Relationships of Magnetic Properties and Heavy Metals Content of Guano in Bat Cave, South Sulawesi, Indonesia

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Abstract
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Keywords
Guano; Magnetic Susceptibility; Heavy Metals; Pearson Correlation

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RESEARCH PAPER

Relationships of Magnetic Properties and Heavy Metals Content of Guano in Bat Cave, South Sulawesi, Indonesia

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Abstract

Bat Cave is one of the caves with guano deposits in the Rammang–Rammang karst area, South Sulawesi, Indonesia. The guano deposits can indicate environmental changes in the cave. This study aims to analyze the magnetic properties and correlation between magnetic susceptibility and heavy metal content in guano. Sampling was carried out in Bat Cave, South Sulawesi, Indonesia, and magnetic susceptibility, XRD (mineralogy analysis), and XRF (heavy metal content analysis) were measured. The results showed that the guano sample contained superparamagnetic grains and stable single domain (SP-SSD) measuring $<0.05$ m with a low magnetic susceptibility value ranging from 7.2 to $147.6 \times 10^{-8}$ m$^3$/kg. The location of caves in karst areas and climate change affect the magnetic grains. The Pearson correlation coefficient analysis results showed that magnetic susceptibility had a negative correlation with the heavy metal content of Fe. Meanwhile, Fe has a positive correlation with the content of other heavy metals such as Cu, Zr, and Nb. Thus, magnetic susceptibility has the potential as a proxy indicator to detect the presence of heavy metals.

Keywords: Guano, Magnetic susceptibility, Heavy metals, Pearson correlation

1. Introduction

Guano has been studied in environmental magnetic studies for ancient climate changes [1] and environmental changes in caves [2,3]. In its development, environmental magnetic studies have been carried out on materials such as urban soils [4–7], iron sands [8–11], river sediments [12–16], lake sediments [17–19], marine sediments [20,21], leachate [22–25], agricultural land [26–28], peatland [29–33], volcanic soil [34], and guano [35–37]. Environmental magnetism involves the relationship of magnetic properties to the process of environmental change due to sediment transport factors, human activities, industrial activities, and agricultural activities [14].

Guano deposits can record environmental changes in caves. Assessment of environmental changes is accompanied by changes in magnetic mineralogy and can be traced through magnetic minerals as carriers of the magnetic properties of guano. Magnetic properties can be reviewed based on the type of mineral, mineral concentration, domain and grain size, and grain shape [38]. Thus, the source of magnetic minerals can be estimated. Magnetic identification and measurement were chosen because their effectivity, quick results, inexpensive, and do not damage the material. This method is complemented by chemical analysis [38,39].

Magnetic minerals are influenced by the content of iron (Fe) which is a ferromagnetic element. Fe can be detected, although its presence in magnetic minerals is small. In environmental magnetic studies, it is proven that the magnetic mineral content is associated with heavy metals content [40,41]. Similarly, magnetic properties can indicate the presence of heavy metals in guano deposits.

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Several studies have been conducted on the relationship between magnetic susceptibility and heavy metal content. The study of the relationship between magnetic susceptibility and heavy metal content of urban topsoil in the arid area of Isfahan, central Iran, showed that heavy metal concentrations (Pb, Zn, Cu, and Ba) were highly correlated with magnetic susceptibility. In contrast, As, Sr, Cd, Mn, V, and Cr show a weak correlation in the topsoil of urban areas [42]. A high positive correlation was obtained between Fe concentration with $\chi_{\text{LF}}$ in several rocks [43]. A high positive correlation was obtained between Cu, Fe, Mn, Zn, and Co with $\chi_{\text{LF}}$. Meanwhile, Ni and Cr did not show a significant correlation with $\chi_{\text{LF}}$. The positive correlation between Cu, Fe, Mn, and Zn is related to industrial activities and urbanization in the study area, increasing heavy metals’ susceptibility and magnetism on the soil surface [44]. A negative correlation was obtained between $\chi_{\text{LF}}$ with CaCO$_3$ and gypsum. The presence of CaCO$_3$ and gypsum as diamagnetic materials causes a decrease in magnetic susceptibility [45].

A study of guano from the Bubau and Mampu Caves in South Sulawesi found a strong correlation between magnetic susceptibility and Fe content [35]. Furthermore, studies on guano from Solek Cave, West Sumatra, found a weak correlation between magnetic susceptibility and Fe content [36]. The study of the relationship between magnetic susceptibility and heavy metal content also found a weak correlation in the guano of Bau–Bau cave, East Kalimantan [46]. These studies prove that magnetic susceptibility correlates with heavy metal content [47,48]. In addition, environmental magnetic studies are associated with magnetic minerals, geochemical parameters, domains, and grain size [39]. Specific magnetic characteristics are influenced by transporting material from the outside environment into the cave through wind or water flow during the rainy season [35]. Furthermore, it is also influenced by the geology of the location studied.

The characterization of magnetic properties and the correlation of magnetic susceptibility with heavy metal content in guano caves in karst environments have not been studied, especially in Indonesia. Therefore, studying the magnetic environment and its relationship with heavy metal content is essential. Thus, this study aims to improve understanding of magnetic analysis and its relationship with heavy metals and test the magnetic susceptibility as a proxy for heavy metals in guano in the karst environment, especially in Bat Cave. Magnetic analysis was performed from the magnetic measurements and heavy metal content, X-Ray Fluorescence (XRF), and X-Ray Diffraction (XRD). The test results are used to describe the relationship between magnetic susceptibility and the heavy metal content of guano.

2. Materials and methods

Bat Cave is located in the Rammang–Rammang Karst Area, particularly Berua Village. Bat Cave has a cave mouth width of about 10 m, a cave width of about 25 m, a cave height of about 50 m, and a length of cave that can be reached about 30 m. Bat Cave is located at an elevation of 54 m 119°40’19.5” east longitude and 4°58’33.0” south latitude.

Guano samples were taken from the Bat Cave in the Rammang–Rammang Karst Area, Maros, South Sulawesi, Indonesia. There are thirty points from the mouth of the cave to the cave’s depth that can be reached 30 m due to the oxygen levels in the cave at a depth of more than 30 m getting smaller, so the cave guider does not allow it. The sampling point locations are shown in Fig. 1. At each sampling point, at a depth of 10 cm the sample was taken and put into polyethylene plastic. The guano samples were prepared in the laboratory by being cleaned of impurities and dried at room temperature. The samples were mashed using pastels and mortar, then sieved using a 100 mesh sieve. At this stage, a sample of guano powder is produced. The guano powder sample was weighed at 15 g using a digital scale and put into a plastic clique.

Magnetic measurements were carried out on samples of guano powder using a Bartington MS2B Susceptibility meter (Bartington Instrument Ltd., Oxford, UK), which operated at low (470 Hz) and high (4700 Hz) frequencies [39]. The measurement results were analyzed using Multisus software. Measurements at two frequencies to obtain magnetic susceptibility depend on frequency ($\chi_{\text{FFD}}$) [49,50] so that the types of magnetic minerals, magnetic mineral domains, and magnetic mineral sources can be interpreted. Based on the results of magnetic susceptibility testing, ten samples with the highest values were selected. The selected guano samples were tested using a Shimadzu Uniquant X X-Ray Fluorescence (XRF) device and analyzed using PCX Uniquant software to determine the magnetic mineral content and heavy metals.

Two samples were selected for X-Ray Diffraction (XRD) testing from ten samples. The samples were put into a beaker and extracted using a bar magnet to separate the magnetic particles and not the magnetic particles contained in the guano sample. The sample is put in a plastic bag and tested. At this stage, a sample of the extracted guano powder is produced. XRD testing using the Rigaku MiniFlex II
type XRD tool to determine the type and concentration of magnetic minerals. It operates at 30 kV voltage, 15 mA current, 0.02° scan width, 4°/min scan rate per time, and 5°-90° scan interval. Qualitative analysis using PDXL2 software with search and match method equipped with ICDD (International Center for Diffraction Data) card 2011. At the same time, the quantitative analysis uses the RIR (Reference Intensity Ratio) method [51,52].

3. Results and discussion

A summary of descriptive statistics of magnetic parameters of the Bat Cave guano sediment sample is presented in Table 1. All magnetic parameters were normally distributed according to the Kolmogorov–Smirnov (K–S) test. Meanwhile, the graph plots of the magnetic susceptibility ($\chi_{LF}$) and frequency-dependent magnetic susceptibility ($\chi_{FD}$) at each point are shown in Fig. 1. The magnetic susceptibility of guano samples ($\chi_{LF}$) ranged from 7.20 to 147.60 $\times$ 10$^{-8}$ m$^3$/kg. The $\chi_{LF}$ profile of the Bat Cave guano sample fluctuated along with the cave depth as far as 15 m from the cave mouth. The lowest $\chi_{LF}$ values are $7.2 \times 10^{-8}$ m$^3$/kg, located at point 20. $\chi_{LF}$ values more than $100 \times 10^{-8}$ m$^3$/kg are located at points 8, 13, 27, and 29. Meanwhile, $\chi_{FD}$ varies from 2.78 to 8.70%.

The $\chi_{LF}$ range of guano samples contains a mixture of (canted) antiferromagnetic and paramagnetic minerals. Meanwhile, $\chi_{LF}$ guano Bat Cave mostly has a relatively low value. The low $\chi_{LF}$ indicates that the guano sample’s iron (Fe) level is also low [53]. Fe content is one of the constituent elements of guano deposits associated with other elements in the Bat Cave. Thus, it is indicated that the Bat Cave is still natural and not influenced by anthropogenic factors. Several studies have reported that the magnetic susceptibility of guano in low-value surface areas is not influenced by

Table 1. Descriptive statistics of the magnetic susceptibility of Bat Cave guano samples ($n = 30$).

<table>
<thead>
<tr>
<th>Descriptive Statistics</th>
<th>Variable</th>
<th>$\chi_{LF}$ ($x 10^{-8} \text{ m}^3/\text{kg}$)</th>
<th>$\chi_{HF}$ ($x 10^{-8} \text{ m}^3/\text{kg}$)</th>
<th>$\chi_{FD}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum</td>
<td>7.20</td>
<td>7.00</td>
<td>2.78</td>
<td></td>
</tr>
<tr>
<td>Maximum</td>
<td>147.60</td>
<td>135.50</td>
<td>8.70</td>
<td></td>
</tr>
<tr>
<td>Range</td>
<td>140.40</td>
<td>128.50</td>
<td>5.92</td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>73.92</td>
<td>69.42</td>
<td>5.64</td>
<td></td>
</tr>
<tr>
<td>Median</td>
<td>70.15</td>
<td>66.60</td>
<td>5.64</td>
<td></td>
</tr>
<tr>
<td>Std. Deviation</td>
<td>26.71</td>
<td>24.13</td>
<td>1.48</td>
<td></td>
</tr>
<tr>
<td>CV (%)</td>
<td>36.13</td>
<td>34.76</td>
<td>26.24</td>
<td></td>
</tr>
<tr>
<td>Skewness</td>
<td>0.55</td>
<td>0.45</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>Kurtosis</td>
<td>1.95</td>
<td>2.10</td>
<td>−0.54</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. Sampling location in Bat Cave, South Sulawesi, Indonesia.
anthropogenic but by the location of the cave and climate [35].

Bat Cave guano samples have a higher $\chi_{LF}$ than $\chi_{HF}$. The bar graph plot of $\chi_{LF}$ and $\chi_{HF}$ is shown in Fig. 2. It can be seen that $\chi_{LF}$ and $\chi_{HF}$ have significant differences in values. Different values of specific mass measurement of magnetic susceptibility at different frequencies will result in frequency-dependent magnetic susceptibility ($\chi_{FD}$), which indicates the presence and amount of superparamagnetic minerals [53]. Variation of $\chi_{FD}$ (2.78–8.70%) indicates that the guano sample belongs to the category of medium $\chi_{FD}$ % in which the guano sample contained an admixture of superparamagnetic (SP) and coarser non-SP grains, or SP grains <0.005 μm [39]. SP behavior is a unique property of the simple domain (SD), with a grain size of <0.03 m. The magnetization is solid but unstable. The thermal energy counteracts the induced magnetization quickly after removing the magnetic field. Its magnetic susceptibility is much greater than that of paramagnetic behavior. SP is characterized by its response to susceptibility measured at different frequencies.

The distribution of domains and magnetic mineral sources in the guano sample was interpreted by plotting a scattering of $\chi_{FD}$ and $\chi_{LF}$ as shown in Fig. 3. The range of $\chi_{FD}$ values from 2 to 10% shows that the domain type is dominated by superparamagnetic (SP) and stable single domain (SSD). SP domain has a finer grain while SSD has a coarser grain [54]. Magnetic mineral sources are indicated to be pedogenic, bacterial magnetosomes, and autogenic or biogenic [39]. These sources can be influenced by climatic factors, namely the transportation of materials through water flowing into the cave and the cave's location in the karst area, namely the minerals that make up the karst, such as calcite (CaCO₃) and gypsum (CaSO₄·2H₂O). The presence of calcite and gypsum as diamagnetic materials causes a decrease in magnetic susceptibility [45]. In addition, it comes from bat droppings and material transported by wind from outside the cave into the cave [36,37]. Therefore, following the interpretation of the $\chi_{LF}$ distribution of the Bat Cave guano sample, the cave is still natural.

XRD analysis was done to identify magnetic mineral content in guano samples. As shown in Fig. 4, the XRD diffractogram of the extracted guano samples. Based on the results of XRD analysis, the guano samples contained magnetite (Fe₃O₄) and hexaferrum (Fe). The calcium indium content was also identified, namely Ca₃In in sample T08 and Ca₈In₃ in sample T29. In addition, the guano sample contains silicon dioxide (SiO₂) and calcium aluminum antimonide (Ca₁₄AlSb₁₁). Minerals Ca₃In, Ca₈In₃, Ca₁₄AlSb₁₁, and SiO₂ are thought to originate from the external environment and enter the cave through water media that drip on the walls of the cave during the rainy season. Meanwhile, magnetite and hexaferrum are thought to have come from the external environment through the wind entering the cave. Elemental calcium in the minerals calcium indium and calcium aluminum antimonide originates from carbonate rocks. Carbonate rocks contain karst constituent minerals such as calcite (CaCO₃), aragonite (CaCO₃), and dolomite (CaMg(CO₃)₂). However, it can also occur in other rocks formed from these minerals and other watersoluble minerals such as gypsum (CaSO₄·2H₂O).
This result is by the $\chi_{FD}$ interpretation regarding the magnetic mineral source of the guano sample.

Fe$_3$O$_4$ is a mineral with solid magnetic properties or high magnetic susceptibility, while CaIn has weak or low magnetic susceptibility. Thus, the guano sample contains a mixture of minerals with strong and weak magnetic properties. Because the concentration of CaIn is greater than Fe$_3$O$_4$, it indicates that the value of magnetic susceptibility in the guano sample is low. It measures the magnetic susceptibility of the Bat Cave guano sample, which was obtained low.

The results of the XRF analysis regarding the heavy metals content in the Bat Cave guano samples with varying concentrations are shown in Table 2. The heavy metals identified were iron (Fe), zinc (Zn), copper (Cu), zircon (Zr), and neodymium (Nb). The heavy metal in guano is indicated as material carrying magnetic properties in the cave. Fe dominated the heavy metal content of the guano sample.

The concentration of Fe in all samples showed low concentrations, thus causing low magnetic susceptibility. The concentration of Fe becomes the controller of the magnitude of the magnetic susceptibility in a sample [36,50,58].

The high concentration of heavy metals indicates the high value of magnetic susceptibility and vice versa. This paper reports that the source influences the magnitude of guano’s magnetic and heavy metal susceptibility. Mixed sources are pedogenesis, bacterial magnetosomes, autogenic, and biogenic [59,60]. Magnetic mineral content can occur naturally due to climatic factors and the location where this source acts as a contaminant [35]. Thus, the magnetic susceptibility parameter can be used as a proxy indicator to detect the presence of heavy metals [47,48].

The Pearson correlation coefficient between susceptibility magnetic and heavy metal content of the guano samples is shown in Table 3. The Pearson correlation coefficient shows how strong the relationship between heavy metals as well as between susceptibility magnetic and heavy metals. The Pearson correlation coefficient between $\chi_{FD}$ and Fe ($r = 0.38$) has a positive correlation (Fig. 5a). Pearson correlation coefficient between $\chi_{LF}$ and Fe ($r = -0.24$) (Fig. 5b), Zn ($r = -0.20$), and Cu ($r = -0.36$) has a negative correlation. The same is true between $\chi_{FD}$ and Zn ($r = -0.39$).

Meanwhile, the Pearson correlation coefficient $\chi_{LF}$ with Zr ($r = 0.13$) and $\chi_{LF}$ with Nb ($r = 0.14$) have a positive correlation. Likewise, the Pearson correlation coefficient $\chi_{FD}$ with heavy metal content (Zr $r = 0.43$ and Nb $r = 0.53$) has a positive correlation. Pearson correlation coefficient $\chi_{FD}$ with Cu ($r = 0.08$) almost does not correlate. The negative correlation of $\chi_{LF}$ with Fe indicates that the low concentration of Fe causes a low magnetic susceptibility value of the guano sample. Fe is a ferromagnetic element affecting the magnetic susceptibility value of guano samples [14,36].

Elements of Fe with other heavy metals such as Cu, Zr, and Nb have a positive Pearson correlation coefficient. Meanwhile, Fe has a negative correlation with Zn ($r = -0.28$). Fig. 6 shows a plot of Fe with
other heavy metals (Zn, Cu, Zr, and Nb). Based on these results, magnetic susceptibility is known as a proxy indicator to detect the presence of heavy metals, where heavy metals are associated with Fe [47,48]. Sources of magnetic susceptibility and heavy metals can be affected by the location of the guano sampling. The guano sample came from the Bat Cave in a karst environment. Location and climate factors affect the Fe content in magnetic minerals [35]. This evidence confirms that the Bat Cave is still natural due to the low magnetic particles of the guano sample. Magnetic particles come from pedogenic components, bacterial magnetosomes, and autogenic or biogenic components. In addition, the presence of heavy metals in the guano samples affects the magnetic particles.

4. Conclusions

Bat Cave guano’s magnetic susceptibility is relatively low and varies from 7.2 to $147.6 \times 10^{-8}$ m$^3$/kg. The guano sample contains fine and coarse superparamagnetic (SP) and stable single domain (SSD) grains with a grain size of $<0.05$ m. The guano
samples contained a mixture of antiferromagnetic and paramagnetic minerals. The value of magnetic susceptibility is influenced by Fe content. Fe element is associated with several other heavy metals such as Zn, Cu, Zr, and Nb. The correlation obtained is dominantly positive. The location and climate factors of Bat Cave in a karst environment obtained is dominantly positive. The location and element is associated with several other heavy elements.

**Conflicts of interest**

No conflict of interest among authors.

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**References**


Analysis of magnetic minerals of iron sand deposit in Sampulungan Beach, Takalar Regency, South Sulawesi using the X-ray diffraction


