Magnetic Susceptibility and Heavy Metal Content of Sediments in the Upstream Citarik River

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Abstract. The Citarik River is one of the Citarum sub-watersheds that originates in the Kareumbi Masigit Forest Conservation Area, Sumedang Regency. The number of human activities around the upstream Citarik River can affect the quality of water and sediment. To identify the anthropogenic effect, we conducted measurements of common parameters used to determine water and sediment quality, namely EC (Electrical Conductivity), TDS (Total Dissolved Solids), and pH. Thus, to analyze the characteristics of sediment, we used magnetic susceptibility measurements, heavy metal content tests, Scanning Electron Microscopy, and Energy Dispersive X-Ray Spectroscopy (SEM-EDS) tests. The results showed that the hydrological parameter values of sediment were still at a predetermined threshold except for pH at several locations. The results of low-frequency magnetic susceptibility (χLF) around (1308.696–3071.020) × 10-8m3/kg while the frequency-dependent magnetic susceptibility ($\chi FD\%$) values around (0.955–2.405) %. Those values have a negative correlation which indicates that the sediment sample has been affected by anthropogenic materials. This is supported by heavy metal test results where almost all elements pass the specified threshold. Furthermore, there is a positive correlation between magnetic susceptibility and heavy metals originating from human activities and the results of the SEM-EDS test indicate the presence of a mineral with a spherule shape where the mineral with that shape is a mineral from anthropogenic activity.

Keywords: Anthropogenic, Citarik River, Heavy Metal, Magnetic Susceptibility

Introduction

Citarum River is the longest river in West Java, which has several Sub-Watersheds, one of the sub-watersheds is Citarik River. The Citarik River passes through three regencies: Bandung Regency, Garut Regency, and Sumedang Regency, with a length of 39.64 km and an area of 4,315.31 ha. The Citarik River originates in the Kareumbi

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Masigit Forest Conservation Area, Sumedang Regency, and flows into the Upper Citarum River in Bandung Regency. The Citarik River is widely utilized by the local population for agricultural irrigation, livestock farming, and industry. Unfortunately, the river also used as a disposal site for household waste [1].

Until the year 2018, it was identified that the water quality of the Citarik River had deteriorated [2]. The natural cause and human activities can be attributed to the degradation. Natural factors may result from volcanic activity, land degradation, rock erosion, and other natural disasters. Meanwhile, human activity can be attributed to the disposal of household and industrial waste, motor vehicle emissions, agricultural and livestock waste. In the same year, 2018, the Citarum Harum Program was introduced, leading to an improvement in the water quality of the river. Although the Citarum Harum Program is still ongoing, there are still many community activities involving the disposal of domestic waste into the watershed. This issue has its roots in the upper reaches of the river, where there are numerous residential areas, as well as agricultural, livestock, and plantation activities in the vicinity of the Upper Citarik River area.

Over the past few decades, the rock magnetism method has been widely utilized to identify environmental issues such as river pollution, by leveraging magnetic parameters (magnetic susceptibility values) as proxy indicators for environmental contamination. This method employed to assess the abundance of magnetic minerals in soil or river sediments samples. Rock magnetism can be used to identify magnetic minerals and their characteristics, such as quantity, grain shape, and grain size [3]. This method to conduct a study on the magnetic properties of river sediments as pollution indicators in the Citarum River, Karawang Regency [4]. On the other hand, it is known that magnetic parameters have a strong correlation with heavy metals, as demonstrated in a study conducted which correlated magnetic parameters with heavy metal content [5]. Heavy metal measurements can assist in analyzing the abundance of pollutant elements within a sample. In addition to identifying the abundance of magnetic minerals through magnetic susceptibility values and determining heavy metal content in sediment samples, the rock magnetism method also analyzes the morphology and mineralogy of magnetic minerals. The morphology of magnetic minerals in contaminated sediment samples will have different shapes compared to sediment samples that have not been polluted [5-6]. Furthermore, there are several other parameters that can support rock magnetism methods. Hydrological parameters for measuring water quality, such as Electrical Conductivity (EC), Total Dissolve Solid (TDS), and pH, can be used as supplementary data and initial analysis.

Thus far, there have been no studies conducted in the area surrounding the upper reaches of the Citarik River, despite the potential impact of the upper Citarik River on downstream flow. Therefore, this research aims to identify the characteristics of magnetic minerals based on magnetic susceptibility value and correlated with heavy metal content to understand the environmental conditions of the upper Citarik River.

2 Method

2.1 Materials

The Citarik River is located at 06° 57' 17" S and 107° 56' 26" E to 06° 58' 2" S and 107° 49' 48" E. The upper Citarik River passes through three different lithological units: Qyu, which is the result of unweathered young volcanic activity, comprising lithologies such as tuffaceous sand, lapilli, breccia, lava, and agglomerate. Some of these materials originate from Mount Tangkubanparahu, while others originate from Mount Tampomas. The second lithological unit is Qvl, formed by old volcanic lava, with a basalt arrangement and some portions having been propylitized. The third lithological unit is Qvu, which is the result of unweathered old volcanic activity, characterized by lithologies including volcanic breccia, lahar, and alternating lava flows [7]. Based on the lithology of the upper Citarik River, it can be determined that these rocks are volcanic products. Materials derived from volcanic products typically exhibit characteristics of high magnetic susceptibility values and belong to the ferrimagnetic group.

This research used sediment as the primary sample and water as the comparative sample for hydrological parameter. Sediment samples were directly collected from the Upper Citarik River and subsequently prepared, extracted, and measured in the laboratory. In-situ measurements of water were conducted at the same sampling points as the sediment sampling using a Hanna Combo Meter type HI-9813-6 pH/EC/TDS/°C Portable Meter. Sediment sampling was carried out along the Upper Citarik River, starting from the river near the entrance of the Kareumbi Masigit Mountain Reserve in Cicalengka District, Sumedang Regency, to the Citarik River in Cimanggung District, Sumedang Regency (Fig. 1). Sampling was conducted at 10 locations along the Upper Citarik River, where the 10th and 5th sampling points were divided into two sampling locations due to the river's flow being divided into two channels.

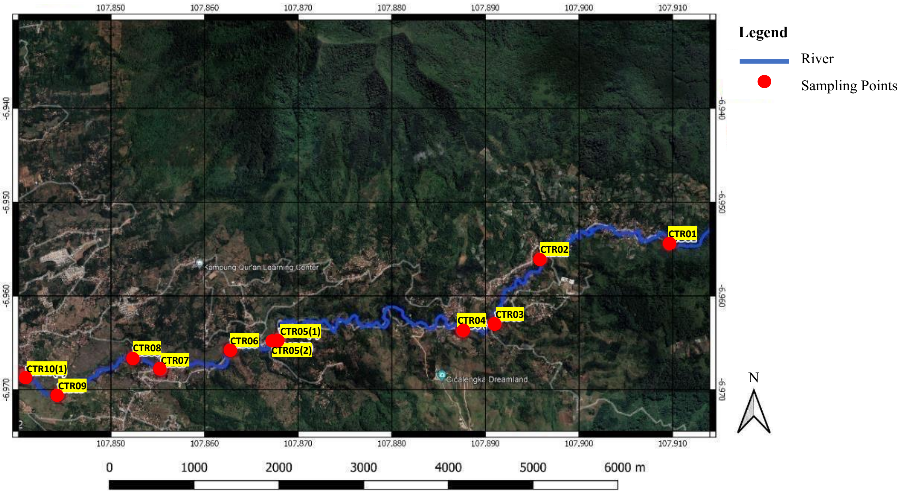

Fig. 1. Map of sampling points of sediments and water along Upstream Citarik River (source: Google Earth Pro, 2019 with modification).

2.2 Magnetic Susceptibility and Heavy Metal Content Measurements

Sample preparation was carried out for sediment samples to undergo magnetic susceptibility measurements. The sediment samples were dried and sieved using a mesh size of 10 to remove impurities, such as plant roots that may have been collected during sampling. Subsequently, the samples were placed into a 10 cm^3 holder for magnetic susceptibility measurements using a magnetic susceptibility meter (Bartington Ltd.) with an MS3B sensor. These measurements were conducted using dual frequencies (low-frequency of 465 Hz and high-frequency of 4650 Hz). The results of the measurements are volume-based magnetic susceptibilities, and the obtained values can be used to calculate mass-based magnetic susceptibilities at both low-frequency and high-frequency (χ_{LF} and χ_{HF}). Frequency-dependent magnetic susceptibility values can be derived from the low-frequency and high-frequency magnetic susceptibility values using the formula $\chi_{FD}\% = [(\chi_{LF} - \chi_{HF})/\chi_{LF}] \times 100$. Magnetic susceptibility values can identify the abundance of magnetic minerals in sediment samples, while frequency-dependent magnetic susceptibility can identify samples with fine grains that show superparamagnetic characteristics.

Magnetic mineral in sediment samples exhibits distinctive morphology. Identifying the morphology of magnetic minerals can aid in reinforcing the analysis of the factors causing changes in magnetic susceptibility values in the samples. Prior to measurement, the samples underwent extraction following the method described by Novala et al. (2019). The mineral morphology was assessed through scanning electron microscope-energy dispersive spectroscopy (SEM-EDS) analysis conducted using the JEOL JSM-6510.

The measurement of heavy metal element content in sediment samples was conducted using inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis. The sample preparation process for ICP analysis involved leaching and wet destructive methods. The ICP-OES measurements were performed using an Agilent Series 700 ICP-OES.

3 Result and Discussion

Figure 2 shows the pH value of water ranges from 6.9 to 7.7 with an average of 7.24, while the pH value of sediment is between 6.1 to 7.0 with an average of 6.49. If the pH value is low, the solubility of the metal will be high, so it can cause greater heavy metal toxicity (Sukoasih et al, 2017). The TDS value of the water sample is in the range of 20 – 77 ppm with an average of 46.08 ppm. While the TDS value of the sediment sample is in the range of 24 – 72 ppm with an average of 40.5 ppm. The EC values of water samples are in the range of 20 – 190 μS/cm with an average of 61.67 μS/cm. While the variation of EC values from sediment samples is in the range of 20 – 90 μS/cm with an average of 44.17 μS/cm. According to WHO, the threshold for TDS value is less than 1000 ppm and the threshold EC value is less than 1500 μS/cm. Variations in TDS and EC values from water samples and sediment samples are still below the threshold indicating good quality.

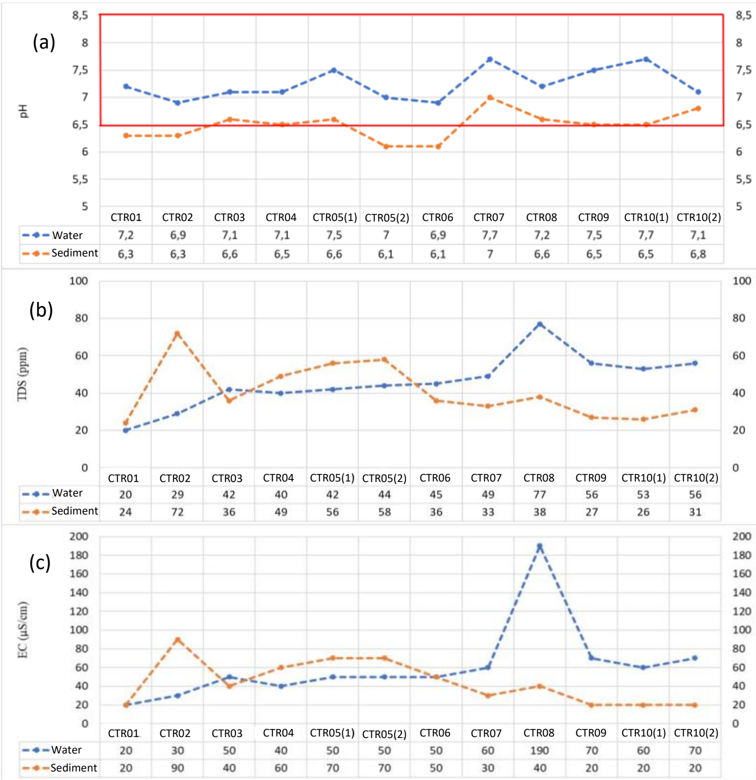

Fig. 2. The distribution data of (a) pH, (b) TDS, and (c) EC values of water and sediments from each sampling points. The red box shows the range of normal pH in the soil.

Low-frequency magnetic susceptibility values (χ_{LF}) are in the range of 1308.696 × 10^{-8} – 3071.020 × 10^{-8} m^3/kg with an average of 1797,178 × 10^{-8} m^3/kg. The value of χ_{FD}% in the sediment sample has a value range of 0.955 – 2.506% with an average of 1.735%. According to Bijaksana and Huliselan (2010), the value of χ_{FD}% with a range of 1 – 4% tends to be found in sediments that have been contaminated by anthropogenic materials. Based on [8] the presence of anthropogenic minerals can be identified by the correlation graph between χ_{LF} and χ_{FD}%. If there is a negative correlation between χ_{LF} and χ_{FD}% then it indicates that anthropogenic minerals contribute more than lithogenic minerals. The scatter diagram between χ_{LF} and χ_{FD}% aims to determine the source of magnetic minerals and their domains (Fig. 3). The Fig 3. shows that the sample in this study belongs to the Stable Single Domain (SSD) or Multi Domain (MD) domain. According to [9], SSD and MD grains were mostly released from anthropogenic sources, while SP (superparamagnetic) grains could be found from pedogenic (natural) sources.

The morphology of magnetic minerals that have an octahedral shape is known as titanomagnetite or magnetite minerals which are identical to pedogenic sources [10-11]. While the morphology of magnetic minerals with a spherical shape indicates that these magnetic minerals come from anthropogenic sources [10]. Fig. 4 shows the shape of magnetic minerals in representative sample (CTR03) from all sample sediment. Fig. 4. is also convincing that the magnetite mineral in the sediment samples, apart from having a pedogenic source, also has an anthropogenic source.

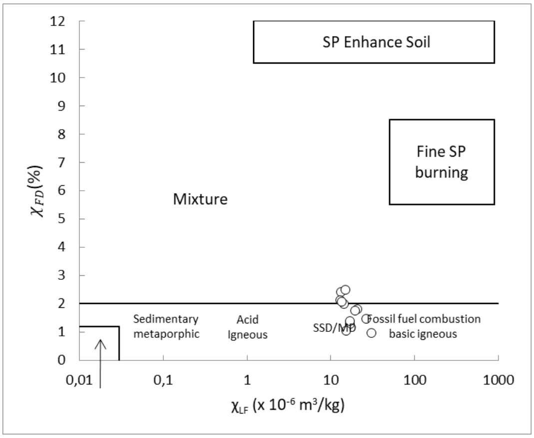

Fig. 3. Schematic diagram of χ_{LF} - χ_{FD}% adopted by Dearing (1999). The black circles show the result of χ_{LF} and χ_{FD}% from sediments sample measurement.

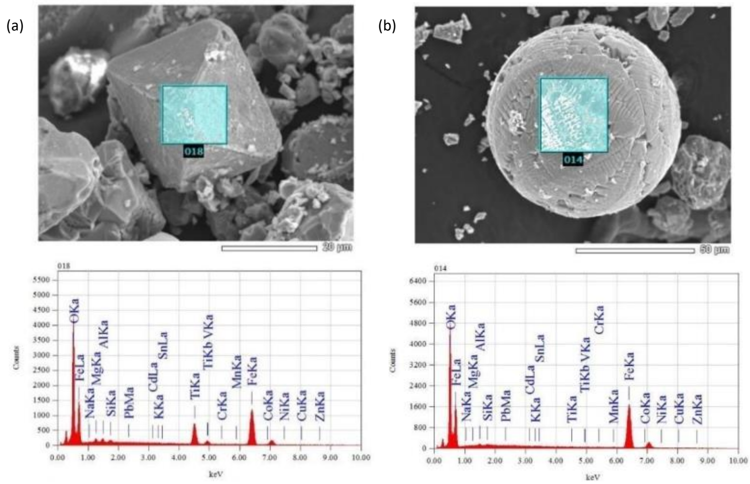

Fig. 4. The morphology of magnetic mineral of representative sample of CTR03. (a) octahedral-shaped magnetic mineral and (b) spherule-shaped magnetic mineral.

Table 1. Concentration of heavy metal content of sediment sample

Element(s)	Contentration (mg/kg)			Average Consen-tration (mg/kg)	Threshold Value (mg/kg)
	CTR01	CTR02	CTR08		
Al	241074,23	147713,81	69602,25	152796,76	-
As	11,56	4,84	7,24	7,88	20(1)

Element(s)	Contentration (mg/kg)			Average Consen-tration (mg/kg)	Threshold Value (mg/kg)
	CTR01	CTR02	CTR08		
Cd	7,40	5,58	6,82	6,60	1,5(1)
Co	75,81	66,62	59,73	67,39	-
Cr	99,76	92,72	74,51	89,00	80(1)
Cu	241,82	211,90	190,98	214,90	65(1)
Fe	14314,78	13281,49	15947,31	14514,52	20000(2)
K	2904,57	3387,07	2224,32	2838,65	-
Mg	727,66	543,51	600,00	623,72	-
Mn	24109,19	17153,60	14046,23	18436,34	248,77(3)
Ni	37,63	29,58	17,91	28,37	21(1)
Pb	79,71	112,91	104,59	99,07	50(1)
Sn	0,64	2,76	0,86	1,42	-
Zn	339,53	294,40	238,05	290,66	200(1)

(1) Australian and New Zealand Environment and Conservation Council Interim Sedimen Quality Guideline (ANZECC ISQG-low, 2000)
(2) Guideline for The Protection and Management of Aquatic Sediment Quality in Ontario (1993)
(3) National Sediment Quality Survey USEPA (2004)

Table 1 shows that almost all heavy metals have values that exceed the sediment quality threshold. Sample selection of CTR01, CTR02, and CTR08 is based on low, medium, and high values of the EC, TDS, and χ_{LF} parameters. Several heavy metals from different locations did not exceed the threshold, i.e. As and Fe as well as Cr and Ni metals at CTR08. There is positive correlation between magnetic susceptibility and some heavy metals derived from human activities. This indicate that the high or low value of magnetic susceptibility influenced by the abundance of certain heavy metal content. A significant correlation can be seen in χ_{LF}-Pb and χ_{LF}-Sn which have a positive correlation value of 0.955 and 0.919. As we know that χ_{LF} could be used as indicator proxy of potential toxic element. According to the United State Environment Protection Agency (USEPA), Pb is a dangerous heavy metal pollutant which is the result of exhaust fumes from the use of motorized vehicles and the Pb element is evidence of pollution from pesticides [12]. Sn is a heavy metal that can come from lithogenic or anthropogenic. Heavy metal Sn is one of the constituent elements of organotin compounds. Organotin compounds are found in pesticides and fungicides. A significant correlation was shown by Cu-Zn of 0.986. The use of fertilizers and pesticides in the long term will accumulate Cu and Zn elements [13].

4 Conclusion

Based on the results of testing hydrological parameters on water and sediment samples is below the threshold although there are several locations that have a pH that is less than the specified threshold. Based on the value of magnetic susceptibility (χLF) of the upper Citarik River sample has a very high value. The frequency-dependent magnetic susceptibility value (χFD%) belongs to the low to medium category, this can indicate that the sample is dominated by anthropogenic material. The analysis is supported by the negative correlation between and (%) which indicates more contribution from anthropogenic material. The significant correlation between magnetic susceptibility with heavy metals Pb and Sn and heavy metals with other heavy metals, Cu-Zn, can be indicated from anthropogenic sources, which are the use of pesticides and fertilizers in the long term. Therefore, in the upstream Citarik River there are indications of pollution although only two heavy metals were found that have a high significance for magnetic susceptibility. This is supported by the magnetic mineral morphology test which shows the presence of spherule grains which indicate from anthropogenic material.

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