

THE IMMOBILIZATION OF HEAVY METALS BY A TROPICAL ANDEPTS TREATED WITH LIME AND ORGANIC COMPOSTS

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ABSTRACT

Heavy metal solubility in soils has been reported to be altered by an addition of lime and/ or organic materials. This research was intended to evaluate the effects of some lime or organic materials on the extractability of heavy metals in an andic soil (Andepts), which is well-known to have an extremely high adsorption capacity with respect to organic compounds and phosphate. Soil sample, collected from South Lampung, Indonesia, lime materials comprising CaCO_3 , $\text{Ca}(\text{OH})_2$, and $\text{CaMg}(\text{CO}_3)_2$, and composts of plant leaf ("alang-alang", corn, casava, and soybean) were used. The soil sample (air dry, 2-mm-sieved) was treated independently with lime (at a level to increase its pH about 2 units) or with organic compost (at 10 Mg ha^{-1}). The mixture was spiked with a standard solution containing 10 mg kg^{-1} Cu, Cd, Mn, and Zn and incubated for 8 weeks at the soils' field moisture capacity. The heavy metals were extracted with DTPA and measured with flame AAS. The results showed that the extractable heavy metals in limed soil (except Cd) were in general greater than those in unlimed soils, probably due to increased concentrations of active soluble organic materials which might have complexed with heavy metals with the increase in soil pH. The organic composts generally did not effect the extractability of heavy metals except Mn, that increased with compost addition in samples not spiked with heavy metals, particularly in samples treated with soybean compost. The insignificant difference in the extractability of heavy metals between the spiked and unspiked soil samples and the lower Mn extractability in spiked soil samples suggested that the Andepts was a good absorber for heavy metals, except for Cd. The majority of Cd added was recovered both in lime- or in compost-treated soils. Based on the % recovery values, the preference of the soil toward the heavy metals followed the sequence of $\text{Mn} > \text{Zn} > \text{Cu} > \text{Cd}$.

Keywords : Lime, organic composts, heavy metals, copper, cadmium, manganese, zinc, Andosols, Andepts.

Andosols or Andepts are soils with unique characteristics, of which their allophanic minerals show an extremely high adsorption capacity with respect to organic compound and phosphate (Paterson *et al.*, 1991). This characteristic is attributed to its larger specific adsorption surface. Thus, andosols can be expected to adsorb great amounts of heavy-metals cations and be a good soil for immobilizing heavy-metals contaminants from various sources.

Similar to those of other soils, the adsorption capacity of Andosols can also be enhanced by an addition of lime and/ or organic materials. The increase in soil pH driven by lime addition may activate the various functional groups including those of the organic origins, which are abundant in this soil; thereby, it may

increase the soil adsorption capacity with respect to heavy metals (Salam *et al.*, 1996; Salam, 1996; 1995; 1993; Helmke *et al.*, 1995; Helling *et al.*, 1964). Salam *et al.* (1996) have demonstrated that addition of some lime materials significantly decreased the extractability of Cu, Cd, Mn and Zn in tropical Ultisols, Oxisols and Alfisols. Some other researchers also report the inverse relationships between the solubility of heavy metals with soil pH (Salam, 1996; Ma and Lindsay, 1995; 1993; 1990; El-Falaky *et al.*, 1991; Workman and Lindsay, 1990).

Organic materials may increase the soil adsorption capacity due to their intrinsic functional groups, mainly carboxyl groups (Rodella *et al.*, 1995; Alloway, 1990; Helling *et al.*, 1964). Parfitt *et al.* (1995) show that the CEC (cation exchange capacity) of the A and B horizons of some New Zealand soils arises mainly from charged carboxyls of organic matter. It is also suggested that the maximum amount of any given heavy metals that can be bound by organic matter is approximately equal to the number of carboxyl groups (Alloway, 1990). A study on the effects of soil pH by McGrath *et al.* (1988) shows that at the same pH the extractable Cu and Zn are smaller in soils with high organic matter than those in soils with low organic matter contents, suggesting that the soil organic matter status indeed plays a significant role in immobilizing heavy metals in soils. In contrast, Rodella *et al.* (1995) show that organic materials can explain only 32% of the soil CEC. However, an inclusion of soil pH increase the organic material contribution to 78% of the soil CEC, indicating that soil pH is also an important factor to consider when using organic materials for soil amendments. The importance of soil pH management is, in fact, not only important for non-specific adsorption but also for specific adsorption, that involves formation of covalent bonds with lattice ions. It is suggested that the latter is more important because its sorption capacity with respect to heavy metals is much higher than that of the former (Alloway, 1990).

An addition of lime and/ or organic materials into Andepts, on the other hand, may also cause totally different effects. The increase in soil pH may ionize H ions not only from its solid phase but also from its soluble organic materials, which are abundant in this soil. Lindsay (1979) suggests that the concentrations of active

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organic complexing agent increase with the increase in soil pH. Complexation by these functional groups may then solubilize heavy metals instead. Similarly, if parts of the organic materials added to soil are soluble, it may solubilize heavy metals accordingly. All these reactions may solubilize heavy metals into the soil solution instead of immobilize them in the soil solids. The addition of organic materials into Andepts may even give no effect on the adsorption capacity of the soil. Parfitt *et al.* (1995) suggest that allophane may react with carboxyl groups of organic matter, thus it may block the heavy metals for the exchange sites of the organic matter. Tan and Dowling (1984) also show that soil organic matter may increase or decrease the soil CEC depending on the soil clay mineralogy.

Data on the adsorption of heavy metals in tropical Andepts is not available in current literature. This experiment was intended to evaluate the changes in the chemistry of heavy metal adsorption in a tropical Andepts treated with lime or organic composts.

MATERIALS AND METHODS

A sample of Andosols (classified as Andepts in the US Soil Taxonomy) was collected from Gisting, South Lampung, Indonesia, in October 19, 1994. After an air-drying, the soil sample was sieved to 2 mm and mixed thoroughly. Selected properties of the soil sample are listed in Table 1.

Table 1. Properties of Andepts[†].

pH	CEC	Exchangeable cations							Heavy metals				C	N	C/N	P	Texture		
		Ca	Mg	K	Na	H	Al	Cd	Mn	Zn	Cu	Sand					Silt	Clay	
cmol.kg ⁻¹							mg.kg ⁻¹				%			mg.kg ⁻¹					
5.51	11.6	8.68	12.0	0.400	0.340	0.335	1.36	0.160	71.7	18.2	1.38	1.54	0.237	6.50	1.82	35.6	22.2	42.2	

[†] Average of 3 replicates

This experiment was conducted in two parts. The first part was intended to study the changes in the chemistry of heavy metals in the soil by lime addition. A plastic container, with a cover, containing 300 g of soil sample was used as an experimental unit. The soil sample was treated with a lime materials (CaCO₃, Ca(OH)₂, or CaMg(CO₃)₂) at a level supposedly to bring its soil pH value about 2 units higher. The level of each lime was calculated based on the neutralizing power of each lime from the level of Ca(OH)₂ determined experimentally to increase the pH of Ultisols about 2 units. The values of the neutralizing powers of the lime materials were 100 for CaCO₃, 109 for CaMg(CO₃)₂, and 136 for Ca(OH)₂. The level of Ca(OH)₂ needed to increase the soil pH of Ultisols about 2 units has been

previously reported (Salam *et al.*, 1996). An experimental unit with soil sample spiked with 10 mg kg⁻¹ of Cd, Cu, Zn and Mn was also prepared by an addition of 40 ml of a standard solution containing 75 mg l⁻¹ of each heavy metal. The mixtures were brought to the soil field moisture capacity with water, covered tightly, and then incubated at room temperature for 8 weeks. The field moisture capacity of the soil was determined by a gravimetry method. For each treatment, a control experimental unit was prepared. Each treatment was replicated 3 times.

The second part of the experiment was intended to study the changes in the chemistry of heavy metals in the soil by addition of organic composts. A plastic container with 300 g of air-dry soil sample was also used as an experimental unit. The soil sample was treated with organic composts (leaf composts of cassava, corn, "alang-alang", or soybean) at 10 Mg ha⁻¹. An experimental unit with soil sample spiked with 10 mg kg⁻¹ of heavy metals (Cd, Cu, Zn and Mn) was also prepared. For each treatment, a control experimental unit was prepared. The mixtures were mixed thoroughly, moistened with water to the soil field moisture capacity, covered tightly, and incubated at room temperature for 8 weeks. Each treatment was replicated 3 times.

The organic composts were prepared with the following technique. About 10 kg of small-chunks of plant leaves was put into a plastic container along with a 250 g of urea and a 200 g of CaCO₃. After a thorough

mixing, the mixture was incubated for 60 days until the organic matter was composted. Intermittent mixing was done every other day to fasten the decomposition process. The composted materials were air-dried and ground before being used in the experiment.

Analysis of the mixtures in both experiments was conducted after the completion of the incubation time. Soil analysis included: pH (soil:water 1:2), *N* NH₄OAc-exchangeable major-cations (exch. Ca, Mg, Na and K), acidity (*N* KCl-Al and H), Bray 1-P, Walkley-and-Black organic C and Kjeldahl total N (for experiment 2), and DTPA-extractable heavy metals. Heavy metal analysis included Cd, Cu, Zn and Mn; Cd was to represent the non-nutrient heavy metals and the rest to represent the nutrient heavy metals.

RESULTS AND DISCUSSION

Changes in the Soil pH

All lime materials significantly increased the soil pH. No difference was observed among the lime materials in increasing the soil pH (Figure 1-A). In average, the lime addition raised the soil pH about 1.13 units in samples not spiked with heavy metals and 1.30 units in samples spiked with heavy metals. These values are definitely much lower than the pH increase caused by the lime treatment in Ultisols, Oxisols, and Alfisols reported earlier (Salam *et al.*, 1996). This observation indicates that this soil possessed a high pH buffering capacity, which might have also been related to the high adsorption capacity of this soil with respect to heavy metals (except Cd). This relationship will be discussed later in a section that follows.

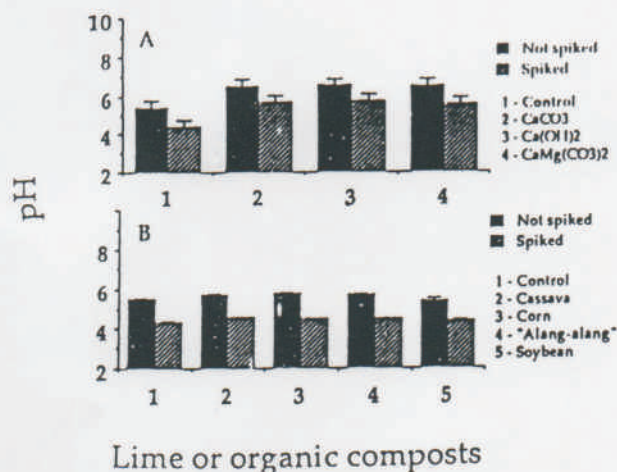


Figure 1. The influence of lime materials (A) and organic composts (B) on soil pH (bar indicates standard error)

Unlike those of Oxisols (Salam *et al.*, 1996), this high pH buffering capacity of Andept seems to originate from the fact that this soil contained allophane as its major component. Allophane is an intermediate product of volcanic ash weathering which is metastable in its nature. The stability of this mineral is sensitive to the changes in soil pH. Paterson *et al.* (1991) show that the range of pH in which this mineral is stable is narrow and becomes narrower with the decrease in the activity of Al^{3+} in soil solution. For example, at Al^{3+} activity lower than 10^{-8} M allophane is stable only in the pH range of 5.5 to 6.5. This range is narrower at Al^{3+} activity lower than 10^{-8} M. Based on this theory, it is probably that the increase in soil pH caused by lime addition had decomposed allophane and released Al^{3+} into soil solution. If this suspicion is true, the Al^{3+} released by the process may explain the high pH buffering capacity of this soil. Aluminium ions may have been hydrolyzed and produced

H^+ ions that neutralized OH^- ions produced by lime addition.

Comparison of the average decrease in the pH of Andepts caused by the addition of the heavy-metal standard solution with those of Ultisols, Oxisols, and Alfisols (Salam *et al.*, 1996) may strengthen the above explanation. The average decrease in soil pH caused by the standard solution in Andepts was 0.96 units, higher than those in Oxisols (0.78 units), Ultisols (0.66 units), and Alfisols (0.49 units) (Salam *et al.*, 1996). In contrast, this observation shows that the Andepts has a lower pH buffering capacity than the other three soils.

This phenomenon is somewhat not reasonable if there was no indigenous soil acidification during the soil incubation. Hydrogen ions produced by Al^{3+} hydrolysis may have acidified the soil, making its pH buffering capacity upon the addition of the standard solution was lower than those of Oxisols, Ultisols and Alfisols. This observation is highly possibly to be associated with the decomposition of allophane that released Al^{3+} .

The addition of organic composts of cassava, corn, and "alang-alang", even though at lower magnitudes than the effect of lime, also significantly increased the pH of Andepts (Figure 1-B). This observation is obviously related to $CaCO_3$ used for composting the organic materials. The fact that soybean compost did not increase the soil pH was probably due to the acid nature of this compost, that could neutralized the effect of $CaCO_3$. This pattern was also observed in soil spiked with heavy metals (Figure 1-B). The addition of the heavy-metals standard solution also significantly lowered the soil pH, probably due to the acidity of the standard solution coupled with Al^{3+} produced by the decomposition of allophane at lower pH.

Changes in the Solubility of Heavy Metals

The effect of lime materials on the extractability of heavy metals in Andepts is very much different from those in Oxisols, Alfisols, and Ultisols reported earlier (Salam *et al.*, 1996), which show that the addition of lime materials significantly decreased the extractability of heavy metals. In contrast, the addition of lime materials into Andepts significantly increased the solubility of heavy metals, except Cd (and Mn with $CaMg(CO_3)_2$ addition) (Figure 2.). This phenomenon is probably associated with the presence of soluble organic matter that might have been present at high concentration in this soil. The functional groups of the soluble organic materials may bind with heavy metal cations if their H ions are dissociated. The increase in the soil pH caused by lime addition may have increased the number of the negative charges that could bind with the heavy metals cations. If this theory holds, it can explain the increase in the extractability of heavy metals by lime addition into this soil.

metals with the addition of particular organic composts and the increase in the extractability of Mn caused by all organic composts are probably related to the increase in the active organic chelating agents (chelating agents with H ions that are bound on their functional groups have been dissociated) induced by the increase in soil pH and/or compost addition. Soybean compost increased the solubility of Mn very significantly, indicating that this material may have introduced high addition of soluble chelating agent into the soil. Direct addition of Mn contained in soybean compost is also possible since soybean, and generally legumes, is a good Mn accumulator from soils.

Table 2. The percent recovery of heavy metals from Andepts treated with lime materials or organic composts.

Treatment	Zn	Cu	Cd	Mn
	% †			
Lime Materials				
Control	(-) 2.20	0.80	93.2	(-) 459
CaCO ₃	4.00	(-) 7.10	87.3	(-) 858
Ca(OH) ₂	(-) 27.0	(-) 3.50	95.4	(-) 812
CaMg(CO ₃) ₂	(-) 22.3	0.300	93.8	(-) 582
Organic Composts				
Control	9.00	(-) 2.50	96.1	(-) 520
Cassava	(-) 80.0	(-) 4.50	95.6	(-) 596
Corn	(-) 30.0	(-) 6.70	99.1	(-) 764
"Alang-alang"	(-) 8.00	1.70	99.3	(-) 839
Soybean	(-) 10.0	2.00	111	8360

† Calculated with an equation of $[(M_{(x)}) - M_{(0)}] * 100 / M$, where $M_{(x)}$ is the extractable heavy metal in soil treated with lime or organic compost x and spiked with heavy metal; x includes CaCO₃, Ca(OH)₂, dan CaMg(CO₃)₂ or cassava, corn, "alang-alang" and soybean composts; $M_{(0)}$ is the extractable heavy metal in soil treated with lime or organic compost x but not spiked with heavy metal; and M is the amount of heavy metal added to soil (in this experiment it is 10 mg kg⁻¹).

As that in soil treated with lime, most of the Cd added into the soil treated with organic compost was not adsorbed. However, the extractability of Zn and Cu in soil spiked with heavy metals was in general not significantly different from those in soil not spiked with heavy metals. The extractability of Mn was even lower in soil spiked with heavy metals. These observations are consistent with those observed in soil treated with lime (Figure 2.), and also show that Andepts is a good absorber for these three heavy metals. As discussed earlier, the disappearance of the added heavy metals is probably due to their adsorption by allophane or precipitation/co-precipitation with the products of allophane decomposition, that might have happened at lower pH caused by the addition of the heavy-metal standard solution. Based on the value of the % heavy-metal recovery, the preference of Andepts towards heavy metals follows the sequence of Mn > Zn > Cu > Cd (Table 2).

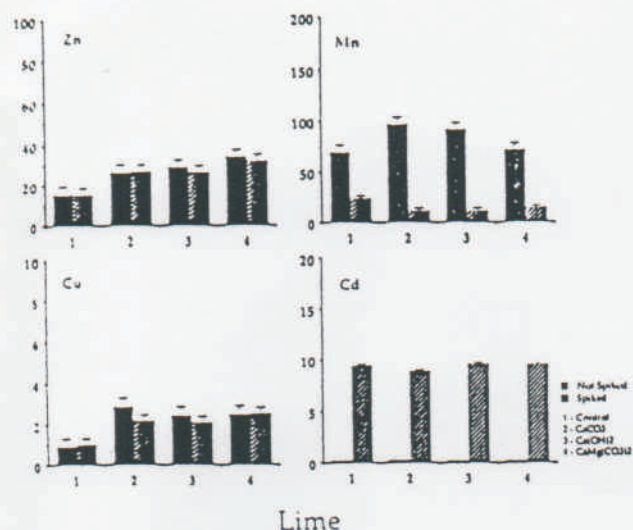


Figure 2. The influence of lime materials on heavy metal extractability (bar indicates standard error)

Unlike those in Oxisols, Ultisols and Alfisol, the extractability of Zn and Cu in soil spiked with heavy metals were not different from those in soil not spiked with heavy metals (Figure 2.). This phenomenon is also shown by the low or negative values of the % heavy-metal recovery from soils (Table 2). The extractability of Mn was even lower in soil spiked with heavy metals than in soil not spiked with heavy metals (shown by the high negative value in Table 2). The disappearance of the added heavy metals to some extent may be explained by two reasons. First, allophane has been shown to possess high adsorption capacity, particularly with respect to phosphates and organic compounds (Paterson *et al.*, 1991). It is obvious that this data also shows that allophane possessed high specific adsorption capacity with respect to heavy metals. Second, due to the metastable nature of allophane, the disappearance of the added heavy metals, and also a part of Mn previously soluble, also can be caused by precipitation/ co-precipitation of these elements with the decomposition products of allophane at a low pH values caused by the acidity of the standard solution. The greater Mn precipitation is probably caused by the insolubility of Mn precipitates at lower pH. In any case, it is obvious that Andepts is a good absorber for these three heavy metals. The major part of Cd was not absorbed by this soil, probably because the magnitude of Cd addition was too high. Cadmium natural concentration in soils is generally a few hundreds $\mu\text{g kg}^{-1}$, much lower than that was used in this experiment.

With a few exception, the addition of organic composts generally did not affect the solubility of Zn, Cu and Cd (Figure 3). Significant increase in some heavy

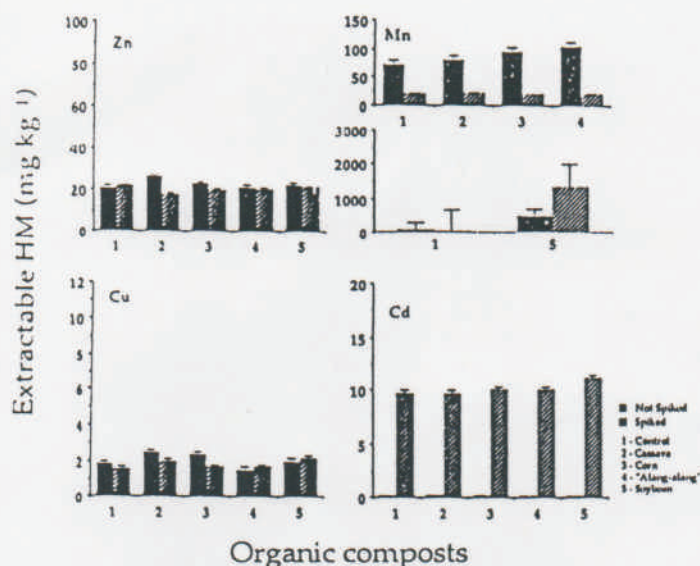


Figure 3. The influence of organic composts on heavy metals extractability (bar indicates standard error).

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