid Mine Drainage. *Waste Management & Research*, Vol. **24** No.2 134-140.

Sanudin, T. & Baba, M. 2007. *Pengenalan Kepada Stratigrafi*. Penerbit UMS, Kota Kinabalu, Sabah.

Schlotz, R. & Uhlig, S. 2006. *Introduction to X-ray Flourescence Analysis (XRF).* Bruker AXS GmbH, Karlruhe, West Germany.

Shan, W., Xinghui X., Chunye L., Xi, C. & Chuanhui, Z. 2010. Levels of Arsenic and Heavy Metals in The Rural Soils of Beijing and Their Changes Ove The Last Two Decades (1985-2008). *Journal of Hazardous Materials*, **179**:860-868.

Sipos, P. 2004. Factors Affecting Heavy Metal Distribution in Forest Soils: Inherited Pedogenic Characteristics. *Eurosoil 2004*. Alvert-Ludwigs-Universitat Freiburg.

Taylor S.R. & McLennan S.M. 1995. The geochemical evolution of the continental crust. Rev. Geophys. 33 241–265.

Terashima, S., Katayama, H., & Itoh, S. 1993. Geochemical Behaviour of Pt and Pd in Coastal Marine Sediments, Southeastern Margin of The Japan Sea. *Applied Geochemistry*, Vol. **8**, 265-271.

Tjia, H.D., Ibrahim Komoo, Che Aziz Ali & Sanudin, T. 1992. Geology of Taman Bukit Tawau, Semporna Peninsula, Sabah. *Geology Survey of Malaysia*, Bulletin 31.

Villaescuasa-Celaya, J.A., Gutierrez-Galindo, E.A & Flores-Munoz, G. 2000. Heavy Metals in The Fraction of Coastal Sediments From Braja California (Mexico) and California (USA). *Environmental Pollution*, **108**:453-462.

Yalcin, A., 2007. The Effects of Clay on Landslides: A case study. *Applied Clay Science* **38**:77-85.

Young, A. 1976. *Tropical Soils and Survey*. Cambridge University Press, Cambridge.