

Distribution of Chromium and Gallium in the Total Suspended Solid and Surface Sediments of Sungai Kelantan, Kelantan, Malaysia

(Taburan Kromium dan Galium di dalam Jumlah Pepejal Terampai dan Permukaan Sedimen di Sungai Kelantan, Kelantan, Malaysia)

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ABSTRACT

Concentration level of chromium (Cr) and gallium (Ga) were measured in the total suspended solid (TSS) and surface sediments to investigate its distribution and anthropogenic inputs along Sungai Kelantan. The in-situ water quality parameters, surface sediment and surface water were collected using calibrated portable YSI water quality meter, ponar grab and water sampler, respectively. The concentration range of chromium and gallium in TSS were from 19-111 µg/g and 153-3762 µg/g, respectively, along the river. While in surface sediment, the concentrations ranged from 16-172 µg/g for Cr and 25-82 µg/g for Ga. The high concentration of Ga in TSS and Cr in sediment would suggest that the anthropogenic inputs takes place in the river channel, which is due to human activities such as sand exploration along Sungai Kelantan. In mobilization towards the estuary, Ga was more easily transported in the TSS from upstream to downstream especially during the wet season. Cr was dominant in sediment due to its affinity towards inorganic minerals and easily being scavenged in the water column during burial onto the riverbed sediment. Spatial distribution was prominent as several factors affecting the distribution along the river channel addresses the lighter gallium and dissolution of chromium towards surface sediment while being mobilize further for overall distribution before sinking in the estuarine region.

Keywords: Heavy metal; monsoonal season; pollutants; river; sediments

ABSTRAK

Aras kepekatan kromium (Cr) dan galium (Ga) telah diukur dalam jumlah pepejal terampai (TSS) dan sedimen permukaan untuk mengkaji taburan dan juga kemasukan sumber antropogenik di sepanjang Sungai Kelantan. Parameter in-situ kualiti air, sedimen permukaan dan air permukaan dikumpul dengan menggunakan YSI meter kualiti air mudah alih yang dikalibrasi, pensampel cekau ponar dan persampel air. Julat kepekatan Cr dan Ga di dalam TSS adalah dari 19-111 µg/g dan 153-3762 µg/g masing-masing, di sepanjang sungai. Manakala di sedimen permukaan pula, julat kepekatan adalah dari 16-172 µg/g untuk Cr dan 25-82 µg/g untuk Ga. Aras kepekatan yang tinggi dalam TSS adalah Ga, manakala Cr dalam sedimen menunjukkan bahawa kemasukan input antropogenik berlaku di dalam aliran sungai yang disebabkan oleh aktiviti manusia seperti penggalian pasir di sepanjang Sungai Kelantan. Bagi mobilisasi ke arah muara, Ga lebih mudah diangkut ke dalam TSS dari hulu ke hilir terutamanya semasa musim hujan. Cr adalah lebih dominan di dalam sedimen akibat keafinan ke arah unsur mineral tak organik dan mudah diskaveng di dalam turus air semasa pengebumian di atas sedimen sungai. Sebaran ruang adalah peranan yang menonjol sebagai salah satu faktor yang mempengaruhi taburan di sepanjang aliran sungai dengan mengenal pasti bahawa Ga yang lebih ringan dan pelarutan Cr ke dalam sedimen permukaan ketika mobilisasi mempengaruhi taburan keseluruhan sebelum terbenam di kawasan muara.

Kata kunci: Logam berat; musim monsun; pencemar; sedimen; sungai

INTRODUCTION

In the aquatic environment, water becomes a necessity for mobilization of several metals (trace metal and heavy metal) which accumulates in water bodies that can trap significant quantities of metals while acting as a reservoir via various hydrocycles within aquatic environments. The presence of metal contaminants exceeding the natural level in the water column would indicate the presence of natural and anthropogenic sources, which leads to serious concerns on aquatic lives at all trophic level. The retention

of metal contaminants is controlled by temporal variations, precipitation and absorption, which later would affect the transport within the water column in riverine channels (Prathumratana et al. 2008).

The climatic influence was governed by the seasonal variations that act on the riverine channel, which triggers intense weathering and erosion on sites affecting the riverine water quality. Seasonal variation in southeast Asia namely southwest monsoon (June to August) and northeast monsoon (October to March) influences the

distribution of gallium (Ga) and chromium (Cr) in the water column (Roseli & Akhir 2014). Further on monsoonal variation causes heavy precipitation and will contribute to a sudden rise in the water level of rivers located on the east coast of Peninsular Malaysia (Suhaila et al. 2010). Winds are strong during the northeast monsoon which creates turbulence resulting in riverbank erosion. Both processes would create an increasing discharge towards the estuarine region, which will indirectly mobilize the gallium and chromium composition along the water column. Many researchers suggested that the temporal variation which is governed by the northeast monsoon would increase the freshwater accumulation along the river into the coastal area of the east coast of Peninsular Malaysia as the fluctuated contents of suspended particulate and trace elements (Akhir et al. 2015; Buranapratheprat et al. 2016).

Heavy metals are one of the main pollutants that influences the biogeochemical cycles within aquatic environments. They occur in natural environments from ore where enriched minerals consist of trivalent ions leading to widespread accumulation in fine sized clay and silt (Bradl 2004). In the water column, absorption and desorption of metal components is dependent on the pH under perpendicular motion while being generated by the scavenging of metals onto finer sediment or the removal in suspended particulates towards the surface sediments (Furness 2018). Elemental contamination along riverine areas arising from rapid urbanization and industrialization has become worrisome as the ecosystem receives anthropogenic waste which persists, bioaccumulates and is toxic which poses a threat to aquatic environments (Reza & Singh 2010). Sand exploitation such as mining, dredging, and riverbank excavation is prominent in developing cities to hasten the building of structures which lead to cities growth. Nevertheless, illegal sand exploitation leads to severe erosion that changes the geography and topology of a region as changes in the fluvial behaviour of river would cause a significant effect towards particle size distribution in suspended sediment in response to sand mining (Sadeghi et al. 2018).

Gallium is present in the form of traces in silicate rocks and minerals while similarly having a geochemistry similar to aluminium. Gallium tends to camouflage in aluminium minerals due to similar ionic radius of aluminium and are found in traces in mica, feldspar, and clay minerals. In mineral morphology, Ga and Al are dominant in feldspar and mica in igneous and metamorphic rocks which are abundant in Sungai Kelantan (Awadalla & Noor 1991). On the other hand, chromium is one of the major metal elements in granitic rocks and ultramafic rocks and its behaviour highly resembles trivalent aluminium (Al^{3+}), leading to widespread accumulation in clay minerals, similar to gallium. Elevated Cr and Ga values in the river indicates the weathering process as a natural occurrence along riverbanks. The introduction of anthropogenic inputs

mainly from mining, ore deposits, deforestation and agriculture, has subsequently polluted Sungai Kelantan (Heng & Singh 1986; Li et al. 2015). In theory, the anthropogenic input backed with the wet season may increase the overall metal concentration and elevates the distribution content, especially Ga and Cr, along Sungai Kelantan. The objective of this study was to identify the sources of gallium and chromium while assessing several factors that influences the distribution of Ga and Cr along Sungai Kelantan. Thus, this paper examines the distribution in Sungai Kelantan while assessing the prominent factors that affect the Ga and Cr concentration along the riverine channel.

MATERIALS AND METHODS

Sungai Kelantan is located in the northern of Peninsular Malaysia with a drainage area of about 12,000 km² and 388 km long from Gua Musang until Kota Bharu (Perera & Lahat 2015) (Figure 1). The river originates from the northeast of Peninsular Malaysia which consist of caves and several limestone outcrops, flowing from several tributaries in the forested mountains. The river receives a variation of annual rainfall, from 0 to 1750 mm, respectively, in dry and wet seasons thus creating annual flood events during severe rainfall. The sampling began on 11 October 2016 and ended 2 days later. Surface water samples were collected using 500 mL polyethylene bottle and surface sediment using the Ponar grab (Table 1).

In the laboratory, the water sample was filtered using pre-weighed glass fibre filter paper ($D = 47$ mm, $\Phi = 0.45$ mm) and dried until constant weight. Filter paper containing TSS was digested with mixture of 10 mL of nitric acid (HNO_3), 5 mL of perchloric acid ($HClO_4$) and 1 mL of hydrofluoric acid (HF) for 2 h in Teflon beaker at 120°C (Daud et al. 2013; Sarimin & Mohamed 2012; Yusoff et al. 2015). The concentrations of chromium and gallium were determined using the Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The Diorite Gneiss Reference Material (SY-4) from Canada Certified Reference Material Project (CCRMP) was used with five replicates of reference materials to identify the effectiveness of the established method and the yield obtained was between 96-98% with results of 34.10 ± 1.2 µg/g for gallium and 10.57 ± 0.4 µg/g for chromium, respectively.

RESULTS AND DISCUSSION

CONCENTRATION OF GALLIUM AND CHROMIUM IN TOTAL SUSPENDED SOLIDS AND SURFACE SEDIMENT

The concentration of gallium and chromium in the TSS and surface sediment fluctuated from upstream to downstream (Table 2). The distance and difference in metal concentration covered from upstream to downstream was applied to observe the relationship between distance and concentration of both elements from their sources where

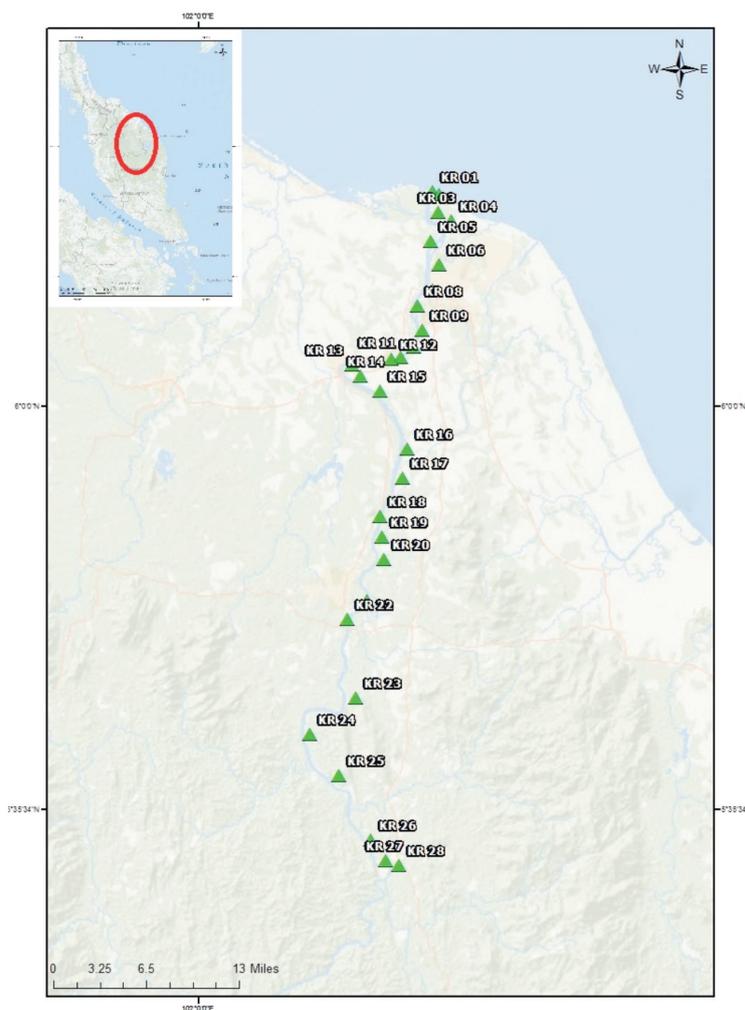


FIGURE 1. Location of sampling at Sungai Kelantan, Peninsular Malaysia

dilution process may take place during mobilization from upstream towards downstream (Amano et al. 2011).

The concentration of Cr ranged from 19.9 - 111.9 $\mu\text{g/g}$ and Ga 153.1 - 3762.2 $\mu\text{g/g}$ in TSS and the highest concentration acquired in Table 2 was KR 1, which is located at the end of downstream. Similarly, readings in Table 2 also show a slight increase towards downstream from 38.4% to 40%, located at station KR 1 to KR 12. The mean concentration for downstream stations of Cr was $58.2 \pm 4.4 \mu\text{g/g}$ and Ga $1307 \pm 72.5 \mu\text{g/g}$ in TSS which were also higher compared to the upstream stations. The mean concentration of station K24 until station K28 suggests that it is a location where trace elements are buried and acts as a bio filter before flowing towards the coast (Teuchies et al. 2013). The abundance of Ga in suspended solid, averaging 910.14 $\mu\text{g/g}$ which is 20 times higher than Cr, averaging at 42.4 $\mu\text{g/g}$ in Sungai Kelantan may due to particle reactivity in which Ga was less readily scavenged and had multiple sources either from atmospheric or terrestrial inputs (Orians & Bruland 1988). Other events such as absorption of particulates during mobilization and resuspension from surface sediment may cause the

sudden increase of Ga in the TSS (Table 2). In any drainage basins, the surficial sediment would become a significant point for increment of metal loading in the water column which generally, recycles the metal content in the sediment through porous media (Matisoff et al. 2017). On the other hand, presence of diffusion acting onto surface sediment may increase the overall metal loading in the water column, thus increasing the Ga concentration where diffusion always accommodates the porous media of sediment which becomes more dominant for the sudden increment of metal concentration in the water column (Bucur et al. 2006). In the meantime, the continuous sedimentation and re-suspension of these fine sediment particles along the river channel might lead to the homogenous pattern in pollutant loadings of total suspended solids along the river (Allen et al. 2017).

The concentrations of both elements in surface sediment ranged from 16.8 - 172.9 $\mu\text{g/g}$ and 25.2 - 82.0 $\mu\text{g/g}$ for Cr and Ga, respectively. The highest concentration recorded was at KR5, for both Ga ($82 \pm 2.4 \mu\text{g/g}$) and Cr ($172.9 \pm 7 \mu\text{g/g}$). Similarly, to TSS, both element concentrations increased downstream. To be precise, the

TABLE 1. Sampling stations of Sungai Kelantan

Station	Date	Latitude (°N)	Longitude (°E)	Temperature (°C)	Salinity (psu)
KR 01	11-Oct-16	06° 13' 00.3	102° 14' 13.9	27.0	1.08
KR 02	11-Oct-16	06° 12' 51.7	102° 13' 98.8	29.1	2.17
KR 03	11-Oct-16	06° 11' 44.5	102° 13' 95.4	29.1	1.60
KR 04	11-Oct-16	06° 10' 75.1	102° 14' 84.4	29.1	0.17
KR 05	11-Oct-16	06° 09' 60.5	102° 14' 07.3	29.6	0.09
KR 06	11-Oct-16	06° 08' 33.8	102° 13' 97.6	28.7	0.06
KR 07	11-Oct-16	06° 07' 04.1	102° 13' 73.7	28.9	0.03
KR 08	11-Oct-16	06° 06' 03.7	102° 13' 18.4	28.7	0.03
KR 09	11-Oct-16	06° 04' 37.5	102° 13' 38.8	29.0	0.03
KR 10	11-Oct-16	06° 03' 34.6	102° 12' 65.4	28.8	0.03
KR 11	11-Oct-16	06° 02' 57.8	102° 11' 77.9	29.0	0.03
KR 12	11-Oct-16	06° 02' 51.1	102° 11' 43.4	29.1	0.03
KR 13	11-Oct-16	06° 01' 89.9	102° 08' 79.4	29.1	0.02
KR 14	12-Oct-16	06° 01' 48.4	102° 09' 52.7	28.8	0.03
KR 15	12-Oct-16	06° 00' 53.5	102° 11' 02.8	28.7	0.03
KR 16	12-Oct-16	05° 57' 25.2	102° 12' 41.8	29.1	0.03
KR 17	12-Oct-16	05° 54' 97.2	102° 11' 85.0	29.2	0.03
KR 18	12-Oct-16	05° 53' 17.7	102° 11' 01.7	29.3	0.03
KR 19	12-Oct-16	05° 52' 04.8	102° 10' 70.8	29.3	0.02
KR 20	12-Oct-16	05° 50' 43.3	102° 10' 77.6	29.3	0.03
KR 21	12-Oct-16	05° 47' 71.5	102° 10' 13.9	29.5	0.03
KR 22	12-Oct-16	05° 46' 64.1	102° 09' 03.9	31.4	0.03
KR 23	12-Oct-16	05° 42' 16.6	102° 08' 94.2	30.3	0.03
KR 24	12-Oct-16	05° 39' 64.2	102° 06' 46.7	30.7	0.03
KR 25	12-Oct-16	05° 36' 93.2	102° 08' 31.1	31.0	0.03
KR 26	12-Oct-16	05° 33' 39.7	102° 10' 27.7	30.7	0.03
KR 27	12-Oct-16	05° 32' 25.4	102° 10' 83.6	30.7	0.03
KR 28	12-Oct-16	05° 32' 06.3	102° 11' 72.5	30.6	0.03

average concentration of Cr in downstream stations, KR 1 until KR 12 was 84.2 ± 2.2 $\mu\text{g/g}$, while in upstream it was 46 ± 1 $\mu\text{g/g}$. In addition, the average concentration of Ga in downstream station KR 1 until KR 12 was 42.7 ± 0.9 $\mu\text{g/g}$ while in upstream was 33.3 ± 0.7 $\mu\text{g/g}$. The concentrations of Cr and Ga found in surface sediment of Sungai Kelantan was portrayed into the fine sediment, where the high surface area/volume ratio increases the potential to bind more heavy metals on its surface (Wang et al. 2017). This effect will increase the overall concentrations of both elements (Table 2). In addition, the redox reaction in sediments will dilute the Cr and Ga concentration onto the surface sediment/water interface which may lead to bioaccumulation over time (Eneji et al. 2011). The estuarine area which is located adjacent to the coast acts as an active filter from river input to the oceans, thus subsequently increasing the heavy metal contents in the surface sediments (Dürr et al. 2011). However, the low mobility of Cr, the dissolution from TSS and resuspension from surface sediments may increase the concentration of Cr more than Ga. Furthermore, the diffusion from the water column towards surface sediment due to the presence of dissolved particulate Cr may increase the total

concentration of Cr in surficial sediment (Homoky et al. 2016). On the other hand, chromium is easily scavenged under several water column cycles and introduces new chromium as shown in Figure 3(b). The less populated Cr within suspended particles also showed that the migration of Cr was not towards the suspended solids, rather than the origin of the heavily dense Cr in the surface sediments (Młynarczyk et al. 2006).

The concentrations of TSS in the water column along Sungai Kelantan increased from 14.0% at upstream to 38.3% at downstream with ranging from 68.8 - 571.8 mg/L. During this study the contents of TSS in Sungai Kelantan (266.73 mg/L) was generally exceeding the maximum threshold limit (150 mg/L) of Malaysia Water Quality Standard (Al-Badaii et al. 2013). The possible reasons for this are due to active logging in the upstream region and many legal or illegal sand mining operations along the riverbank. In addition, most sewage discharged into the river are untreated (Hashim et al. 2014; Sheikhy Narany et al. 2017). The TSS contents in Sungai Kelantan was higher than some industrialized rivers such as Tigris River (average = 46.48 mg/L), Mankyung River (average = 14.08 mg/L) and deforested river such as Mekong River (average = 45

TABLE 2. Concentrations of gallium and chromium in the total suspended solid and surface sediment

Distance from estuary	Station No (KR)	TSS (mg/L)	Ga in sediment ($\mu\text{g/g}$)	Cr in sediment ($\mu\text{g/g}$)	Cr in TSS ($\mu\text{g/g}$)	Ga in TSS ($\mu\text{g/g}$)
0-20 km	1	68.8	42.13 \pm 0.92	74.19 \pm 1.82	111.95 \pm 4.40	3762.23 \pm 94.89
	2	77.2	44.41 \pm 0.85	91.72 \pm 2.24	106.42 \pm 6.29	3433.44 \pm 145.26
	3	178.6	44.94 \pm 0.65	94.34 \pm 3.13	73.88 \pm 6.28	1096.61 \pm 7.28
	4	215.6	40.80 \pm 0.46	91.07 \pm 2.24	69.95 \pm 3.88	910.54 \pm 24.10
	5	243.6	82.05 \pm 2.49	172.96 \pm 7.06	61.37 \pm 7.15	1241.19 \pm 114.56
	6	263.8	41.04 \pm 1.01	84.88 \pm 0.93	52.59 \pm 6.14	832.72 \pm 66.44
	7	298.8	33.34 \pm 0.87	71.39 \pm 2.22	43.85 \pm 4.92	743.50 \pm 101.42
	8	305	35.38 \pm 0.35	78.38 \pm 1.82	39.08 \pm 4.33	743.03 \pm 16.14
	9	313.4	35.58 \pm 0.78	76.78 \pm 1.24	35.54 \pm 1.88	769.58 \pm 115.76
	10	285.2	34.59 \pm 1.01	63.22 \pm 1.69	39.00 \pm 3.85	978.31 \pm 57.35
	11	330.2	35.35 \pm 0.82	57.95 \pm 0.95	31.81 \pm 3.91	676.86 \pm 7.43
	12	286.8	43.01 \pm 0.91	53.80 \pm 1.65	33.75 \pm 0.25	501.70 \pm 120.49
20-40 km	13	400	30.09 \pm 0.72	41.28 \pm 0.63	28.47 \pm 1.10	261.10 \pm 130.40
	14	282	32.15 \pm 0.63	63.18 \pm 1.27	28.18 \pm 2.01	370.96 \pm 7.28
	15	384.4	33.11 \pm 0.72	60.89 \pm 2.11	22.02 \pm 4.54	513.35 \pm 40.24
	16	351.8	34.29 \pm 1.26	63.40 \pm 3.20	29.43 \pm 2.57	338.92 \pm 32.13
	17	279	33.20 \pm 0.81	58.40 \pm 2.54	31.29 \pm 1.92	697.84 \pm 134.83
	18	248	29.01 \pm 0.47	61.48 \pm 1.09	32.95 \pm 1.70	476.02 \pm 93.39
40-60 km	19	571.8	40.82 \pm 0.64	21.58 \pm 0.95	19.99 \pm 3.00	153.16 \pm 92.11
	20	498.4	29.04 \pm 0.25	54.18 \pm 1.09	22.07 \pm 1.04	171.43 \pm 25.60
	21	240	25.27 \pm 0.44	41.49 \pm 1.33	25.52 \pm 5.97	459.81 \pm 5.86
	22	105.2	35.29 \pm 0.81	31.57 \pm 0.92	49.77 \pm 1.84	1956.59 \pm 108.93
	23	192.2	27.54 \pm 0.49	49.18 \pm 0.53	32.52 \pm 4.03	631.95 \pm 31.15
60-80 km	24	163.6	39.91 \pm 0.90	16.80 \pm 0.46	33.39 \pm 1.53	731.90 \pm 136.93
	25	308	32.03 \pm 0.79	57.99 \pm 0.91	28.28 \pm 2.82	388.43 \pm 103.67
	26	347.2	31.58 \pm 0.56	53.67 \pm 0.76	26.68 \pm 1.76	331.39 \pm 13.44
	27	110	30.85 \pm 0.81	55.26 \pm 1.46	36.40 \pm 0.63	1122.54 \pm 70.94
	28	120	32.57 \pm 0.56	46.40 \pm 1.83	42.00 \pm 1.26	1188.77 \pm 19.67

mg/L) and Sibuti River (average = 0.11 mg/L) (Gandaseca et al. 2011; Kim et al. 2009; Prathumratana et al. 2008; Varol et al. 2012). Due to constant anthropogenic inputs (i.e. sand mining and logging activities) and continuous mobilization or dispersion by monsoonal seasons (Ansari et al. 2000), the fluctuating pattern of suspended solid along Sungai Kelantan was prominent (Table 2).

Concentrations of Cr in surface sediment was 1.7 times higher than the Ga obtained from Sungai Kelantan during this cruise. These values are similar as those reported in Tsurumi River, Japan (57.93-279.63 µg/g), Sakarya River, Turkey (29.7-252.7 µg/g) and Dunajec River, Poland (10 - 1600 µg/g) (Dundar & Altundag 2018; Mohiuddin et al. 2010; Pawlikowski et al. 2006). However, the Nile River, Egypt reported a high concentration of Cr in sediment during March 1987 ranging from 169 - 5618 µg/g compared with Sungai Kelantan (Elsokkary & Muller 1990). The researcher claimed that the high concentration in Egypt is due to washout during the flooding season, discharge from industrial effluent and agricultural wastewater into the Nile River. However, studies on Ga in TSS are limited considering Ga is a trace metal component and has higher affinity towards aluminium (Al), creating preferences of Al over Ga. In addition, most of the reports regarding Ga in rivers were related to gallium arsenide (GaAs) which is related to the production of photovoltaic cells and semiconductors (Sturgill et al. 2000; Yang & Chen 2003). Furthermore, the source of gallium and chromium in this study was due to anthropogenic inputs and subsequently the rainfall event affected the concentration level of both studied elements in Sungai Kelantan. Reports from similar events show that monsoon-dominated areas are vigorous in leaching the anthropogenic elements in the water column and active riverbed. This hastens the transport process which is sourced from the runoff and terrestrial area thus increasing the heavy metal concentrations (Manjunatha et al. 2001). In addition, the post monsoonal season increases the erosion and weathering of igneous rocks and sedimentary layers while introduction of

anthropogenic inputs that are easily absorbed and become reducible phases into the water column elevates the total concentration of heavy metals during mobilization (Alagarsamy 2006). At the same time, the high pressure within the northern hemisphere due to the cold surge becomes a prominent factor for the increment in rainfall as the intense cold dry air blows out from the continent and absorbs water vapour while it crosses the Pacific Ocean and South China Sea bringing a large amount of moisture by winds. Furthermore, Wardah et al. (2011) suggested that Sungai Kelantan receives moderate rainfall, reaching 35 mm/h along the riverine area and bearing high pressure in the region, thus affecting the mobilization bonding TSS with gallium and chromium towards the offshore region (Figure 2).

Runoff from sand mining activities and land reclamation along Sungai Kelantan may have entered the river and an increment in both elements may suggest that they are active in physical process especially during the rainfall season (Figure 2). High mobility of gallium ions (Ga^{3+}) was present during the weathering process, while immobile chromium ions (Cr^{3+}) which formed under several minerals e.g., $FeCr_2O_4$, $PbCrO_4$ and $Ga(OH)_3$ (Bénézeth 1994; Koleli & Demir 2016) were readily available to replace Fe and Mg into igneous rocks during erosion. In the meantime, gallium is capable of camouflaging as aluminium (Al) where similarities lie in ionic radius in the mica, feldspar and amphibole thus become a dominant host of metamorphic rocks, similar to Al which formed under $CuGaS_2$ and $Ga(OH)_3$ minerals. Previous studies in Sungai Kelantan shows that land degradation and deforestation resulted in serious weathering of soils and rock sourced from the nearby mountainous region which affected the concentration of heavy metals and suspended solids along the river (Shaari et al. 2015; Wang et al. 2017). Another major river such as Yangtze River showed the sediment accumulation from various sized catchment areas dissolved the terrestrial input onto surface sediments under various process (i.e. absorption and coagulation). Terrestrial runoff

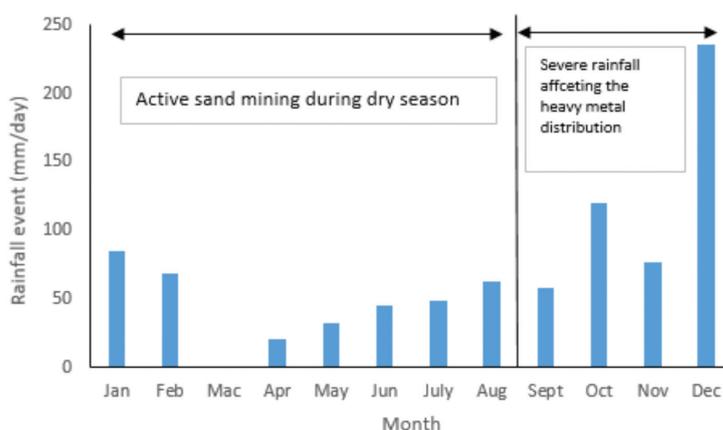


FIGURE 2. Annual frequency distribution of rainfall event in mm/h at Sungai Kelantan

Data from: Kota Bharu Monthly Climate Averages (2019)

which contained trace elements (Ga and Cr) were mainly absorbed by the variety of minerals and oxides and was significantly constrained by grain size (Ip et al. 2007; Liu & Fan 2011; Yuan et al. 2014).

DISTRIBUTION OF CHROMIUM AND GALLIUM IN TOTAL SUSPENDED SOLID AND SURFACE SEDIMENT

The distribution of both elements along Sungai Kelantan fluctuated in suspended solids and surface sediments with both elements potentially attaching to suspended solids in the water column and moved towards the estuary where high increment was shown in the estuary stations, KR1 and KR2 (Table 2). Pearson correlation tests show Cr ($r = -0.659$, $p = 0.000$) and Ga ($r = -0.716$, $p = 0.000$) with respect to TSS shows that suspended particles were encumbered with heavy metals due to anthropogenic input thus TSS was unable to facilitate a particulate transport in the river (Schwientek et al. 2013) (Table 3). In addition, the sudden increment of gallium in TSS and afterwards the sudden rise of TSS content for following stations of KR21, KR20 and KR19 were due to active sand mining operations at the upper stream e.g. at station KR22. The mobilized TSS from the upper stream stations were dispersed through Sungai Kelantan, which made the Ga and Cr concentrations fluctuate along the channel. Furthermore, stronger negative correlation of Ga content in TSS ($r = -0.716$, $p = 0.000$) with the amount of TSS would suggest that direct inputs

from precipitation may increase the concentration of Ga in suspended solids (Wardah et al. 2011). That means that heavy rainfall will influence the erosion rates occurring along river thus increasing the output of gallium and chromium into Sungai Kelantan, which will eventually increase the gallium concentration in TSS by more than 20 times (Suhaila et al. 2010). In addition, the positive correlation of Cr in TSS versus Ga in sediment ($r = 0.463$, $p = 0.013$) and Cr in sediment ($r = 0.507$, $p = 0.006$), suggests that the resuspension of sediment may increase the concentration of Cr in TSS whereby the scavenging of metal components by TSS occurred during active mixing whilst being mobilized towards the estuary.

The distribution of Cr was more dominant than Ga in surface sediment which became a fluctuated distribution at all stations except station KR5 (Figure 3(b)). Through statistical analysis, both Ga in sediment and Cr in sediment ($r = -0.0767$, $p = 0.000$) may come from similar anthropogenic sources which were scavenged by the suspended matter or deposition onto surface sediment. The highest reading found at station KR5 was due to anthropogenic input (i.e. sand dredging and land reclamation) being flushed in the aquatic system, which consecutively, given that Cr^{3+} was far better at sorption and bioavailability in surface sediment increased the concentration at that particular station (Yen & Rohasliney 2013). In addition, the urbanization due to growth in

TABLE 3. Correlation between several variables in Sungai Kelantan

Parameter	Testing	Correlations				Contents of TSS	Distance from estuary
		Ga in sediment	Cr in sediment	Ga in TSS	Cr in TSS		
Ga in sediment	Pearson Correlation	1	.767**	.314	.463*	-.150	-.455*
	Sig. (2-tailed)		.000	.104	.013	.447	.015
	N	28	28	28	28	28	28
Cr in sediment	Pearson Correlation	.767**	1	.285	.507**	-.186	-.600**
	Sig. (2-tailed)	.000		.142	.006	.343	.001
	N	28	28	28	28	28	28
Ga in TSS	Pearson Correlation	.314	.285	1	.906**	-.716**	-.334
	Sig. (2-tailed)	.104	.142		.000	.000	.083
	N	28	28	28	28	28	28
Cr in TSS	Pearson Correlation	.463*	.507**	.906**	1	-.659**	-.542**
	Sig. (2-tailed)	.013	.006	.000		.000	.003
	N	28	28	28	28	28	28
TSS	Pearson Correlation	-.150	-.186	-.716**	-.659**	1	-.022
	Sig. (2-tailed)	.447	.343	.000	.000		.910
	N	28	28	28	28	28	28
Dist. from estuary	Pearson Correlation	-.455*	-.600**	-.334	-.542**	-.022	1
	Sig. (2-tailed)	.015	.001	.083	.003	.910	
	N	28	28	28	28	28	28

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

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

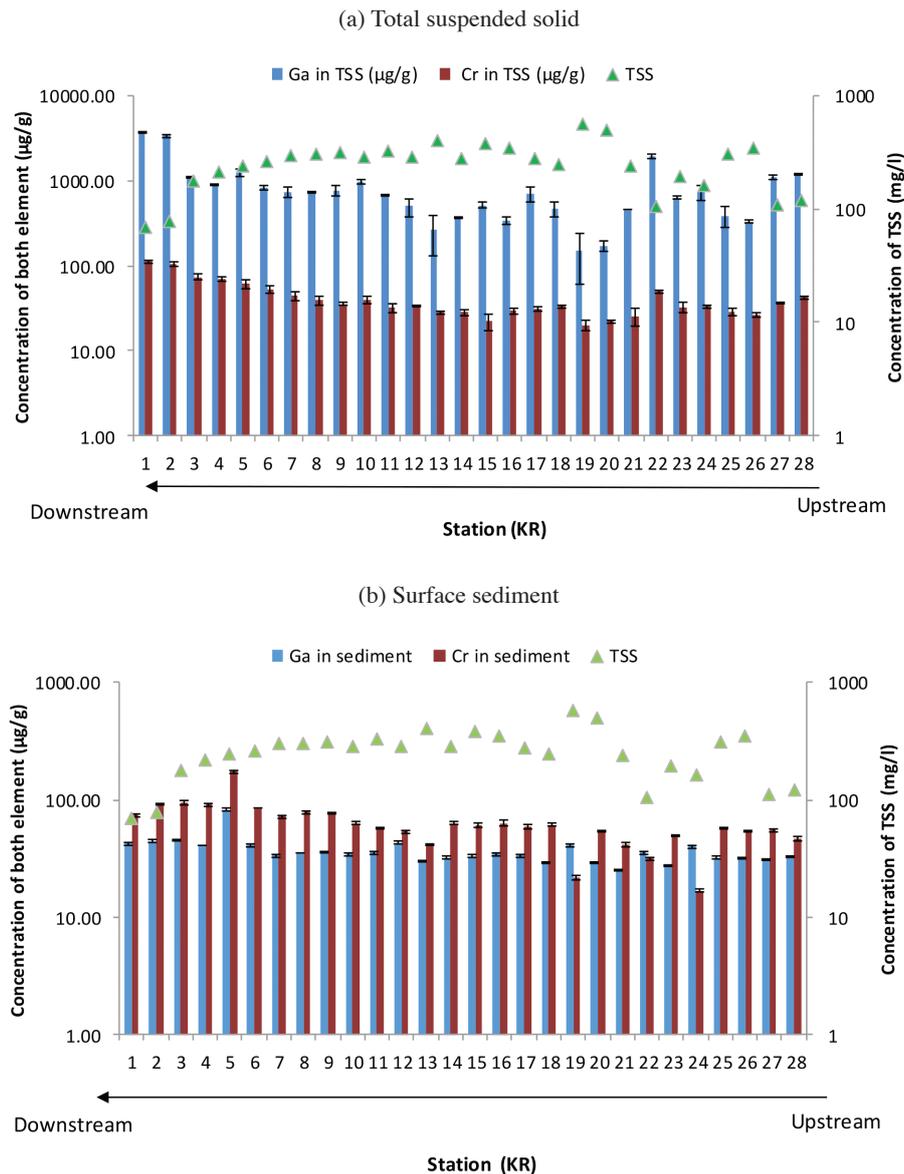


FIGURE 3. Distribution of gallium and chromium in various stations

Note: in log (10) scale

population may lead to increment in land usage, thus subsequently leading to higher pollutant concentration. A previous study on Sungai Kelantan showed high pollutant load prior to monsoon and post monsoon which was consistent with land usage along Sungai Kelantan, while high value of pollutants were recorded in urbanized areas due to large runoff events in some areas (Abdulkareem et al. 2018).

The negative statistical correlation between contents of both elements in sediment and TSS with the distance from the estuary (Table 3) indicating the dilution process of both elements in sediment and TSS occurred during travelling from upstream to the estuary area (Furness 2018). In addition, the resuspension and diffusion of TSS onto the surface sediment and the deposition onto the active riverbed of sediment may have increased the overall

concentration along Sungai Kelantan ($r = 0.507$ $p = 0.006$), this is significant as the physical processes occurring in the water column acted directly onto the surface sediment. Furthermore, distance covered by Cr content in TSS decreased ($r = -0.542$ $p = 0.003$) due to the active scavenging by the particulate matter for deposition, thus increasing the concentrations at all stations.

Although the overall distribution of Ga is much lower than Cr, statistical analysis may decrypt the status behind the Ga distribution. For both metals, the Ga and Cr concentration in sediment was significant ($r = 0.767$ $p = 0.000$), which would indicate the burial in the active riverbed sediment was almost similar as the concentration in the riverbed sediment. Through deposition onto surface sediment, the Ga concentration in sediment was not related to TSS which suggests that several sources (runoff, erosion,

precipitation or through active resuspension) occurred in water column (Shiller & Bairamadgi 2006; Yuan et al. 2018). In contrast, the Cr in TSS may contribute to the scavenging onto particulate matter due to metal bonding between Ga and Cr, thus contributing to the deposition of Ga in the riverbed sediment. Similar to Cr in sediment, Ga dilution acting onto sediment ($r = -0.455$, $p = 0.015$) occurred along the river system which diluted the metal concentration as more distance was covered but comparing to the Cr in sediment ($r = -0.600$, $p = 0.001$), Ga was much weaker in comparison due to terrestrial input which was dominant in Sungai Kelantan.

CONCLUSION

Concentrations of Ga and Cr were found to fluctuate along Sungai Kelantan. Sand mining, land reclamation and rainfall events were major factors controlling the concentrations of both elements. Distribution of Ga and Cr was influenced by the presence of physical process which acted on surface sediment or within the water column. Lastly, the chemical properties of Ga and Cr being easily reducible may have caused the fluctuations at all stations.

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