Magnetic characterization and heavy metals pollutions of sediments in Citarum River, Indonesia

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Abstract. Magnetic methods have been successfully used for pollution detection and mapping in riverine environment. These methods are considered faster and easier compared to conventional analytical methods. In this study, sediment samples from Citarum River, the largest river system in West Java Province and main water supply for more than 10 million people, were measured for their magnetic characteristics and heavy metals content to test the effectiveness of magnetic methods in detecting heavy metals pollution. Magnetic measurements include measurements of magnetic susceptibility (MS), isothermal remanent magnetization (IRM) saturation, and anhysteretic remanent magnetization (ARM) decay. The results show that mass-specific MS values tend to decrease from upstream to downstream, from 1127.3 to 393.2 × 10⁻⁸ m³kg⁻¹. In all samples, the dominant magnetic mineral is found to be magnetite based on the IRM saturation field. The magnetic grains are predominantly multi domain (MD). Geochemical analyses showed that all water and sediment samples contain Fe, Cd, Co, Ni, Pb, Zn, As, Hg, and Mn. The heavy metals content varies irregularly in sediment samples although a negative correlation is found between heavy metals contents and magnetic parameters.

1. Introduction
Studies of magnetic parameters and their interpretation of pollution have been used in several different environments, such as soil, sediment and vegetation since the 1980s [1]. A strong correlation between magnetic and heavy metal parameters indicates the magnetic measurements as a proxy of heavy metal content is acceptable if the magnetic susceptibility exceeds a certain value [2]. The magnetic parameters of sediment and its relation to heavy metals in several rivers in various countries have been studied [1, 3 – 8]. This method is practical and useful for detecting and mapping pollution around modern industrial cities [7]. In Indonesia, the study of magnetic parameters for river sediments have carried out for the Citarum River in Karawang area [9], Tabalong River in South Kalimantan [10] and for the suspended sediment of the Citarum River [11].

Citarum River is the longest river in West Java, Indonesia. The Citarum River is sourced from Wayang Mountain and empties into the Java Sea. The Citarum River flows through 12 districts and the Citarum River is the source of water for three dams: Saguling, Cirata and Jatiluhur. The Citarum River is in tropical climates with high rainfall and humidity throughout the year. In general, the average annual rainfall ranges from 2000 mm to the downstream area in the north, up to 4000 mm for the upstream area in the southern part of the mountain region. The annual evaporation rate for lowland areas is 1,600 mm, while for the lowlands is 1,400 mm [12].
The existence of the Citarum River is very important for the economy because the industry along the Citarum River accounts for 20% of GDP (Gross Domestic Product) [12]. However, the socio-economic activities along the Citarum River are not accompanied by responsible waste management. This resulted in the state of the river being generally heavily polluted [12]. In order to avoid increasingly critical conditions, the mapping and monitoring of pollution status should be done as a quality control of the Citarum River. The heavy metal concentration of river sediments can be used to reveal the intensity and extent of local and regional pollution. However, commonly used geochemical methods (such as AAS and ICP-MS) are relatively complex, take a time and expensive. Therefore, for large-scale mapping or monitoring of pollution, it is more appropriate to use environmental magnetic methods. In this study, the sediment from Citarum River, West Java, Indonesia measured magnetism parameters and heavy metal content to find out what magnetic parameters can be used as an indicator of estimation of heavy metal pollution as an alternative method in monitoring the sediment quality of the Citarum River.

2. Materials and Methods

Four samples of Citarum River sediments (CITA 1 – CITA 4) used in this study were collected from along the Citarum River which started from Balekambang (CITA 1) as upstream area which was an agricultural area and ended in Nanjung (CITA 4) (Figure 1). Samples were collected in November 2014 during the dry season.

In the laboratory, the sample is dried by aerated at room temperature [14]. The dried sample is inserted into the standard holder (25.4 mm in diameter, 22 mm in height, and 10 cm³ in volume). Before performing the measurement of magnetic parameters, the sample is weighed using an Ohaus analytical scale.

The measurement of magnetic parameters performed is mass-normalized magnetic susceptibility (χ) using dual frequencies with a magnetic susceptibility meter (MS2 susceptibility meter by Bartington Instrument Ltd., Witney, UK) producing low-frequency (460 Hz) mass-specific magnetic susceptibility (χ_{LF}) and high-frequency (4600 Hz) mass-specific magnetic susceptibility (χ_{HF}). A new parameter
termed $\chi_{FD}$ (%) could be derived from the value of $\chi_{LF}$ and $\chi_{HF}$ defined as $\chi_{FD}(\%) = 100\% \times (\chi_{LF} - \chi_{HF}) / \chi_{LF}$ [2]. $\chi_{FD}(\%)$ indicates the presence of super paramagnetic (SP) grains [15]. Then, all of the samples were subjected to ARM (anhysteretic remanent magnetization). ARM was induced in a steady field of 0.05 mT imposed on a peak alternating magnetic field of 70 mT. The ARM was given inside in a Molspin AF (alternating field) demagnetizer and the ARM intensity was measured using a Minispin magnetometer (both instruments are product of Molspin Ltd., Newcastle upon Tyne, UK). All samples were also subjected to temperature dependent mass-specific magnetic susceptibility using magnetic susceptibility meter MS2 (with sensor MS2WFP by Bartington Instrument Ltd., Witney, UK). Later, all samples were also subjected to isothermal remanent magnetization (IRM) analyses by placing them in increase magnetic field at room temperature using an electromagnet. The IRM acquired at 1,000 mT is referred to as saturation isothermal remanent magnetization (SIRM). All IRM measurements were performed in Institute Teknologi Bandung, Indonesia. All samples also subjected to AAS (atomic absorption spectrometry) analyses to know the heavy metals content at Laboratory of Marine Geology Research and Development Centre Bandung, Indonesia.

3. Results and Discussion

Figure 2 shows the result of IRM analyses. The IRM acquisition curves for all samples show that the magnetic field of $1/2$SIRM belowed 100 mT, inferring that the predominant magnetic mineral in the samples is a low coercivity magnetic mineral such as magnetite ($Fe_3O_4$) [15]. The presence of magnetite was also confirmed by the results of temperature dependent mass-specific magnetic susceptibility (Figure 3). Results from temperature dependent mass-specific magnetic susceptibility for all shows that the value of temperature dependent mass-specific magnetic susceptibility were close to 0 at a temperature of about 550°C in heating process, it is indicates the presence of magnetite minerals.

![Figure 2](image-url)
Figure 3. Behaviours of the susceptibility versus temperature sediment samples of Citarum River.

Table 1 summarizes the results of magnetic measurements. The value of $\chi_{LF}$ of the samples (CITA 1 – CITA 4) varied from $393.2 \times 10^{-8}$ m$^3$ kg$^{-1}$ (CITA 4) to $1127.3 \times 10^{-8}$ m$^3$ kg$^{-1}$ (CITA 1). Comparing the river sediment to that from elsewhere such as Ponnaiyar River, India [5] and Lianshui River, China [7], the value of $\chi_{LF}$ in the Citarum River were relatively high. The value of $\chi_{LF}$ from upstream (CITA 1) is highest than others and tended to decrease downstream (CITA 4).

Table 1. Summary of magnetic parameters of sediment samples of the Citarum River.

| Sample | $\chi_{LF} \times 10^{-8}$ m$^3$ kg$^{-1}$ | $\chi_{FD}$ (%) | MDF$_{ARM}$ (mT) | SIRM (Am$^2$kg$^{-1}$) | %magnetite |
|--------|-----------------------------------------|-----------------|-----------------|------------------------|-------------|
| CITA 1 | 1127.3                                  | 2.49            | 11.5            | 0.083                  | 0.091       |
| CITA 2 | 473.5                                   | 3.91            | 11.0            | 0.033                  | 0.037       |
| CITA 3 | 466.6                                   | 2.98            | 11.0            | 0.032                  | 0.035       |
| CITA 4 | 393.2                                   | 3.15            | 10.0            | 0.027                  | 0.030       |

Table 1 also shows the variation of $\chi_{FD}$ values for Citarum River samples that vary from 2.49(%) (CITA 1) to 3.91(%) (CITA 2). These results show that all samples contain SP grains [16]. Figure 4 shows the decay of ARM as a function of the peak demagnetizing field. Using Lowrie-Fuller test [17] the median destructive field or MDF$_{ARM}$, the magnetite grains in the samples were classified as MD (Multidomain) range. Saturated isothermal remanent magnetization (SIRM) is the intensity of remanence during the induced field is 1 T. Since magnetite was the predominant mineral in the samples, the abundance of magnetite in the samples can be estimated from $%_{magnetite}$, which is $%_{magnetite} = \text{SIRM} / J_{s_{\text{magnetite}}}$ where $J_{s_{\text{magnetite}}}$ is the saturation magnetization for magnetite (9.2 Am$^2$kg$^{-1}$) [18]. Table 1 shows...
the magnetite contents in the samples estimated from SIRM / \( J_s^{\text{magnetite}} \) that varied from 0.030 (CITA 4) to 0.091 (CITA 1).

Abundance of magnetite minerals from upstream (CITA 1) were higher than other samples, and decreases downstream. This is expected due to the high \( \chi_{LF} \) value in the upstream (CITA 1), where the \( \chi_{LF} \) value is depend on the magnetic mineral and its abundance in the sample. It is known that magnetite minerals have the highest \( \chi_{LF} \) values among other magnetic minerals [14].

![Figure 4. ARM decay profiles for typical sediment samples of Citarum River.](image)

Table 2 also shows the results of AAS analyses for all sediment and water samples. The content of Fe in the sediment samples varied from 156 ppm from upstream (CITA 1) to 13 ppm from downstream (CITA 4), and tended to decrease downstream. Fe content is a dominant element because it has the highest heavy metal content when compared to other elements.

**Table 2. Summary of AAS analyses of sediment and water samples of the Citarum River.**

| Component | Water | | Sediment |
|-----------|-------|---|---|---|---|---|---|---|
| (ppm) | CITA 1 | CITA 2 | CITA 3 | CITA 4 | CITA 1 | CITA 2 | CITA 3 | CITA 4 |
| Fe | 156 | 241 | 68 | 13 | 125 | 150 | 160 | 204 |
| Cd | 0.017 | 0.033 | 0.006 | NA | 0.012 | 0.017 | 0.02 | 0.049 |
| Co | 0.1 | 0.15 | 0.03 | 0.01 | 0.09 | 0.08 | 0.07 | 0.08 |
| Ni | 0.07 | 0.19 | 0.06 | 0.02 | 0.05 | 0.09 | 0.11 | 0.23 |
| Pb | 0.21 | 0.7 | 0.17 | 0.03 | 0.2 | 0.3 | 0.49 | 0.59 |
| Cu | 0.21 | 0.69 | 0.21 | 0.04 | 0.18 | 0.35 | 0.45 | 0.62 |
| Zn | 0.27 | 10.85 | 1.04 | 0.31 | 0.21 | 4.6 | 1.79 | 0.52 |
| Ag | 0.002 | 0.006 | 0.001 | 0.091 | NA | NA | 0.001 | 0.002 |
| Hg | 0.07 | 0.91 | 0.98 | 0.14 | 0.28 | 0.42 | 1.05 | 1.12 |
| As | 0.022 | 0.043 | 0.01 | 0.001 | 0.017 | 0.045 | 0.033 | 0.049 |
Table 3 shows the results of the correlation test between heavy metal content in the sediments, it is found that almost all heavy metals except Fe, Co, Mn and Zn, were positively correlated to Fe. This shows that Fe can be used as an indicator of the presence of other heavy metals in the Citarum River sediment. Figure 5 shows a negative correlation between Fe content with magnetic parameter $\chi_{LF}$ ($r = 0.773$) and SIRM ($r = 0.770$). Figure 5 also shows a negative correlation between Fe content in the sediment and water ($r = 0.725$).

Table 3. Summary of $r$ of Fe and heavy metals content in sediment and water samples of the Citarum River.

| Component | Water  | Sediment |
|-----------|--------|-----------|
|           | $r$    | $r$       |
| (ppm)     |        |           |
| Cd        | 0.9932 | 0.9651    |
| Co        | 0.9944 | -0.4334   |
| Ni        | 0.9278 | 0.9907    |
| Pb        | 0.9205 | 0.9337    |
| Cu        | 0.9083 | 0.9814    |
| Zn        | 0.7997 | -0.1450   |
| Ag        | -0.6755| 1.0000    |
| Hg        | 0.3265 | 0.8481    |
| As        | 0.9905 | 0.8067    |
| Mn        | 0.7008 | -0.0656   |
Figure 5. Relationship among $\chi_{LF}$ and Fe (a), SIRM and Fe (b) in sediment samples, Fe content in water and sediment (c).

An increase in Fe content from upstream to downstream be indicates an increasing downstream pollutant load. A negative correlation between Fe content and $\chi_{LF}$ indicates that the magnetite mineral content decreases downstream. This can be caused by several factors, such as: the decreasing concentration of magnetic minerals downstream due to the increase of nonmagnetic sediments from the tributaries, especially from Cikapundung River and Cisangkuy River thus decreasing the value of $\chi_{LF}$ samples, decreasing magnetite mineral content in sediment due to sand mining activities around the Citarum river in the area around CITA 2, and the possibility of the adsorption of pollutant particles by iron oxide thereby reducing the magnetic concentration of the sediment [18].

Conclusions
Based on the results of the study of magnetic and heavy metal parameters in the Citarum River sediment it is known that the highest $\chi_{LF}$ value is upstream and tends to decrease downstream with magnetic minerals carrier is multidomain magnetite. The decrease in the value of $\chi_{LF}$ is influenced by the reduced magnetite abundance. Fe content is positively correlated to $\chi_{LF}$ and SIRM which show that magnetic parameters $\chi_{LF}$ and SIRM can be used as proxies of Fe. Since Fe is also positively correlated to heavy metals (except Co, Zn and Mn) then Fe can be a proxy for the presence of heavy metals in the Citarum River sediments.

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