Magnetic Susceptibility and Hydrogen Cyanide Levels as Proxy Indicator for Gold Mining Pollution in River Sediment

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ABSTRACT

Sumbawa’s Kuris River is one of the rivers contaminated by the island’s traditional gold mine. In order to detect contaminant levels, we examine the magnetic susceptibility, HCN levels, and the heavy metal contents on the river’s surface sediment. Environmental pollution has been widely assessed using a combination of magnetic properties and geochemical analysis. The goals of this research are to discover how magnetic susceptibility (χ) can be used as a first-order proxy for pollution. The relation between susceptibility and HCN is of particular interest, as this is a major contaminant associated with gold mining. The surface sediment samples were collected at ten different locations along the rivers. The magnetic susceptibility was determined using the Bartington MS2B, and the hydrogen cyanide (HCN) concentration was determined using Argentometric titration. The element content was determined by an Atomic Absorption Spectrometer (AAS). The low-frequency
magnetic susceptibility ($\chi_{lf}$) ranges from 71 to 115×10^{-8} m^3/kg, with an average of 97×10^{-8} m^3/kg, and the $\chi_{fd}(\%)$ analysis ranges from 2% to 4%. The presence of spherical iron oxides, which are indicative of combustion byproducts, was also confirmed by SEM. The samples have low magnetic susceptibility but high levels of Hg and HCN. AAS results showed high Fe, Zn, and Cu concentrations in river sediments, with more variable concentrations of Hg, Mn, As, Cr, and Au. Because Fe, Cu, As, Hg, and HCN have a significant Pearson's correlation with $\chi_{fd}(\%)$, this parameter can be a useful indicator for contamination caused by gold mining waste.

Keywords: Geochemistry, hydrogen cyanide (HCN), magnetic susceptibility, river sediments, tailings

INTRODUCTION

Tailings from traditional gold mines in Sumbawa, Indonesia, are allegedly the source of serious pollution in this region's environment, including rivers and lakes, residential and agricultural areas, and, eventually, the sea. This type of pollution can be caused by the direct disposal of gold mining processing waste or the runoff from waste collection areas, typically located near rivers during rainy seasons (Bruno et al., 2020). Lake Lebo in Taliwang is an example of river pollution because the Suning and Seran Rivers feed it, and it overflows into the Brang Rea River. The Hg levels in the lake’s fish are above the hazard level (Junaidi et al., 2019). Humans, particularly their hair and livestock, are affected (Anderson, 2010; Donato et al., 2007; Junaidi et al., 2019). Human consumption of contaminated fish or livestock meat can have short- and long-term negative consequences. Anthropogenic contamination has also been observed to affect bacterial communities in China’s Jiaolai River, increasing the Ni content in its sediment (Li et al., 2016).

Geochemical data, such as anomalous levels of heavy metals in an area, are frequently used to assess the degree of contamination of soils or sediment (Salomão et al., 2021). The study used elemental analysis obtained from atomic mass spectrometry (AMS) at the Tembi River in Iran was discovered an increase in Cd, Cr, Cu, Fe, Pb, Ni, and Zn concentrations in sewage both upstream and downstream of the entry point (Shanbehzadeh et al., 2014). Similar studies in rivers showed heavy metal contamination was conducted in India’s Beas River (Kumar et al., 2018), rivers in Kabul, Pakistan (Ali & Khan, 2018), the urban river in the Philippines (Decena et al., 2018), rivers in Ukraine (Alokhina, 2021), and Vistula River in Poland (Szczepaniak-Wnuk et al., 2020). Heavy metal pollution in sediment was also assessed in Ghana’s Pre Basin using the geo-accumulation index (Igeo), which tracked As, Pb, Zn, Mn, Cr, Ni, and Fe using atomic absorption spectroscopy (AAS) (Duncan et al., 2018). Heavy metal tracking can also be used in the case of leather factory tanning waste that has polluted the river. Cr tracking is used in this case to determine pollutant waste (Świetlik & Trojanowska, 2016). Geochemistry methods for monitoring pollution
can be combined with magnetic methods; magnetoresponse for arsenic pollution tracking is one example (Ouyang et al., 2020). There are numerous examples in the literature, such as research into coastal sediments (Ravisankar et al., 2018; Suresh et al., 2011), topsoil (Ouyang et al., 2020); snow deposits (Alfonsi et al., 2021), and sediments in a reservoir (Chaparro et al., 2020). In Indonesia, a combination of geochemical and magnetic methods has been used to study lacustrine sediment at Lake Limboto in Sulawesi (Yunginger et al., 2018), sediment of Citarum River in West Java (Sudarningsih et al., 2017), and sediment in Brantas River in East Java (Mariyanto et al., 2019a; Mariyanto et al., 2019b).

Few studies have used magnetic properties in conjunction with geochemistry analysis to track contamination associated with gold mining. Jordanova et al. (2013) demonstrated that sediment from the floodplain of the Ogosta River in Bulgaria exhibits enhanced magnetization, which can be linked to high concentrations of As, Pb, Zn, and Cu. This study compared the magnetic susceptibility of river sediments from the Labuan Kuris River in Sumbawa, Indonesia, to geochemical elemental data and hydrogen cyanide (HCN) concentration. Artisanal gold mining occurs along the river, and mine waste frequently enters the river. For comparison, samples also were taken from processing wastes at mining sites.

**METHODS**

Hijrah and Labuan Kuris areas of Sumbawa, Indonesia, were chosen for sampling because of the high artisanal gold mining activities. Labuan Kuris River receives input from mining processing waste, particularly waste associated with the first processing stage, known as Gelondong, labeled GL. Tong (labeled as TG) is a secondary processing stage. Here gold-containing rocks are ground in the first stage, and the gold is bonded with Hg. The left-over material from the first stage is processed again in the second stage using HCN and Pb. After the GL and TG treatment, surface river sediment (SP) and ground rock samples were collected. Figure 1 depicts the location of the sampling sites. SP1 was obtained from the upstream trial of Kuris River, while SP10 was acquired from the downstream trial near an estuary mangrove forest at an inlet leading to the sea.

Surface sediments were taken 1 kg and placed in a plastic bag for transport to the laboratory. Three samples were collected from each site: one from the left bank facing downstream, one from the center of the river, and one from the right bank. The sediment was then washed and filtered with distilled water and a 325-mesh sieve. After drying at room temperature, the sample was ground into powder and placed in a standard cylindrical plastic holder for magnetic measurement. A digital weight balance was used to weigh the samples. The magnetic susceptibility of all samples was measured using Bartington Magnetic Susceptibility Meter MS2B in two frequencies, 470 Hz, $\chi_{lf}$ and 4700Hz, $\chi_{hf}$. Frequency-dependent magnetic susceptibility, $\chi_{fd}$(%), was defined using Equation 1 (Dearing, 1999):
Several representative samples were prepared from the remaining powder for chemical elements analysis using Atomic Absorption Spectrometer (AAS) and HCN concentration measurement using argentometric titration. The magnetic minerals extracted from several samples were morphologically tested for tailing using scanning electron microscope (SEM) analysis.

RESULTS

AAS was used to determine the elemental concentration in all river surface sediment samples and the three tailing samples. Table 1 shows the results of the AAS magnetic susceptibility and HCN analysis. The Fe concentrations in the river and the tailing samples are significantly higher than other elements. Earlier reported XRF results also confirmed it. In sediment rivers, the elements with the highest concentrations are Si and Fe, followed by Mn, Al, Ca, and K. Meanwhile, Ba, Cu, Cr, Zn, and Ti have relatively low concentrations (Juliansyah et al., 2020). The concentration of heavy metals varies. On average, the tailing samples have the highest concentrations of Au, As, and Hg, while the river sediments have higher concentrations of Mn, Zn, Cu, and Cr.
The concentration of HCN in river sediments ranges from 45 (SP 8.2) to 75 (SP 2.2) ppm, with an average of 62 ppm. The concentration of HCN in the river is still smaller than the two samples from Gelondong and Tong, which are about 100 ppm, smaller than the concentration of HCN in the gold mine soil in China, which is about 70.55 ppm (Shehong et al., 2005), and higher than that reported result from Brazil, which is around 0.83 - 1.44 ppm (Prereira & Neto, 2007).

The TG sample has the highest concentration of HCN as weighed by argentometric titration. It is expectable because HCN is used in the Au extraction processes. Although it should not be used in GL processing, the high HCN concentration indicates that the substance is being used to some extent. There is a considerable concentration in the river sediment, especially at SP 6.2 and SP 7.2, indicating that HCN is entering the river ecosystem. It may be coming from the GL waste tailing that enters the river. It also holds for sites SP 1.2 and SP 2.2, which are upstream from the present mining and processing sites used by the local population. It suggests that the local runoff from GL processing is broader than the immediate processing area.

Magnetic susceptibility varies in river sediment samples; the χlf ranges from 71 to 115 ×10^-8 m^3/kg. The susceptibility, measured in low and high frequencies, is consistent (Figure 2a). It varies according to its location at a site, but no consistent difference exists (Figure 2b). χfd(%) is low in samples from the river and is between 2.6% to 4.8% (Figure 2c). It suggests that the grains are larger than 17 nm (Hrouda, 2011). These low values suggest that the ferromagnetic particles are blocked and do not exhibit superparamagnetic

### Table 1
Magnetic susceptibility, elemental analysis obtained from AAS, and argentometric titration for HCN detection

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>χlf (10^-8 m^3/kg)</th>
<th>χfd (%)</th>
<th>Au</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
<th>Ni</th>
<th>Cd</th>
<th>Fe</th>
<th>Cr</th>
<th>Mn</th>
<th>V</th>
<th>As</th>
<th>Hg</th>
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<tr>
<td>SP 1.2</td>
<td>95.17</td>
<td>3.31</td>
<td>&lt;0.06</td>
<td>52</td>
<td>12</td>
<td>110</td>
<td>1</td>
<td>52200</td>
<td>36</td>
<td>4925</td>
<td></td>
<td>116</td>
<td>3.923</td>
<td>70.17</td>
<td></td>
</tr>
<tr>
<td>SP 2.2</td>
<td>103.67</td>
<td>3.57</td>
<td>&lt;0.06</td>
<td>49</td>
<td>&lt;12</td>
<td>108</td>
<td>&lt;1</td>
<td>52300</td>
<td>30</td>
<td>3535</td>
<td></td>
<td>128</td>
<td>5.061</td>
<td>75.10</td>
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<td>4.01</td>
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<td>-</td>
<td>-</td>
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<td>-</td>
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<td>SP 4.2</td>
<td>71.72</td>
<td>2.64</td>
<td>0.13</td>
<td>46</td>
<td>82</td>
<td>93</td>
<td>&lt;1</td>
<td>45000</td>
<td>34</td>
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<td></td>
<td>121</td>
<td>2.692</td>
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<td>SP 5.2</td>
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<td>4.29</td>
<td>0.74</td>
<td>51</td>
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<td>74</td>
<td>&lt;1</td>
<td>46700</td>
<td>31</td>
<td>1426</td>
<td></td>
<td>107</td>
<td>9.639</td>
<td>59.52</td>
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<td>SP 6.2</td>
<td>108.39</td>
<td>3.97</td>
<td>1.61</td>
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<td>65</td>
<td>7</td>
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<td>105</td>
<td>987</td>
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<td>212</td>
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<td>1.36</td>
<td>57</td>
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<td>85</td>
<td>&lt;1</td>
<td>49000</td>
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<td>98</td>
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<td>4.83</td>
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<td>&lt;12</td>
<td>101</td>
<td>&lt;1</td>
<td>51900</td>
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<td>129</td>
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<td>GL 1 K</td>
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<td>6.19</td>
<td>34</td>
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<td>17</td>
<td>&lt;5</td>
<td>30300</td>
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<td>47</td>
<td>248</td>
<td>68.57</td>
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<tr>
<td>TG 1 H</td>
<td>140.46</td>
<td>0.52</td>
<td>0.3</td>
<td>15</td>
<td>186</td>
<td>&lt;15</td>
<td>&lt;5</td>
<td>20600</td>
<td>18</td>
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<td>30</td>
<td>265</td>
<td>28.16</td>
<td>109.80</td>
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<tr>
<td>GL 1 H</td>
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<td>218</td>
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<td>191</td>
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</table>

The concentration of HCN in river sediments ranges from 45 (SP 8.2) to 75 (SP 2.2) ppm, with an average of 62 ppm. The concentration of HCN in the river is still smaller than the two samples from Gelondong and Tong, which are about 100 ppm, smaller than the concentration of HCN in the gold mine soil in China, which is about 70.55 ppm (Shehong et al., 2005), and higher than that reported result from Brazil, which is around 0.83 - 1.44 ppm (Prereira & Neto, 2007).
behavior (Dearing, 1999). Eight GL samples were taken from different mine processing locations, and the $\chi_{lf}$ is between 20.39 and $112.8 \times 10^{-8}$ m$^3$/kg with the average $\chi_{lf}$ of $(60.64 \pm 35.08) \times 10^{-8}$ m$^3$/kg. The TG samples have a slightly higher $\chi_{lf}$ compared to the GL samples, with values between 32.16 and $140.4 \times 10^{-8}$ m$^3$/kg and an average of $(90.43 \pm 35.08) \times 10^{-8}$ m$^3$/kg. The samples from the tailing wastes have the $\chi_{fd}$(%) of between 0.5% and 2.3%, which is lower than in the river sediment.

The magnetic minerals were extracted from Gelondong and Tong tailings samples with a hand-permanent magnet and analyzed using SEM (Figure 3) to aid in identifying ferromagnetic minerals in the tailings. Many magnetic phases were irregular in shape and size, but there were also spherules (Figure 3a and 3b, right). Some irregularly shaped grains are iron oxide, but they may also contain Si and, to a lesser extent, Al or Cr (Figures 3a and 3b, left). Magnetic minerals with spherules have a 30–50 m diameter and are pure iron oxides that could be magnetite (see the EDAX data in the bottom right of Figures 3a and 3b). The surface may be smooth or have an orange skin texture (Figures 3a & 3b, right). These spherules are commonly found in combustion processes in, for example, factories and automobiles (Kelepertzis et al., 2019; Wang et al., 2017; Zajzon et al., 2013).
DISCUSSION

The magnetic susceptibility of low frequency, $\chi_{lf}$ in the surface sediment of Kuris River is influenced by lithogenic and anthropogenic input. The average magnetic susceptibility of this area is $104.8 \times 10^{-8}\text{ m}^3/\text{kg}$, which is lower than other areas in Indonesia, such as Brantas.

*Figure 3.* The SEM capture of magnetic minerals and composition of extraction results using EDAX show that magnetic minerals are dominated by Fe content in a representative: (a) Gelondong sample; and (b) Tong sample.
River with 3022.9 × 10^{-8} \text{ m}^3/\text{kg} (Mariyanto et al., 2019a) and Cikapundung River with 734.7 × 10^{-8} \text{ m}^3/\text{kg} (Sudarningsih et al., 2017) in Java, where the contribution of volcanic sources is larger. Its magnetic susceptibility dependence frequency, $\chi_{fd}(\%)$, is about 3.1%. This value is larger than that of the Brantas River (1.03%) and is similar to the reported value from the Cikapundung River. The values of more than 2% mean that the grain size of the magnetic minerals is smaller and that it is the contribution by anthropogenic input as reported in Cikapundung River. Other areas, such as Lake Limboto, have magnetic susceptibility in the same order as this study (Yunginger et al., 2018). Therefore, the magnetic susceptibility of the samples from Kuris River is not largely affected by volcanic but by anthropogenic input, as found in the tailing samples.

The high Fe content is related to the high lithogenic contribution to the sediment in the river. The lower Fe concentration in the TG sample suggests that some of the Fe contents were removed during the second step of the Au extraction process. Here the residue sample of Gelondong inserted into the vertical spinning Tong will make heavy metals, including Fe, seep into the bottom of the disposal pond, which reduces the ingress of Fe into river sediments. It would also explain the lower Mn, Zn, and Cu concentration in the tailing samples. It should be noted that the GL samples have a higher concentration of Au compared to TG samples and river sediment. It indicates that the GL processing does not bind all the Au in the first processing step; Au is removed after the second step. Au is also relatively low in the river samples but slightly higher at SP6.2 and SP7.2. These two sites also have high Hg concentration, on the same level as in the TG samples.

HCN levels in tailing waste and river samples are both high. It is important to note that the values in the river sediments exceed the government’s 0.02 ppm threshold (Government Regulation of the Republic of Indonesia, 2001). The negative correlation between $\chi_{fd}(\%)$ and HCN, Cu, Fe, As dan Hg suggests that $\chi_{fd}(\%)$ can become a quick first-order proxy to monitor HCN levels in river sediments. The correlation indicates an increase in the magnetic domain and the formation of possible strong compounds, i.e., Fe - CN and/or Au - CN, and weak compounds, such as Ag - CN and/or Cu - CN. The formation of these compounds may occur in the environment, as described in previous studies (Jaszczak et al., 2017). Further research should be conducted along other rivers that flow through areas of artisanal gold mining to determine how robust this correlation is. It has been established that the Tong waster area or tailing ponds have a relatively high frog fatality rate, which may be linked to the high HCN concentration (Donato et al., 2007). A method that allows for rapid first-order monitoring of a large area would be beneficial, allowing more time-consuming or expensive methods to focus on areas where the environment may be threatened. Figure 4 shows the correlation between $\chi_{fd}$ or $\chi_{fd}(\%)$ with different major elements as determined from AAS. Pearson’s correlation list is available in Table 2. There is a good correlation between $\chi_{fd}$ and Fe content in the river sediments, but this does not hold for the tailing.
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Figure 4. Linear correlations that are statistically significant for: (a) Fe versus $\chi_{lf}$; (b) Cu versus $\chi_{lf}$; (c) Fe versus $\chi_{fd}$ (%); (d) Cu versus $\chi_{fd}$ (%); (e) As versus $\chi_{fd}$ (%); and (f) HCN versus $\chi_{fd}$ (%). Note. Open symbols are not considered in the respective correlation

sample (Figure 4a), and a particularly good correlation with Cu when all samples are considered. It suggests that the lithogenic component of river sediments controls $\chi_{lf}$. A significant correlation between magnetic susceptibility of low frequency and Fe element was also reported from the surface sediment of the Brantas River (Mariyanto et al., 2019a).
Table 2

Pearson Correlations (R) between magnetic susceptibility and elements 1) using only river sediments; 2) including GLIH

<table>
<thead>
<tr>
<th></th>
<th>Xhf</th>
<th>Xlf</th>
<th>Xfd</th>
<th>Cu</th>
<th>Fe</th>
<th>Cr</th>
<th>Mn</th>
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<tr>
<td>Xlf</td>
<td>-0.240</td>
<td>-0.70</td>
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<tr>
<td>Xfd</td>
<td>0.012</td>
<td>0.796**</td>
<td>0.830**</td>
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<tr>
<td>Cu</td>
<td>0.157</td>
<td></td>
<td></td>
<td>0.831**</td>
<td>0.906**</td>
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<tr>
<td>Fe</td>
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<td>0.200</td>
<td>0.301</td>
<td>0.401</td>
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<tr>
<td>Cr</td>
<td>0.101</td>
<td>0.107</td>
<td>0.292</td>
<td>0.316</td>
<td>0.596</td>
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<tr>
<td>Mn</td>
<td>-0.071</td>
<td>-0.052</td>
<td>-0.656**</td>
<td>-0.837**</td>
<td>-0.812**</td>
<td>0.828**</td>
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<tr>
<td>As</td>
<td>-0.448</td>
<td>-0.505</td>
<td>-0.620**</td>
<td>-0.786**</td>
<td>-0.587</td>
<td>-0.023</td>
<td>-0.522</td>
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<tr>
<td>Hg</td>
<td>-0.125</td>
<td>-0.042</td>
<td>-0.768**</td>
<td>-0.834**</td>
<td>-0.822**</td>
<td>-0.262</td>
<td>-0.300</td>
<td>0.840**</td>
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* p < 0.05, ** p < .005

Figure 5. The mapping of low-frequency magnetic susceptibility and Hg and HCN content along Kuris River and some point of tailing area

Furthermore, strong significant correlations are seen between $\chi_{fd}(\%)$ and Cu and HCN and between $\chi_{fd}(\%)$ and Fe and As. (Figure 4). Usually, high correlations are shown by $\chi_{lf}$ and some heavy metals as well as in other polluted sediment, but in this case, a good correlation is present between $\chi_{fd}(\%)$ and some pollution inputs like HCN. In this case,
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where an anthropogenic input is not strong enough, $\chi_{fd}(\%)$ may serve as a good proxy indicator of pollution. It is different from the fact that the wastes of mining activities are heavy metals (Morales et al., 2016). The high correlation between Hg and HCN suggests that those elements and compounds are used in high concentrations in the second step of gold binding. Figure 5 illustrates magnetic susceptibility as well as Hg and HCN content of all surface sediment samples collected along Kuris River, including the gold mining waste.

Figure 5 depicts the mapping for the levels of magnetic susceptibility, HCN, and Hg content in each sampling point as a result of Kuris River’s dominant pollutant input, which represents how much pollutant enters the river where agriculture and residential areas are irrigated by the river. Based on this evidence, we can estimate how much HCN and Hg will pollute agricultural soils over time if traditional mining cannot be stopped or improved with immediate waste management. As previously stated, cyanide weakens the human body and causes various diseases, such as hypothyroidism, renal damage, and miscarriages (Jaszczak et al., 2017).

CONCLUSION
Kuris River sediments have an average $\chi_{lf}$ of $97 \times 10^{-8}$ m$^3$/kg, which is relatively low compared to other rivers in Indonesia, generally contributed by volcanic materials. The correlation between $\chi_{lf}$ and lithogenic elements suggests the dominant influence of the component. There is no trend in $\chi_{lf}$ along the river flow, which supports the notion that, in this case, the contribution of anthropogenic $\chi_{lf}$ is minor. $X_{fd}(\%)$ indicates that the magnetic minerals are larger than SP. The correlation between $\chi_{fd}(\%)$ and HCN and other elements such as Cu, Fe, As, and Hg suggests that $\chi_{fd}(\%)$ may be used as the first-order proxy for HCN, As, and Hg content in sediment for nonmagnetic pollutant input, particularly in the case of gold mine tailing.

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