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Magnetic Susceptibility Properties of Pesticide Contaminated Volcanic Soil

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Abstract. Pesticides, unfortunately, are still widely used in many countries as way to eradicate agricultural pests. As they are being used continuously over a long period of time, they accumulate as residues in soils posing serious threats to the environment. In this study, we study the changes in magnetite-rich volcanic soils that were deliberately contaminated by pesticide. Such changes, in any, would be useful in the detection of pesticide residue in contaminated soils. Two different types of magnetically strong volcanic soil from the area near Lembang, West Java, Indonesia were used in this study where they were contaminated with varying concentrations of pesticide. The samples were then measured for magnetic susceptibility at two different frequencies. The measurements were then repeated after a period of three months. We found a reduction of magnetic susceptibility as well as a reduction in SP (superparamagnetic) grains proportion in contaminated soil. These might be caused by pesticide-induced magnetic dissolution as supported by SEM analyses. However the impact of pesticide concentration as well as exposure time on magnetic dissolution is still inconclusive.

Keywords: Pesticide, Volcanic soil, Magnetite, Magnetic grain.
PACS: 91.25.fd

INTRODUCTION

Pesticides are widely used worldwide by farming communities to exterminate pest, insects, and other plant diseases. In the long run, however, the use of pesticide is harmful to the environment. Prolong use of pesticide lead to residual accumulation in soils and also in agricultural products. Several types of pesticides stay long as they have half-life of about 20 years more [1]. Pesticide residue in our food chain has been known to cause illnesses ranging skin disease to cancer [2]. The maximum residue limits (MRLs) for pesticide differs from one country to another ranging from 0.3 mg/kg in the USA to 9.2 mg/kg in Australia [2].

Monitoring pesticide residue in soil is of great interest to soil and environmental scientists. The process is often carried out by chemical analyses which are often expensive and laborious. In this study, we investigate the effectiveness of rock magnetic methods in identifying pesticide residue in volcanic soil. In places like Java, volcanic soil is the predominant type of soil and is very important economically. Compared to other analytical methods, rock magnetic methods are relatively inexpensive, fast, and non-destructive [3-5]. In this study the rock magnetic method is represented by the measurement of magnetic susceptibility. The rock magnetic methods would be complemented by visual and compositional analyses using scanning electron microscopy (SEM). SEM provides information about the shape, size and morphology but also the chemical compositions of magnetic grains. The use of SEM analyses in rock magnetic studies has been well documented in the literature [6].

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METHODS

Volcanic samples were obtained from Bukit Tunggul Cinchona Plantation (6° 50′ 5.1948″ S; 107° 43′ 42.1148″ E, elevation 1499 masl) located about 25 km to the northeast of Bandung, the capital-city of West Java Province. The soil samples were obtained from a soil-outcrop about 3 m in height. They were obtained from two distinct layers, namely the topmost organic layer (horizon 1) and the blackish block and ash-flow deposit (horizon 2). Within each horizon, thirty cylindrical samples (2 cm in diameter and 2.2 cm in height) were obtained at about 10 cm intervals. Thus, there were 60 samples in this study. First ten samples from each horizon were considered to be the control samples. The second ten samples from each horizon were contaminated by pesticide with varying concentration. The first concentration is made by mixture of 5 ml pesticide with 45 ml aqua bidest distilled water, the second concentration is of 10 ml pesticide with 40 ml of aqua bidest, the third concentration is of 15 ml of pesticide with 35 ml of aqua bidest etc. The tenth concentration was only pure pesticide. The second ten samples were kept for three months before analyses. The last ten samples were treated similarly to the second ten samples, but they were kept until 6 months.

All the samples were subjected to magnetic susceptibility measurement. This was carried out on a a Bartington MS2 system (Bartington Instruments Ltd., Oxon, UK) equipped with a dual frequency sensor (type MS2B), respectively at 470 and 4700 Hertzs. The measured values are given as mass-specific magnetic susceptibilities at low or 470 Hz frequency (χ_{LF}) and as that at high or 4700 Hz frequency (χ_{HF}). In general, parameter χ_{LF} is often referred as the bulk-magnetic susceptibility that approximates the total concentration of Fe-bearing minerals in the samples. In this study we use a parameter termed frequency-dependent susceptibility or FDS that approximates to the proportion of superparamagnetic (SP) ferrimagnetic minerals. In this study FDS is defined as Eq. (1).

$$\chi_{FD\%} = 100\% \times \frac{(\chi_{LF} - \chi_{HF})}{\chi_{LF}} \qquad (1)$$

Later selected samples were subjected to SEM analyses on a JEOL scanning electron microscope type 3060LA (Jeol Ltd, Japan) that is equipped with BSE (Back Scattering Electron) and EDX (Energy Dispersive X-Ray) features. BSE capability is important in imaging grains high sizable iron or metallic content, while that of EDX allows the estimation of elements through their oxides. Magnetic grains were extracted from the samples by mixing the samples with aqua bidest to form very thin slurries. A plastic covered strong neodymium magnet was then placed and stirred inside the slurries. Extracted magnetic grains were then placed in a covered petri dish ready for SEM analyses.

RESULTS AND DISCUSSION

Table 1 shows the average values of magnetic parameters χ_{LF}, χ_{HF}, and $\chi_{FD\%}$ of control samples for horizon1 and horizon 2. Samples of horizon 1, in general, has more Fe-bearing minerals than that of horizon 2 as indicated by their higher χ_{LF} values. This might be due to magnetic enhancement towards the soil surface. Although the samples of horizon 2 have lower magnetic concentration, they have greater variation in SP content as shown by their $\chi_{FD\%}$ values.

TABLE 1. Results of magnetic measurement for control samples in both horizon 1 and 2.

Horizon	χ_{LF} (10^{-8} m^3/kg)	χ_{HF} (10^{-8} m^3/kg)	$\chi_{FD\%}$ (%)
Horizon 1	779.5 ± 69.3	751.5 ± 55.2	3.4 ± 2.2
Horizon 2	421.0 ± 35.5	399.8 ± 21.8	4.9 ± 3.3

For contaminated samples of horizon 1, the results of magnetic measurement are summarized in Fig. 1. Fig. 1a show that the χ_{LF} of contaminated samples (both 3 and 6 months) are significantly lower than that of control samples inferring that the presence of pesticide might reduce the quantity of Fe bearing minerals in volcanic soil. Moreover, the presence of pesticide might also reduce the proportion of SP grains in volcanic soils as shown by the lower values of $\chi_{FD\%}$ in contaminated samples (Fig. 1b). Both Figs. 1a and 1b, however, do not clearly shown the impact of pesticide concentration as well as the exposure time to the above changes. Higher concentration of pesticide does not necessarily means greater magnetic reduction. Similarly, longer exposure time (6 months) does not necessarily means greater magnetic reduction.

Fig. 2 summarizes the results of magnetic measurements for contaminated soils of horizon 2. Like that in horizon 1, the χ_{LF} values of contaminated samples in horizon 2 are also significantly lower than that of control samples (Fig. 2a). The $\chi_{FD\%}$ values of these samples are also lower than that of control samples (Fig. 2b). Moreover, the results for contaminated samples of horizon 2 also show that there is no significant impact of the impact of pesticide concentration as well as the exposure time to magnetic reduction.

Thus it is plausible that the smallest concentration of pesticide in this study is more than enough to initiate the magnetic reduction or dissolution. Increasing the pesticide concentration might have little effect. Similarly, the shortest exposure time to pesticide (3 months) might be sufficient to initiate the process of magnetic reduction so that longer exposure time (6 months) would have similar results.

Figs. 3 and 4 show the results of SEM analyses for control samples as well a contaminated samples in horizons 1 and 2 respectively. Fig. 3a depicted typical magnetic grains extracted from control samples. Marked grain in this picture depicts the abundance of bitetrahedral-shaped iron oxide, magnetite lite which is often associated with titanium. Such grain is typically found in volcanic soil [7]. In general, magnetic grains from control samples have relatively smooth surface (Fig. 3a) while that from contaminated samples have rough or cracked surface (Figs. 3b and 3c) suggesting the presence of magnetic dissolution process [6]. Magnetic grains shown in both Figs. 3b and 3c were extracted from the most contaminated samples after 3 and 6 months respectively.

Similar to that of horizon 1, magnetic grains extracted from control samples in horizon 2 also have relatively smooth surface (see marked grain in Fig. 4a). Magnetic grains extracted from contaminated samples in horizon 2 also show evidence of early stage of dissolution in fractured surfaces (see marked grains in Figs. 4b and 4c). Few smaller magnetic grains were also seen attached to larger grains. This might be due to growth of new but non-SP magnetic grains as the overall values of $\chi_{FD\%}$ in contaminated samples are lower than that of control samples.

Higher concentration of pesticide is expected to speed up magnetic dissolution process. Prolonged exposure is also expected to increase the severity of dissolution. However, there is no evidence for either expectation in SEM analyses.

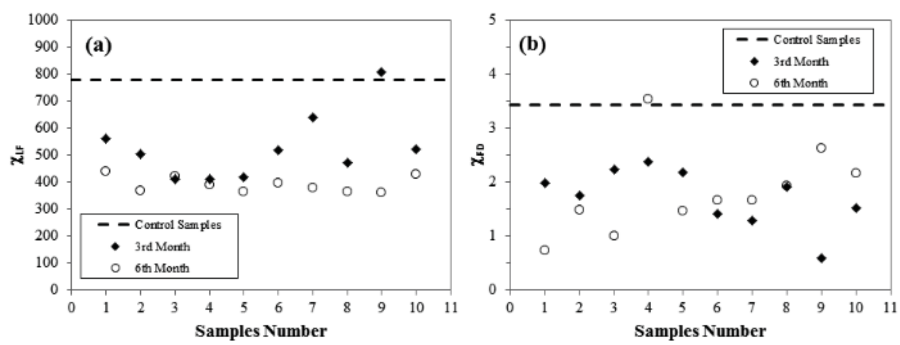

FIGURE 1. Results of magnetic measurement for contaminated volcanic soil samples from horizon 1 presented as variation of χ_{LF} (a) and $\chi_{FD\%}$ (b).The dashed lines indicate the average values for control samples. The sample numbers in the abscissa refers to pesticide concentrations. Smaller number means lower pesticide concentration.

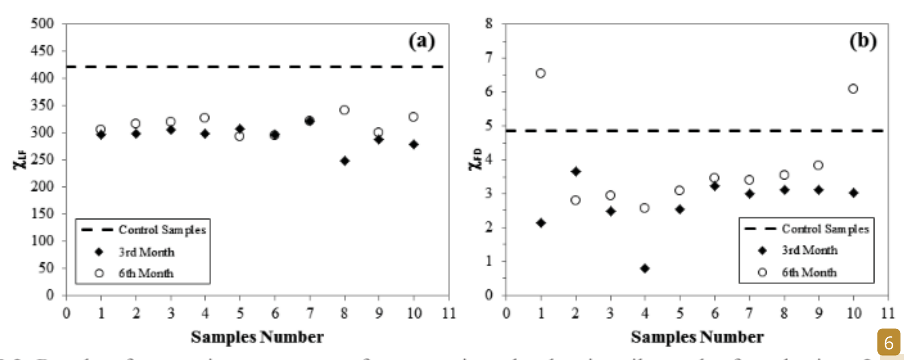

FIGURE 2. Results of magnetic measurement for contaminated volcanic soil samples from horizon 2 presented as variation of χ_{LF} (a) and $\chi_{FD\%}$ (b).The dashed lines indicate the average values for control samples. The sample numbers in the abscissa refers to pesticide concentrations. Smaller number means lower pesticide concentration.

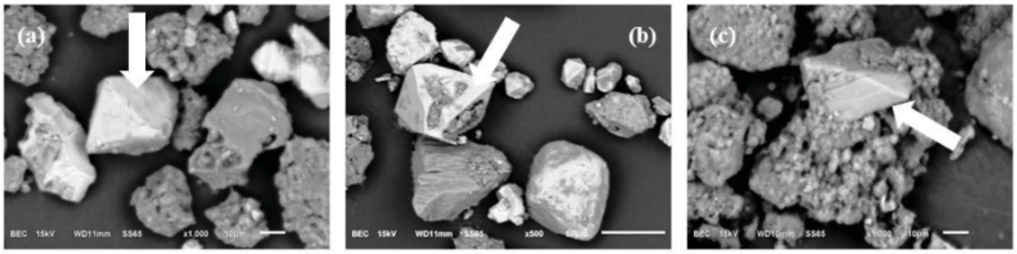

FIGURE 3. SEM images of magnetic grains extracted from samples from horizon 1. (a) grains from control sample, (b) grains from 3 months contaminated sample, and (c) grains from 6 months contaminated sample. See text for specially marked grains.

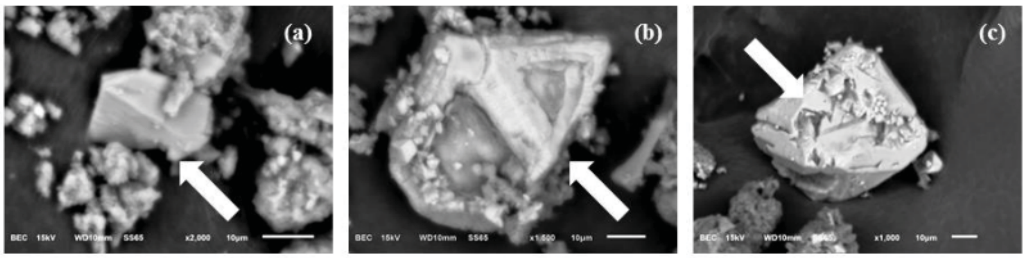

FIGURE 4. SEM images of magnetic grains extracted from samples from horizon 2. (a) grains from control sample, (b) grains from 3 months contaminated sample, and (c) grains from 6 months contaminated sample. See text for specially marked grains.

CONCLUSION

Magnetic measurements and SEM analyses on control and contaminated volcanic soil samples show that the presence of pesticide in volcanic soils not only reduced the abundance of Fe-bearing minerals but also reduced the proportion of SP grains. This finding is important in the quest to find an alternative method in pesticide detection. The quantity of contaminant and the time exposure to contaminant might play a significant role in the reduction process but they roles were found to be inconclusive

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