Nickel and Chrome Pollution Identification in the Coastal Area of Kulon Progo, Yogyakarta

Identifikasi Polusi Nikel dan Kromium pada Wilayah Pantai di Kulon Progo, Yogyakarta

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ABSTRACT

Kulon Progo is located in the southern part of Yogyakarta Special Province, Indonesia. The regency is famous of some tourist beach points. This study discusses the composition of beach sand samples in three coastal areas in Kulon Progo: Karangwuni, Glagah, and Congot in relation to environmental issues. Seven samples of four locations were megascopically described and analyzed using XRF and ICP-MS for geochemistry contents. Four of samples are beach sands from the surface whilst the others were collected from about 50 cm below surface. Box plots show maximum Cr outlier and minimum most of REE outliers in the group of beach sand samples. Nickel and chrome tenor anomalies were detected in samples from the coastline of Karangwuni and Glagah. On the other hand, neither Ni and Cr anomalies were identified in the two samples 200 m from the seashore of Karangwuni nor the two samples near Congot seashore. In the polluted location, the two heavy metals are relatively concentrated in the surface. Two volcanic rock samples from the andesite domain are selected to trace the origin of the heavy metals. The wastes of base metal mining in northern Kulon Progo together with urban activities and several industries in Wates were then transported through the Serang River to Indian Ocean. Tidal currents help the heavy metals to be deposited in the coastal areas near the mouth of Serang River. This study also concluded that people gold mining activity in Sangon is not the source of Ni and Cr pollution to the coast of Kulon Progo.

Keyword: geochemistry, beach sand, Kulon Progo, heavy metal pollution.

ABSTRAK

Kulon Progo berlokasi di bagian selatan Provinsi Daerah Istimewa Jakarta, Indonesia. Kabupaten ini terkenal dengan beberapa lokasi wisata pantai. Studi ini membahas mengenai komposisi pasir pantai pada tiga lokasi pantai di Kulon Progo: Karangwuni, Glagah, dan Congot terkait dengan masalah lingkungan. Tujuh percontoh dari empat lokasi penelitian telah dideskripsikan secara megaskopis dan dianalisis kandungan geokimianya menggunakan XRF dan ICP-MS. Empat percontoh merupakan pasir pantai yang berasal dari permukaan sedangkan percontoh lain berasal dari substansi 50 cm di bawah permukaan. Box plot dengan jelas menunjukkan keberadaan maximum outlier pada Cr dan minimum outlier pada banyak elemen REE pada kelompok percontoh pasir pantai. Anomali tinggi nikel dan krom terdeteksi pada seluruh percontoh yang berada dekat tepi pantai di Karangwuni dan Glagah. Namun demikian, tidak terdapat anomali Ni dan Cr pada dua percontoh yang berasal dari area 200 m sebelum tepi Pantai Karangwuni maupun dua percontoh dari Pantai Congot. Pada titik yang tercemar polusi, dua logam berat ini lebih terkonsentrasi

pada bagian permukaan. Dua batuan vulkanik dari wilayah andesit dipilih dalam menelusuri asal-muasal logam berat tersebut. Sampah sisa penambangan logam dasar bersama dengan aktivitas perkotaan dan industri di Kulon Progo telah terbawa oleh aliran Sungai Serang menuju Samudra Hindia. Arus bolak-balik air laut membantu logam berat tersebut terendapkan di wilayah pantai dekat muara Sungai Serang. Studi ini juga menyimpulkan bahwa penambangan emas rakyat di Sangon bukanlah sumber pencemaran Ni dan Cr di tepi pantai Kulon Progo

Kata kunci: geokimia, pasir pantai, Kulon Progo, polusi logam berat

INTRODUCTION

Process operating in three majors of natural system at the earth surface, namely atmosphere, ocean, and land surface are responsible for shaping the coastal zone. The zone is extremely dynamic, because the interaction between the three different sets of processes makes the coastal zone as a zone of transfer of material from the land surface to the ocean system, with sediments eroded by rivers and/or glaciers and moved to the beach and near shore. In some areas accumulation of sediments may add to the land mass (Davidson-Arnott, 2010). The coastal zone is subject to the constant change: minute by minute as waves break and currents move alongshore; daily with high and low tides; monthly with tidal cycles; yearly with seasonal changes in the wave approach and storm energy; and over the longer term with changes of climate and sea level (Bush and Young, 2009). A large proportion of the world population is concentrated in the coastal zone, including almost all of major cities. Many of human activities pose an environmental threat to coastal systems, both physical and biological, through pollution, siltation, dredging, infilling, and a host of other activities that alter the way natural systems operate. Ensuing global climate change that will have a far reaching impact on the coastal belt is also influenced by anthropological activities (Chattopadhyay, 2010).

The information of physiochemical and ecological settings of natural environments and changes caused to them by earth processes and anthropogenic activities are provided in quaternary and recent sediment characters in near shores and rivers (Al-Juboury, 2009). The sediments are considered as important indicators for the rate of pollution in aquatic environments: rivers, seas and oceans (Nasr *et al.*, 2006). Baseline levels against current conditions are probably to establish to investigate a possibility of pollution. Heavy metals, such as cadmium, mercury, lead, copper, zinc, nickel, and chrome are regarded as serious pollutants of aquatic ecosystem because of their environmental persistence, toxicity, and ability to incorporate

into food chains (Kishe-Machumu and Machiwa, 2003). Moreover, various activities within urban environment are often vastly accelerated, inevitably rendering the urban environment particularly susceptible to environmental degradation and contamination (Wong *et al.*, 2006). Kulon Progo is a coastal regency in Yogyakarta Special Province on Java Island. Wates is the capital of Kulon Progo Regency and is classified as an urban area with various industries which may influence the coastal environments.

The objective of this study is to measure the composition of seven selected beach sand samples in correlation to environmental aspects in Kulon Progo. The box plot method is applied to identify any extreme values. Two volcanic rocks from the andesite domain were selected to estimate natural and anthropogenic influences of Ni-Cr composition in the selected beach sand samples.

Regional Geology

The studied area is in the coastal area of Kulon Progo Regency on the southern part at the Yogyakarta Quadrangle (Rahardjo *et al.*, 2012). Kulon Progo comprises four sedimentary formations which from the oldest to the youngest are the Nanggulan, Kebobutak, Jonggrangan, and Sentolo Formations. The Early Miocene to Pliocene Sentolo Formation consists of conglomerate overlain by tuffs in the upper part base of the formation. Conglomerate, tuffaceous marl, calcareous sandstone, limestone, and corraline limestone built the Jonggrangan Formation in Lower Miocene that interfingered with the lower part of the Sentolo Formation. Kebobutak Formation is the other name of van Bemmelen Old Andesite Formation and surrounds the intrusive andesite unit. The Kebobutak Formation is composed successively of conglomerate, sandstone, tuffaceous shale, and silt which is Late Oligocene - Lower Miocene in age, and sedimented over the Nanggulan Formation. The Nanggulan Formation, the oldest rock

formation in Kulon Progo, consists of sandstone with intercalation of lignite, sandy marl, claystone with limonite concretion, sandstone, and tuff. Nanggulan Formation was assigned to be deposited at Eosen to Early Oligocene using planktonic foraminifera test (Harjanto, 2011).

Kulon Progo experienced two phases of tectonic activities in minimum. The Kebobutak Formation was uplifted in Late Oligocene to Lower Miocene on the peak tectonic activity in Mid-Java. Southwest-northeast and north-south cross-section produced horizontal faults, foldings, and fractures in Kebobutak Formation and filled with andesite, dacite, and quartz veins. The next tectonic activity occurred in Late Miocene to Quaternary era which reoriented the north-south force to northeast-

southwest. Faultings, brecciations, and fracture formations were dominant in the second tectonic activity (Harjanto, 2011 after Soeria-Atmadja *et al.*, 1994). Andesite was emplaced earlier and was intruded by dacite in Miocene (Rahardjo *et al.*, 2012). Young volcanic deposits of Merapi Volcano, collovium and alluvium are the three nearest Quaternary units. Tectonic intensity of Kulon Progo region may be measured upon the morphometry on its Quaternary deposit development as recent sedimentary process. The studied area is located in the domain of alluvium in the Yogyakarta Quadrangle (Rahardjo *et al.*, 2012) which is built of gravel, sand, silt, and clay along coastal plain. Geological map around coastal area of Kulon Progo and sampling locations are shown in Figure 1.

Figure 1. Geological map of researched area. Four sampling points were located in the south coast of Kulon Progo, while two andesites were situated around Gunung Ijo (modified from Rahardjo *et al.*, 2012)

DATA AND DESCRIPTION

Seven beach sands (GPJ 36, GPJ 37, GPJ 38, GPJ 39, GPJ 40, GPJ 42, and GPJ 43) were obtained from three coastal areas in Kulonprogo, namely Karangwuni (2 locations, 4 samples), Glagah (1 location, 1 sample), and Congot (1 location, 2 samples). GPJ 36 and GPJ 37 were attained about 200 m before the seashore of Karangwuni in location 1, whilst GPJ 38 and GPJ 39 were taken just near the seashore of the beach in location 2. GPJ 36 and GPJ 38 were taken from surface, whilst GPJ 37 and GPJ 39 are subsurface samples approximately 50 cm below the surface. GPJ 40 is the surface beach sand from Glagah, about 2,5 km northwest of location 2. The other two coastal samples were gained in Congot and located approximately 2,5 km from location 3, that are GPJ 42 (surface) and GPJ 43 (subsurface). The three coastal areas, especially Glagah, are tourist sites and are normally crowded during holidays. Studied samples were taken such far away from the tourist sites to minimize anthropogenic contamination in relation to tourist waste as shown in Figure 2a. Two rocks of the andesite unit (RK 22 and RK 68), about 10 km from the coast of Kulon Progo, were added to investigate anthropogenic impacts of heavy metals anomaly in the three coastal areas. RK 22 is greyish, porphyritic, medium grained plus phenocryst andesitic rock in Ngaseman Village, while RK 68 is volcanic samples on the edge of Bendungan River with high counts of mafic minerals megascopically. Sampling locations are shown in Figure 1.

Before instrument measurements, samples were washed and dried outdoor for one day minimum. Whole samples were then crushed with jaw crusher and were grounded using a ball mill to gain particle size of ~200 mesh. Basically, there are two main sample preparation techniques for measurement of sample powders with XRF, namely, pressed pellets and fused beads. The first technique was applied in this study because it keeps sample homogenous, minimizes cross contamination, reduces the sample size, and has high sensitivity although the accuracy is not as good as fused beads. Pressed pellets are prepared by pressing loose sample powders filled in a ring or cup using a set of dies and a press machine. The ease of pelletization depends on sample characteristics and grain size, and can be improved by sufficient pulverization (Takahashi, 2015). The pressed pellets were analyzed with the Advant XP x-ray fluorescence method (XRF) for major oxide measurement. Loss on Ignition (LOI) analysis is an important factor of geochemistry analysis as a simple method for estimating the content of organic matter and carbonate minerals.

REE content of the selected rock samples were analyzed using quadrupole X-Series Thermo Fisher Scientific's Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) as shown in Figure 2c. Nitric acid (ultra pure grade), formic acid (ultra pure grade), and perchloric acid (pro analysis grade) were the solvents in sample digestion. The digestion procedure was done carefully because incomplete dissolution of highly resistant minerals

Figure 2. a) Greyish andesite from Ngaseman Village (RK 22); and b) The X-Series Thermo Fisher Scientific's Inductively Coupled Plasma - Mass Spectrometry ICP-MS that was used in this study.

in rock samples may cause biased results for a number of trace and rare earth elements (Bayon *et al.*, 2009). Full suite of rare earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) and some other trace elements (Sc, Ni, Cr, V, Rb, Sr, Y, Ba, Zr, Nb, Th, and U) were analyzed. This study measured Ni and Cr contents in RK 22 and RK 68 which were not analyzed in the previous the study (Irzon, in prep²). The CPSs (counts per second) of one blank and six levels of calibration solutions (0.1, 1, 5, 10, 25, and 50 ppb)

were measured to produce the calibration curves of analyzed elements. Computer programme of the ICP-MS device transformed element CPS of samples to concentrations using the previous calibration curves. AGV-2 and GBW 7112 were the two certified reference materials used in this study to certify the quality of measurement results.

INTERPRETATION AND DISCUSSION

Box Plot of The Whole-rock Composition

Table 1. Composition of Selected Beach Sands in This Study Plus Two Volcanic Rocks from the Andesite
a) Domain: a) major oxides; b) trace elements; and c) rare earth elements

Sample	SiO ₂ (%)	TiO ₂	Al ₂ O ₃	Fe ₂ O _{3T}	MnO	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Total
GPJ 36	50.05	0.90	18.94	9.56	0.22	9.71	4.01	3.77	1.46	0.29	0.79	99.70
GPJ 37	48.16	1.07	16.16	12.64	0.25	10.19	4.97	3.71	1.22	0.32	1.10	99.79
GPJ 38												
GPJ 39												
GPJ 40												
GPJ 42	42.22	2.13	11.00	22.06	0.36	11.55	7.42	1.61	0.83	0.43	0.35	99.96
GPJ 43	38.99	2.69	10.84	26.13	0.38	10.36	6.96	1.90	0.77	0.38	0.57	99.97
RK 22	50.80	0.59	20.49	7.77	0.16	7.68	5.71	3.47	0.87	0.22	2.25	100.01
RK 68	47.15	1.00	22.30	9.48	0.17	10.39	2.94	2.96	0.72	0.10	2.79	100.00

b)

Sample	Sc (ppm)	V	Cr	Ni	Rb	Sr	Y	Zr	Nb	Ba	Th	U
GPJ 36	20.55	359.50	25.96	16.67	34.25	629.00	24.31	86.25	4.85	385.50	9.43	7.08
GPJ 37	24.14	466.90	32.31	21.89	29.76	527.30	26.06	79.34	4.58	531.80	6.52	3.85
GPJ 38	39.45	971.50	847.90	402.10	16.87	277.90	33.20	65.27	4.09	285.10	4.07	2.91
GPJ 39	16.23	357.40	210.90	265.00	7.48	99.00	11.69	27.74	1.87	183.60	2.11	1.78
GPJ 40	26.62	610.40	210.90	243.10	9.52	85.87	20.89	39.35	0.14	115.80	4.08	3.79
GPJ 42	36.83	860.70	38.93	21.27	20.24	311.40	31.71	73.88	2.32	337.00	5.00	3.20
GPJ 43	34.59	1070.00	58.81	30.73	17.95	268.90	28.41	65.29	3.40	255.60	3.02	1.57
RK 22	10.99	148.50	20.98	12.82	19.67	323.70	14.66	65.48	3.92	254.60	n.a.	n.a.
RK 68	18.74	254.80	34.85	19.77	11.47	329.90	16.79	58.03	2.45	226.90	n.a.	n.a.

c)

Sample	La (ppm)	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
GPJ 36	16.01	35.79	0.59	17.86	3.39	1.68	4.12	0.62	3.82	0.75	2.12	0.44	3.53	0.45
GPJ 37	14.77	29.31	0.15	17.26	3.09	1.58	4.00	0.60	3.74	0.76	2.13	0.45	2.83	0.42
GPJ 38	13.48	27.73	0.46	19.50	5.17	1.64	5.24	0.79	4.78	0.94	2.64	0.56	3.30	0.48
GPJ 39	7.81	10.09	0.04	7.35	0.20	0.83	1.27	0.40	2.56	0.51	1.44	0.29	1.87	0.28
GPJ 40	11.42	21.54	0.02	15.51	3.08	1.17	2.91	0.60	3.79	0.73	2.07	0.43	2.54	0.38
GPJ 42	13.73	27.37	0.30	19.61	4.81	1.68	4.81	0.78	4.73	0.92	2.61	0.54	3.38	0.50
GPJ 43	12.75	24.68	0.10	16.66	3.57	1.38	3.83	0.65	4.12	0.77	2.23	0.45	2.73	0.40
RK 22	13.27	23.13	n.a.	12.52	0.80	1.26	2.35	0.41	2.53	0.52	1.41	0.31	2.07	0.30
RK 68	9.94	15.05	n.a.	9.67	0.43	1.26	1.74	0.46	2.99	0.61	1.73	0.37	2.36	0.35

SiO_2 , Al_2O_3 , Fe_2O_{3T} , and CaO are the major oxides in the seven selected beach sand samples with average abundances of 49%, 17,5%, 11%, and 10% respectively. Three oxides are relatively minor which are TiO_2 (0.98% in average), P_2O_5 (0.31%), and MnO (0.23%). Fe_2O_{3T} and SiO_2 contents are relatively in broader range of 10 - 26% and 39 - 50% respectively in comparison to other oxides. Samples from Karangwuni are more silicic (49% of SiO_2 in average) than samples from Congot (40% SiO_2 in average). In contrast, Fe_2O_{3T} content in the beach sands from Congot is twice than samples from Karangwuni. Moreover, higher MgO composition in GPJ 42-GPJ 43 than GPJ 36-GPJ 37 confirms that there are more mafic character of beach sand in Congot as mafic rocks are typically contain more Fe and Mg (Rakovan, 2009; Irzon and Baharuddin, 2016). Elements composition of selected samples are displayed in Table 1

Geochemical data analysis for environmental problems with statistical tests based on assumptions of normality, independence, and identical distribution are rather tricky, because they may not

be warranted. A solution would be to use the box plot for the identification of extreme values (Reimann *et al.*, 2005). The box plot basically divides the ordered values of the data into four 'equal' parts (quartile group 1, 2, 3, and 4), by determining the median value (displayed as a line in the box), and then by doing the same for each of the halves. The central box contains approximately 50% of the data which is bounded by upper and lower quartiles. The 'inner fence' is defined as the box extended by 1.5 times the length of the box towards the maximum and the minimum. The upper and lower 'whiskers' are then drawn from each end of the box to the farthest observation inside the inner fence. Any values beyond these whiskers are defined as data outliers and marked by a special symbol. Maximum outlier is higher than the upper whisker whilst minimum outlier is smaller than the lower whisker. The box plot method is applied in this study to reveal any anomalies in selected samples as it is used in various environmental studies (*e.g.* Reimann *et al.*, 2005; Kelepertsis *et al.*, 2006; von Eynatten and Tolosana-Delgado, 2011). Typical model of box plot is drawn in Figure 3.

Figure 3. Typical of blockplot components which consists of: median, upper and lower quartiles in the box fence, upper wishker, and lower wishker. Any data that is plotted outside the wishkers is classified as minimum/maximum outliers

All selected beach sand samples are considered suitable to be united as Irzon (in-press) concluded that the andesite is the source rock of coastal sediments in Karangwuni, Glagah, and Congot. Geochemistry data of this study is segmented into four groups to simplify in understanding about element distribution. There are trace elements >100 ppm, trace elements <100 ppm, light rare earth elements (LREE), and heavy rare earth elements (HREE) (Figure 4). Vanadium is the most abundant trace element (610 ppm in average) which is followed by barium and zircon on the average of 285 ppm and 280 ppm respectively. The low Ba content in GPJ 40 (115 ppm) (Congot, location 4) is classified as minimum outlier (Figure 4a and 4b). The box plots of Cr and Ni are different from other trace elements which median of these heavy metals are very close to the bottom part of the inner fence. The lower whiskers on these two heavy metals are very narrow that indicate an anomaly. Cr composition in GPJ 38 (847 ppm) is detected as maximum outlier and much higher than the upper whisker, whilst the abundant Ni in the sample is

not considered as an extreme value. Even though the low contents of Ba in GPJ 40 (115 ppm) and Sc in GPJ 39 (16 ppm) are detected as minimum outliers; they are very closed to the low whisker and are not classified as anomalies.

Box plot denotes that cerium and neodymium are the major light rare earth elements with median value of 25 ppm and 16 ppm respectively while dysprosium content (3.93ppm) is the highest compared to other heavy rare earth elements (Figure 4c and 4d). Most of rare earth elements on the selected beach sands show minimum outlier except praseodymium, europium, and lutetium. Total rare earth elements content of subsurface sample in location 2 (near Karangwuni seashore, 35 ppm) is much lower than the REE median value from the studied beach sands (74 ppm). Total REE in surface samples are higher than that of subsurface samples in the two coast areas: Karangwuni and Congot as shown in Table 1. Nevertheless, REE comparison of surface to subsurface in Glagah cannot be discussed as there is no subsurface sample was analyzed in this study.

Figure 4. Box plots of the seven selected beach sands from the coast of Kulon Progo. (a) trace elements >100 ppm; (b) trace elements <100 ppm; (c) light rare earth elements (LREE); and (d) heavy rare earth elements (HREE).

Pollution Identification

Twelve trace elements plus full suite off REE content of surface to subsurface in three location were analyzed and may be compared from location 1, location 2, and location 4. However, subsurface beach sand from location 3 were not sampled in this study. The composition of Sr, Rb, Zr, Th, and U in the surface of the three coast locations are relatively more concentrated than the samples 50 cm below the surface, whilst other trace elements are without any similarities. Trace elements composition of GPJ 38-GPJ 39 (location 2) and GPJ 40 (location 3) is different with other samples. The three samples contain much higher Cr and Ni but lower Rb, Sr, Zr, and Ba than GPJ 36-GPJ 37 (location 1) and GPJ 42-GPJ 43 (location 4). Two rivers discharge to the south coast near the studied location in Yogyakarta, namely Bogowonto and Serang River (Rahardjo *et al.*, 2012, Figure 1). Bogowonto River feeds sediment to the beach in Congot (Location 4) whilst elemental composition of location 2 and location 3 are relatively controlled by the influence of sediments derived from Serang River. The difference on geochemistry content on coastal sediments is largely affected by dissimilar input from the flows (*i.e.* Kasper-Zubillaga *et al.*, 2007; Malick *et al.*, 2011; Armsrong-Altrin *et al.*, 2012). However, element composition of location 1 is considered not be influenced by the Serang River as it is situated far from the flow and approximately 200 m before the coast.

Wide differences in Cr and Ni contents are detected between the two samples far from seashore (location 1) to the other three samples from the coastline around the mouth of Serang River (location 2 and location 3). The average Ni concentration in the two samples 200 m before Karangwuni coast line (GPJ 36 and GPJ 37, location 1) is 19.28 ppm. In contrast, Ni are much more abundant in the seashore samples, there is 333 ppm in average of GPJ 38 and GPJ 39 (Karangwuni Coast) and 210 ppm in GPJ 40 (Glagah Coast) even though location 2 and location 3 are separated within 2.5 km. The same contradiction is shown in Cr composition comparison between before seashore group to coast line group in ratio of 29:646 ppm. On the other hand, before seashore group contains much higher Sr (277 ppm in average) than the other group (154 ppm in average). Cr, Ni, and V are relatively more concentrated in subsurface relative to the surface at location 2 and location 4. Conversely,

GPJ 38 contains more Cr, Ni, and V than GPJ 39 of location 1. This higher concentration of Cr, Ni, and V in the surface sample than sample from 50 cm below the surface reflecting anomalous enrichment at Karangwuni Beach as these elements and Fe generally increase with depth (Kribek *et al.*, 2010).

Anthropogenic pollutants discharged from industrial, domestic and agricultural wastewater. The wastes then can become river-transported metal pollutions (Angelidis and Aloupi, 2000). Sediment served as sinks for most of the metals in aqueous phase and monitoring of the sediment with the determination of heavy metals is fundamental to the realization of pollutants (Al-Juboury, 2009; Ho *et al.*, 2010). The high contents of Ni and Cr in the seashore samples around the mouth of Serang River is a strong pollution indication. This is because the two elements are normally associated with the presence of ultramafic rocks (Angelidis and Aloupi, 2000) whilst there is no ultramafic rock is detected around Kulon Progo and even in Yogyakarta Quadrangle (Rahardjo *et al.*, 2012). Ni and Cr concentrations in GPJ 38, GPJ 39, and GPJ 40 are much bigger than Taylor and McLennan upper continental crust and average continent crust of 44-105 and 85-185 ppm, respectively (after Ho *et al.*, 2000) to confirm that the heavy metals were not present naturally.

Irzon (in prep²) stated that the andesite is most possibly the source rock of coastal sediment of Kulon Progo based on chemical index of alteration (CIA) value, major oxides ratios ($\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$, and $\text{Al}_2\text{O}_3/\text{TiO}_2$), REE spider diagram, and correlation coefficient calculation. In order to investigate Ni and Cr composition in the andesite, two most mafic samples of previous study (Irzon, in prep¹) were selected as secondary data: RK 68 and RK 22. RK 68 is relatively more mafic than RK 22 based on SiO_2 content of 47.15% and 50.80% respectively. Ni-Cr are relatively concentrated in igneous (ultra)mafic rocks (*i.e.* Garnier *et al.*, 2008; Arndt *et al.*, 2010; Schlatter and Stensgaard, 2014) to explain the higher content of these elements in RK 68 rather than RK 22. Ni and Cr contents in the sample from location 2 and location 3 are much higher than RK 68 and RK 22, whilst Sr composition is lower (Table 1). These anomalies concluded that heavy metals in location 2 and location 3 are not only affected by the source rock composition but also by the anthropogenic impacts.

Urban environments are polluted by a number of different sources such as road traffic, industry, waste incineration, waste sites, crematoria and incineration of coal, oil and wood (Ottesen and Langedal, 2001). The Government of Kulon Progo Regency (2014) confirmed that industries are located near the Serang River. Although most of these industries might have adequate waste water treatment plants. It is also estimated that effluent-related metals enter the Serang River and are transported by suspended particles and colloids to the Indian Ocean which separate Karangwuni and Glagah. Tidal currents help the outflow particles and colloids from the mouth of Serang River to the Indian Ocean to spread and be deposited as coastal marine sediments. Heavy metals particles are difficult to get to GPJ 36-37 location because it is far from Serang flow and is separated more than 200 m from seashore to explain the low Ni-Cr compositions in the samples in comparison to coastline samples.

Progo, Serang, and Bogowonto are the three watersheds in Kulon Progo Regency. Serang River is relatively more special as it flows through urban

flow through populous area which may become the source of pollution and explains the low Ni-Cr composition in the sediments near the mouth of this river in Congot.

Folk gold mining in Sangon, northwestern part of Kulon Progo, started since more than a decade ago with limited waste treatment plant. Gold processing using amalgamation technique has resulted in contamination of mercury in the stream sediments as shown by high values of Hg, Pb, Zn, As, and Cd (Setiabudi, 2005). The mining wastes of the mines were discharged into Plampang River without detoxification, degradation, and water treatment which may affect public health in the mine area and surrounding. Plampang River and Bogowonto River are united near Karangsari to flow southward to Indian Ocean. The estuary of the river is relatively near location 4 in Congot. The low Ni-Cr content in GPJ 42 and GPJ 43 indicates that gold mining activity is rather correlated to Cd, Cu, Pb, Hg, and Zn pollutions but not Ni and Cr as was described in Lake Victoria, Tanzania (Kishe-Machumu and Machiwa, 2003).

Table 2. Pollution factors in Serang watershed (The Government of Kulon Progo Regency, 2014). BOD = Biological Oxygen Demand, COD = Chemical Oxygen Demand, TSS = Total Suspended Solids.

No.	Source of Pollution	Number	Pollution Parameter
1.	Health Service	17	BOD, COD, TSS, NH ₃ , PO ₄ , oil
2.	Automotive Workshop	21	Oil and fats, pH, detergent
3.	Batik Industry	12	BOD, COD, TSS, oil, pH
4.	Tapioca Industry	1	BOD, COD, TSS, cyanide, pH
5.	Tofu and Tempe Industry	10	BOD, COD, TSS, sulfide, pH
6.	Printing Industry	2	Pb, blue methylene, oil, pH
7.	Gas Station	6	Oil
8.	Farm	11	BOD, COD, TSS, sulfide, ammonia, pH
9.	Hotel and Restaurant	9	BOD, TSS, detergent, oil and fats, pH

area of Wates and is vulnerable to anthropogenic pollution (The Government of Kulon Progo Regency, 2014). Nine sources of pollution on Serang watershed are described in Table 2. The report revealed about the highest Cr content in the water of Serang River reached 120 ppm whilst Ni was not measured. The anthropogenic activities around Wates most possibly the source of Ni-Cr pollution as previously was explained by Wong *et al.* (2006). On the other hand, Bogowonto does not

CONCLUSIONS

The box plot denotes abnormal elemental values of the seven beach sand samples from the coast in Kulon Progo. High anomaly is detected in Ni-Cr content whilst most of rare earth elements show minimum outliers. Anthropogenic activities most possibly influence the high Ni and Cr composition in samples near the mouth of Serang River. On the other hand, the two heavy metals are relatively low

in the samples in Congot because they are influenced by Bogowonto River which flows through a rural area. Cr and Ni are more concentrated in the surface, whilst Rb, Sr, Zr, and Ba are in the subsurface sample of polluted locations. Folk gold mining activity in Sangon is rather correlated to Cd, Cu, Pb, Hg, and Zn pollutions but not Ni and Cr.

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