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HEAVY METALS IN WATER AND SEDIMENT FROM LIWAGU RIVER AND MANSAHABAN RIVER AT RANAU SABAH

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ABSTRACT

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The Liwagu River is one of the most reliable river systems in Ranau which had experienced a mudflows event due to massive landslide of Mount Kinabalu. The aim of this study is to determine the water quality and compare the level of heavy metals in water and sediment of the Liwagu River and a non-impacted mudflows of Mansahaban River. Water and sediment were collected from four sampling stations on each river. Water samples were filtered with 0.45 µm membrane filter and acidified to pH<2 and conducted by means of ICP-OES while AAS was used for sediment analysis prior to aqua regia digestion method for the determination of five heavy metals (Cd, Cr, Cu, Pb and Zn). The Paired T-test shows that there were significant different between impacted and non-impacted river especially for turbidity, conductivity, temperature, Cu_w , Cr_w , Zn_w , Cd_s , Cr_s and Cu_s , ($P<0.05$). Liwagu River shows the Cu concentration in sediment and water were exceeded the Guideline for the Protection and Management of Aquatic Sediment quality in Ontario and Interim National Water Quality Standards (INWQS): >110 mg/kg and >0.02 mg/L, respectively. The correlations coefficient shows that there were significant relationship between heavy metals in water and sediment from Liwagu and Mansahaban River ($0.413<r<0.888$, $p<0.05$). For conclusion, the quality of water from both river are fairly the same but not for the sediment. However, further in depth investigation is needed to identify a wider perspective towards the behavior of heavy metals prior to mudflows event in Ranau, North Borneo of Malaysia.

KEYWORDS

Ranau, North Borneo, Mudflow event, Water Quality, Heavy Metal, Sediment.

1. INTRODUCTION

The earthquake triggered in Ranau on 5th June 2015 with 5.9 magnitude has brought massive disturbance not only on the man-made infrastructure but also the natural landscape of Mount Kinabalu itself. A group researchers clarified that the occurrence of an earthquake may create or influenced other natural phenomena to occur as it may be refer as natural disaster that arise from one factor connected to another [1]. This nature can be seen through the massive landslide which happened as a result from the earthquake. The removal of part of the land on the foot hill of Mount Kinabalu at the same time has affected the natural vegetation [2]. Moreover, the soils presence in hill side of a mountain is important in terms of the security of the land, whereas the erosion due to enormous amount of rainfall as well as a tremor resulting from earthquake can be reduced [3]. In addition, the protection of land on the hilly side is more secure when it is covered by trees, as the root system is highly responsible to hold the soils together form sloping down the hill. Primarily, the reduction of top soils regarding to the landslide in Mount Kinabalu has altered this function which ultimately allows more reduction of soils caused by the tremor resulting from aftershocks. Basically, aftershock has a small magnitude of earthquake occurs after the main earthquake triggered in certain region [4]. Additionally, the aftershock has lengthened the process of erosion on the foot hill of Mount Kinabalu which eventually caused more soils to rush down the hills. This process has largely contributed to the process of sedimentation resulting from the streams carrying mud [5]. The process of sedimentation can be described when the water associated with mud are flowing through a river channels and eventually settled down when they encountered obstacle along the way or as the water streams will eventually slow down [6]. The settlement of mud accumulates in the lower land of Liwagu River can be seen along the river which overly change the structure of the irrigation.

The intervention of water that mixed with sediment will endangered the biota environment as well as the small vegetation which lies in the river in such way that these ecosystems will be killed due to the severe condition [7]. Fish may die in this situation where they have insufficient amount of oxygen supply as the water becomes polluted with portion of soils and exhibit high amount of metals concentrations caused by the fact that the sedimentation exposed heavy metals elements into the river streams which then diluted along with streams. In fact, the small vegetation which lies across the water channel are also reducing either caused by the erosion of river bank or the inability of receiving light to carried out photosynthesis due to the presence of turbidity. The reduction of vegetation along the Liwagu River has resulted from such event.

As consequence, the removal of large amount of sand and debris which allowed the process of accumulation of soil and not only changes the structure of the Liwagu River yet also altering the water supply in Ranau [8]. Further emphasize into this case, a researcher added that the strong streams which caused by the discharged of temporary dammed by the landslide sweep tons of vegetation across the river [9]. This situation has affected the supply of water in Ranau, where the intake station of water plant is forced to be closed caused by the risk of huge streams and the quality of the water itself. As the quality of water been a key factor in influencing the water supply, heavy metals pollution has become one of the concerned pollution in this situation [10].



Figure 1: The sedimentation and the color of water change after mudflow event

Whereby, some researchers claimed that the occurrence of heavy metals into the river system can appear from the mudflows events resulting from the aftershock which lengthen the sedimentation on the hilly side of mountain [11]. Primarily, heavy metal is an essential nutrient that presence in soils and important for the development of living organism however hazard at certain point of their concentration and most importantly they are not permanently fixed in soils [12]. In other words, it may be removed or transported by soils and water as a typical removal agent in trophic land. Since the Liwagu River triggered by the mud flowing streams situation thus, additional metals concentration may be dispersed from this event. Furthermore, other researchers has mentioned that river are one of the reliable agent of transporting heavy metals contaminants [13]. With respect to its mobility, hence this contaminant may be distributed across the irrigation system for agricultural activities.

Prevalently, the lower land of Ranau is covered by the ultrabasic soils [14]. Since this part of land is uniformly elevated in terms of landscape, thus the distributions of water are accessible through the irrigation which channelled from the Liwagu's streams. A group researchers added that by considering the fact that the heavy metals are able to retain their presence in sediment and running water, there is a high potential for this contamination to be distributed along the Liwagu River [15]. Additionally, the contamination of heavy metals will endanger the exposed plant as well as human through the water supply [16].

Moreover, the awareness towards this pollution need to be emphasize. Thus, this study was carried out to determine the current status of water quality and heavy metals (Cd, Cr, Cu, Pb and Zn) in water and sediment from Liwagu River as impacted river and compared to Mansahaban River as non-impacted river after mudflow event. This study focus on the analysis of heavy metals namely, as accordance to the state that claimed that these elements comprised the highest heavy metals concentration detected in fresh water system as well as the surface sediment [13,17]. Hence, these elements refer as the potential occurring heavy metals in Liwagu River.

2. METHODOLOGY

2.1 Study sites

The study was conducted in the district of Ranau, Sabah, North Borneo of Malaysia. Ranau district experienced an annual rainfall of 2500 mm per year with average temperature at 10°C on the higher land while increasing up to 30°C on the lower land. Primarily, Ranau is a rural district which comprise of a total population of 94,029 where more than 85% of these populations are Dusun [18]. Geographically, Ranau comprise of a hilly elevation of land where the highest land peak presence is the Mount Kinabalu whereby it is known as the highest mountain in South East Asia with 4096 meter in height. Additionally, the locals in Ranau contributed to agriculture, tourism and self-employment and government employees which composed of 50%, 7% and 13% respectively [19]. To cope with this level of population, the domestic use of water in Ranau is highly dependent on the Liwagu River. Prevalently in Ranau, Liwagu River and Mansahaban River are the main reliable sources of water distribution (Figure 2 & 3). The amount of water is available as a source for agricultural, households and commercial activities [9].

Sampling was conducted in two different geological setting of river whereby the water and sediment samples were taken simultaneously from four selected location along the Liwagu River and Mansahaban River respectively. The sampling site with coordinates is shown in Table 1. The sampling stations was chosen because of the community livelihood that depending on the water supply from the river especially for agricultural activity, paddy plantation, freshwater fish pond and tagal area (Tagal is the conservation area for freshwater fish belong to community at an area, fishing not allowed for some period of time and punishment will apply if unfilled the tagal's rules) [20]. The Sampling was done few months after the mudflow event; on 9 February 2016 and 9 March 2016.

Table 1: Sampling stations at Liwagu River, Ranau Sabah

Station	Liwagu River	Descriptions	Mansahaban River	Descriptions
S1	557'4.59"N 116 38'58.97"E	Water Catchment area	05 56' 03. 3"N 116 41' 09.7"E	Tagal area
S2	557'27.03"N 116 39'44.23"E	Agriculture area	05 56' 44.0"N 116 41' 24.1"E	Fish pond area
S3	557' 25.65"N 116 40'2.35"E	Paddy plantation area	05 57' 26.9"N 116 41' 28. 7"E	Tagal area
S4	557'11.13"N 116 40'34.07"E	Paddy plantation area	05 58' 53. 6"N 116 40' 28. 8"E	Tagal area



(a) Station 1



(b) Station 2



Figure 2: The sampling stations at Liwagu River, Ranau Sabah



Figure 3: The sampling stations at Mansahaban River, Ranau Sabah

2.2 In-situ parameters and Analysis of water

The in-situ parameter were taken along the Liwagu and Mansahaban River which were the pH value, turbidity, temperature, Dissolve Oxygen (DO) and Electrical conductivity (EC) by using YSI meter. Calibration technique was applied to the portable meter before used to optimize the functions for measurement reading recovery.

The polyethylene bottles were used to collect the water samples from the study sites. Polyethylene bottles were cleaned by soaked into 5% of HNO₃ for all night and rinse with distilled water, additionally this will ensure that the safety of bottles from any undesirable matter. Next, the water sample was taken by submerging the polyethylene bottles into the water surface for a depth of 20 cm to exclude suspended matter and nitric acid was added until pH <2 for preservation before analyzed the samples by using Perkin Elmer Optima 5300DV Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES) [17].

2.3 Sediment Digestion

Sample sediment were dried thoroughly in an oven for 2 days with temperature of 105 °C in order to remove all the moisture before being sieved through 0.65 µm stainless steel mesh [21]. In later stage, the digestion method for aqua regia were carried out at a very cautious mode

due to the acid presence in this method. As accordance to a study, the total amount of Cd, Cr, Cu, Pb and Zn in sediments normally applying the aqua regia's method as a procedure due to their simplicity and adaptability [22]. The aqua regia solution made by the mixing of HNO₃ and HCL acid and added to 1 g of the sediment (<0.65 µm). Later, the samples were boiled for a period of 2 hours with maximum temperature of 110°C. As it settled down, the samples passed through 0.45 µm membranes filter and added the deionized water until it reach 50 ml before analyzed with FAAS.

3. RESULTS AND DISCUSSIONS

To analyse the ranges of acceptable amount of heavy metals elements in the surface water, Mansahaban River (1km away from Liwagu River) was used as a reliable and comparable data as this river does not affected by the mudflows event, in fact Mansahaban River at the same time is a preserved river or known as a "tagal" river. Hence it was subjected to Mansahaban River as a baseline representative river in Ranau to indicate the ranges of heavy metals present in Liwagu River after the mud flows events with a non-impacted river. Thus, the concentration of heavy metals in water and sediment from four sampling station along two rivers were determined respectively in two distinct sampling period. The result shows in Table 2.

Table 2: The results (range and mean concentrations) of in-situ parameters and heavy metals in water and sediment from Liwagu and Mansahaban river, Ranau Sabah.

Media	Parameters	Liwagu River				Mansahaban River			
		Samp 1	Samp 2	Mean	SD	Samp 1	Samp 2	Mean	SD
In-situ	Dissolve oxygen (mg/L)	7.56-9.86	7.50-8.23	8.18	0.73	6.3-7.7	6.1-8.1	7.14	0.67
	pH	7.56-9.00	7.57-8.53	8.16	0.48	7.97-8.24	6.1-8.09	7.58	0.76
	Turbidity (NTU)	12.22-20.66	3.38-14.29	14.55	5.80	2.31-7.69	2.54-8.71	5.68	2.62
	Conductivity (µs/cm)	215.30-432.56	236-380	347.98	78.77	275.63-340.90	224.17-314-67	281.55	38.59
	Temperature (°C)	25.53-30.80	26.03-31.00	28.18	2.16	25.10-29.87	25.70-32.47	28.91	2.54
Water	Cd (mg/L)	<0.0001-0.0005	<0.0001	0.0004	0.0001	<0.0001-0.0005	<0.0001	0.0003	0.0002
	Cr (mg/L)	0.0072-0.0139	<0.0001	0.0088	0.0024	0.0050-0.0138	<0.0001-0.0042	0.0161	0.0339
	Cu (mg/L)	<0.0001-0.0932	<0.0001-0.0230	0.0240	0.0248	<0.0001-0.0188	<0.0001-0.0058	0.0072	0.0076
	Pb (mg/L)	0.0026-0.0099	<0.0001-0.0047	0.0077	0.0236	0.0018-0.0054	<0.0001	0.0037	0.0010
	Zn (mg/L)	0.0023-0.0424	0.0055-0.0105	0.0161	0.0247	0.0012-0.0106	0.0039-0.0110	0.0048	0.0039
Sed	Cd (mg/kg)	0.22 - 2.08	0.60 - 4.35	1.81	1.30	0.95-1.10	0.70 -1.20	0.96	0.18
	Cr (mg/kg)	62.43 - 174.28	60.75 - 121.45	93.61	51.16	67.65-155.70	70.90 - 162.50	106.52	58.14
	Cu (mg/kg)	114.55-390.65	10.50 - 93.50	137.16	116.29	18.35-45.10	8.07 - 43.10	29.05	15.08
	Pb (mg/kg)	14.75- 32.55	6.55 - 25.05	21.34	7.67	4.55 - 28.60	4.45 - 18.15	13.24	11.23
	Zn (mg/kg)	16.02 - 51.35	25.7 - 55.80	35.32	22.09	29.50 - 69.30	25.70 - 55.80	45.89	24.19

(Below detection limit = <0.0001)

3.1 In-situ parameters

According to a study, the water quality of Liwagu River was considered as excellent before the mud flow event in year 2011, respectively [23]. Similar to this study where the concentrations of the parameters (DO, pH, EC and temperature) were found safe for human consumption but unfortunately not for drinking water because of the turbidity is exceeded the permissible limit of INQWS and Drinking water standard (Table 6). The result shows that the Liwagu River has seriously impacted by mud flow after the earthquake natural disaster. The Paired T-test proved that there were significant different between first sampling and second sampling that shows the Liwagu River condition is still unstable and the water quality keep on changing ($p < 0.05$, Table 3). In additions, the high amount of annual rainfall per year may cause the river is not easy to recover again as before. However, the mud flow event has significantly introduced an interesting impact to the water quality where the concentration of DO, EC and temperature were on considerable range of INQWS and its shows that the water received more nutrients and energy from new sediment that traps in the areas. The correlation coefficient shows that there were interaction relationship between in-situ parameters in water was occurred actively at Liwagu River compared to Mansahaban River ($0.742 < r < 0.798$, $p < 0.05$, Table 4).

3.2 Heavy metals in Water and Sediment

The heavy metals concentrations in water at Liwagu River and Mansahaban River show significant different between two sampling period ($p < 0.05$). While, in sediment there is only Liwagu River shows the significant different especially for Cd, Cr and Cu (Table 3). The concentration of heavy metals in water and sediment at Liwagu River were still below the concentration that found from Mamut River [24,25]. Mamut River has known as acid mine drainage area due to the Mamut Copper Mining (MCM) activities since 1975 until 1999 [25]. The comparisons of the heavy metals were at Table 6 and 7. In additions, the mean concentrations of heavy metals in water and sediment have found below the Interim National Water Quality Standard for Malaysia (Class II) (INWQS) and The Guideline for the Protection and Management of Aquatic Sediment quality in Ontario. However, some of the heavy metal has more than both guideline levels when maximum concentration counted especially for Cu (Table 2). According to the correlation coefficient analysis, there were significant different between Cu in water and sediment also with other elements ($-0.431 < r < 0.608$, $p < 0.05$, Table 4 & 5). Maybe it was due to the MCM historical activity where Cu was the key of connectors element for both water and sediment at Liwagu and Mansahaban River [26-28].

Table 3: Paired T-test between sampling at Liwagu and Mansahaban River, Ranau Sabah.

Location		Heavy Metals	Mean	Variance	Observations	df	t-Stat	t-Critical	P-value	Sign
Liwagu River (Impacted)	In-situ	Dissolve oxygen (mg/L)	8.43	0.9879	12	11	1.298879	0.2848	3.1824	> 0.05
		pH	8.24	0.3477	12	11	0.717561	0.5249	3.1824	> 0.05
		Turbidity (NTU)	18.2575	16.2804	12	11	11.18392	0.0015	3.1824	< 0.05
		Conductivity (µs/cm)	357.465	9537.1129	12	11	1.119735	0.3444	3.1824	> 0.05
		Temperature (°C)	28.34	6.1998	12	11	0.572478	0.6071	3.1824	> 0.05
	Water	Cd (mg/L)	0.0001	3.45E-08	12	11	1.8638	0.0892	2.2010	> 0.05
		Cr (mg/L)	0.0088	5.62E-06	12	11	12.8158	5.90E-08	2.2010	< 0.05
		Cu (mg/L)	0.0235	0.0006	12	11	1.4994	0.1619	2.2010	> 0.05
		Pb (mg/L)	0.0124	0.0005	12	11	1.6799	0.1211	2.2010	> 0.05
		Zn (mg/L)	0.0236	0.0005	12	11	2.3757	0.0368	2.2010	< 0.05
	Sediment	Cd (mg/kg)	1.1058	0.4132	12	11	-3.5210	2.2010	0.0048	< 0.05
		Cr (mg/kg)	106.0333	1571.5733	12	11	3.0111	2.2010	0.0118	< 0.05
		Cu (mg/kg)	220.0667	10818.6574	12	11	4.9129	2.2010	0.0005	< 0.05
		Pb (mg/kg)	22.6750	26.5657	12	11	1.1994	2.2010	0.2556	> 0.05
Zn (mg/kg)		34.2108	205.1815	12	11	-0.3946	2.2010	0.7007	> 0.05	
Mansahaban River (Non-Impacted)	In-situ	Dissolve oxygen (mg/L)	7.1750	0.38	12	11	0.440732	0.6892	3.1824	> 0.05
		pH	8.0800	0.01	12	11	2.852232	0.0650	3.1824	> 0.05
		Turbidity (NTU)	5.1725	8.53	12	11	-0.90294	0.4331	3.1824	> 0.05
		Conductivity (µs/cm)	301.1325	908.53	12	11	7.548012	0.0048	3.1824	< 0.05
		Temperature (oC)	28.0275	4.48	12	11	-4.37849	0.0221	3.1824	< 0.05
	Water	Cd (mg/L)	0.0001	2.70E-08	12	11	1.7578	0.1065	2.2010	> 0.05
		Cr (mg/L)	0.0192	0.0014	12	11	1.6547	0.1262	2.2010	> 0.05
		Cu (mg/L)	0.0066	5.74E-05	12	11	2.3877	0.0360	2.2010	< 0.05
		Pb (mg/L)	0.0037	1.08E-06	12	11	12.4514	7.95E-08	2.2010	< 0.05
		Zn (mg/L)	0.0030	7.45E-06	12	11	-3.0701	0.0107	2.2010	< 0.05
	Sediment	Cd (mg/kg)	0.9875	0.0082	12	11	1.1957	2.2010	0.2570	> 0.05
		Cr (mg/kg)	94.5767	1778.7496	12	11	-1.3878	2.2010	0.1927	> 0.05
		Cu (mg/kg)	30.4958	101.5102	12	11	0.9922	2.2010	0.3424	> 0.05
		Pb (mg/kg)	15.2042	80.5852	12	11	1.0884	2.2010	0.2997	> 0.05
Zn (mg/kg)		51.1875	312.4437	12	11	1.2120	2.2010	0.2509	> 0.05	

Table 4: The correlations between parameters for Liwagu River, Ranau Sabah.

	DO	pH	Turbidity	EC	Temp	Cd _w	Cr _w	Cu _w	Pb _w	Zn _w	Cd _s	Cr _s	Cu _s	Pb _s	Zn _s
DO	1														
pH	.569	1													
Turbidity	-.221	-.434	1												
EC	.768*	.742*	.756*	1											
Temp	-.706	-.402	.484	.798*	1										
Cd _w	-.177	-.050	-.499	-.178	-.234	1									
Cr _w	.573	.191	.476	-.141	-.246	.249	1								
Cu _w	-.429	-.224	-.500	.054	.038	.143	.058	1							
Pb _w	-.007	-.467	-.073	.105	-.232	.535*	.242	.158	1						
Zn _w	.215	-.097	-.361	-.222	-.379	.587*	.339	.226	.888*	1					
Cd _s	-.111	.495	-.293	-.174	-.007	-.160	-.574**	-.015	-.205	-.175	1				
Cr _s	.456	.084	.491	-.054	-.211	.192	.598**	-.487*	.109	.071	-.493*	1			
Cu _s	-.411	-.124	-.115	.208	.343	-.040	.584**	.358	.090	.180	-.533**	-.075	1		
Pb _s	-.029	-.014	.238	.104	.101	-.088	.339	-.107	-.068	.058	.137	.190	.186	1	
Zn _s	.217	-.036	-.024	-.168	-.412	.395	.003	-.158	.193	.234	.413*	.216	-.431*	.270	1

Table 5: The correlations between parameters for Mansahaban River, Ranau Sabah.

	DO	pH	Turbidity	EC	Temp	Cd _w	Cr _w	Cu _w	Pb _w	Zn _w	Cd _s	Cr _s	Cu _s	Pb _s	Zn _s
DO	1														
pH	.358	1													
Turbidity	-.152	-.649	1												
EC	-.612	.444	-.277	1											
Temp	.733*	-.163	.254	-.723*	1										
Cd _w	-.619	-.398	.203	.280	-.278	1									
Cr _w	.295	-.335	.514	-.529	.509	-.031	1								
Cu _w	.029	-.740*	.271	-.606	.326	-.002	.608*	1							
Pb _w	.393	-.008	.212	-.396	.025	.143	.299	.423*	1						
Zn _w	-.074	-.749*	.320	-.537	.116	-.195	-.213	-.357	-.478*	1					
Cd _s	.036	-.270	.378	-.065	.354	-.022	.027	.030	.165	-.177	1				
Cr _s	.136	-.008	-.249	.112	.225	-.198	.260	.390	-.369	.128	.048	1			
Cu _s	.408	.501	.177	.100	.046	-.265	.165	.070	.221	-.305	.354	.161	1		
Pb _s	.151	.274	.354	.187	.057	.245	-.075	-.228	.249	-.492*	.387	-.204	.509*	1	
Zn _s	-.060	.072	.406	.205	.127	.473*	-.171	-.289	.244	-.473*	.291	-.328	.222	.871**	1

*. Correlation is significant at the 0.05 level (2-tailed) ** Correlation is significant at the 0.01 level (2-tailed).

Table 6: The water quality standard and drinking water standard

Parameters	Interim National Water Quality Standard for Malaysia (Class I) (INWQS)	Mamut River (Ali <i>et al.</i> , 2004)	Kipungit River (Ali <i>et al.</i> , 2004)	Liwagu River (Fera <i>et al.</i> , 2013)	This Study
DO (mg/L)	7.00	7.7±0.3	7.5±0.2	6.19-7.79	6.1-8.23
pH	6.5-8.5	6.15±0.43	7.30±0.9	6.34- 8.30	6.1-8.53
Turbidity (NTU)	5	-	-	-	2.31-20.66
EC (µs/cm)	1000	318±6.0	40.2±1.6	0.05- 0.14	215-432
Temperature (°C)	-	-	-	19.27-24.87	25-32
Cd (mg/L)	-(Class IIA=0.01)	0.37	0.15	-	0.0004
Cr (mg/L)	-(Class IIA=0.05)	0.71.	-	-	0.0161
Cu (mg/L)	-(Class IIA=0.02)	-	-	-	0.0240
Pb (mg/L)	-(Class IIA=0.05)	2.08	-	-	0.0077
Zn (mg/L)	-(Class IIA=5.00)	2.18	-	-	0.0161

Table 7: The sediment quality standard

Parameters	The Guideline for the Protection and Management of Aquatic Sediment quality in Ontario (Persaud <i>et al.</i> , 1993)	Mamut River (Bibi <i>et al.</i> , 2015)	This Study
Cd (mg/kg)	0.6-10	-	0.96-1.81
Cr (mg/kg)	26-110	-	93.61-106.52
Cu (mg/kg)	16-110	40.8-1347.54	29.05-137.16
Pb (mg/kg)	31-250	0.49-49.68	13.24-21.34
Zn (mg/kg)	120-820	43.87-68.41	35.32-45.89

4. CONCLUSION

The turbidity, Cu_{water} and Cu_{sediment} were the best indicator to determine the water and sediment recovery for the Liwagu River after impacted by mud flow event. The quality of water from both river (Liwagu and Mansahaban River) are fairly the same but not for the sediment. However, further in depth investigation is needed to identify a wider perspective towards the behavior of heavy metals prior to mudflows event in Ranau, North Borneo of Malaysia.

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