TRANSLOCATION OF HEAVY METALS IN COLUMNS OF A TROPICAL SOIL TREATED WITH LIME AND ZEOLITE

TRANSLOKASI LOGAM BERAT DI DALAM KOLOM TANAH TROPIKA YANG DIPERLAKUKAN DENGAN KAPUR DAN ZEOLIT

Abdul Kadir Salam
Fakultas Pertanian Universitas Lampung

Abstract *Heavy metals are decrimental to human health and their solubilities and movements in soils to most likely influence their accumulations in human organs trough food chains. This study was conducted to observe heavy metal solubility and movements in columns of a tropical soil treated with lime and/or zeolite. Unlike Zn, most of an added Pb, Cd, and Cu were immobilized in topsoil. Lime effectively reduced the heavy metal (Pb, Cd, Cu, and Zn) solubility and retarded their movements due to the lime role in enhancing the soil pH. Zeolite and its interaction with lime show no consistent effect on heavy metal solubility and movements in the soil columns.*

Keyword : heavy metals, heavy-metals movements, tropical soils.

Abstrak *Logam berat berbahaya bagi kesehatan manusia dan kelarutan serta pergerakannya di dalam tanah dapat mempengaruhi tingkat akumulasi di dalam organ tubuh manusia melalui rantai makanan. Penelitián ini bertujuan untuk mempelajari kelarutan dan pergerakan logam berat di dalam kolom tanah tropika, yang diperlakukan dengan kapur dan atau zeolite. Tidak seperti Zn, sebagian besar Pb, Cd, dan Cu dimobilisasi oleh tanah atas. Kapur secara efektif mengurangi kelarutan logam berat (pb, Cd, Cu, dan Zn) dan meperlambat pergerakannya karena kapur mampu meningkatkan nilai pH tanah. Zeolit dan interaksinya dengan kapur tidak memberikan pengaruh yang konsisten terhadap kelarutan dan pergerakan logam berat di dalam kolom tanah.*

Kata kunci: logam berat, pergerakan logam-berat, tanah tropika.

INTRODUCTION

The accumulation of heavy metals in human tissues has been a concern in environmental sciences, particularly of metals coming into human bodies trough soil system (Salam et al., 1997; Kabata pendias and Pendias, 1992; Alloway, 1990; Lagerwerff, 1982) There are basically two major routes truth which heavy metals in soils water and be available to plants. Their intake by plans in the first step that enables heavy metals to come into the food chains in which human being is one of the components. Second, the soluble heavy metals may move in the soil profiles trough or with soil water and may reach the ground water. Depending on the utilization of the ground water, heavy metals may eventually come into human bodies, directly trough drinking water or indirectly trough food chains. Aside from reducing the heavy-metals disposals into the soil system, effort to reduce the intake of heavy metals by human beings are two major methods: (1) reducing intake of heavy metals by plants and (2) retarding the movements of heavy metals in the soil profiles. These two methods can be performed by immobilizing heavy metals in the soil methods.

The capacity of soil absorb heavy metals is limited, but basically it can be unchanged by several methods. Among which the additions of zeolite and/or lime are the most reasonable, particularly for the tropical soils, that have low cation exchange-capacity (CEC) and high amounts of pH-dependent charges. Zeolite is a mineral that process high CEC (Zelazny and Calhoun, 1982). Additions of zeolite into soil are expected to increase the soil adsorption capacity with respect to heavy metals and to retard their movements in soil profiles. Recently, Affandi et.al. (1993) show that additions of zeolite to soil depressed the adsorption of some heavy metals by spinach. The additions of zeolite might have decreased the solubility of heavy metals and thereby decreased their intake by the plants. Data on the effect of this mineral on heavy metal movements in tropical soils in scantily.

Lime may exchange soil pH. The increase in soil pH may cause the release of hydrogen ions from various functional groups found in soils. This process my then enchant the soil CEC or the capacity of soils to adsorb the soluble metals and, hereby, may reduce the soluble metals in soils (Salam, 1995; Tyler and McBride, 1982, Helling et.al, 1964). Some data on these phenomena are available in current literature (Salam, 1995; 1993; Salam and Maswah, 1994; Fahad, 1987). Salam (1995; 1993) showed that addition of lime decreased the solubility of Cd, Cu, and Zn in soils amended with sewage sludge and lime 15 years before the observation. Salam and Mawah (1994) showed that lime additions in a tropical soil significantly decreased Fe, Mn, Zn, and Cu extractable by DTPA (diethylenettiaminepentaacetic acid). Welch and Lund (1989) also showed that the vertical distance of Zn translocation in soil was inversely correlated with soil pH. However, data on the effect of lime on the heavy metals movements in tropical soils not available.

This study was intended to observe the movements of some heavy metals (Pb, Cd, Cu, and Zn) by evaluating the changes in the solubility of these metals in columns of a tropical soil treated with zeolite and/or lime. Lead and Cd were chosen to represent the none-plantnutrient heavy metals while Cu and Zn to represent the plant-nutrient heavy metals.

MATERIALS AND METHODS

Soil samples and other Experimental Materials.

Soil samples (classified as ultisols in the US soil taxonomy), I. e topsoil (0-20 cm) and subsoil (20-40 cm), were collected from a cornfield in Bajaragung, Central Lampung, Indonesia. After an air-drying, each soil sample was ground, screened to 2 nun, and thoroughly mixed. The soil samples of both layers were clayey, relatively acid and low in CEC and detectable-Al. Soil pH, CEC, organic C, total N, and base elements of the topsoil sample were all higher than those of the subsoil sample. Some selected physical and chemical properties of topsoil and subsoil are listed in table 1.

Calcite (CaCO3) was used to increase the soil pH. The zeolite used was clinoptilite ((CA,Na2)(Al2Si7Oig)6H2o) purchased from PT Minatama Mineral Perdana(ECC-International) with the following properties: particle diameter 1-3 nun, pH 6.7 surface area 7.625 m g and CEC 95-160 cmolckg-1. Standard heavy metals was a single solution containing Pb, Cd, Cu, and Zn, each with a concentration of 50 ppm, diluted from their respective stock standard solution each with a concentration of 1000 ppm in I N HN03- Water for the leaching experiment was close to neutrality (pH 6.92) and contained 0.47 ppm Zn and undetectable Pb, Cd, and Cu by flame atomic adsorption spectrophotometer (flame AAS).

Experimental Procedures

The Experiment was conducted in a laboratory of by using columns made of transformation plastic sheets. The columns have 10 cm in diameter and 50 cm in total height. A container with a diameter of about 10 cm and some small holes in its bottom to drain some free water during the leaching experiment was fitted in the column bottom. Soil sample was added in the columns in such a way that the thickness of either topsoil or subsoil in the columns was about 20 cm, similar to the soil layers sampled in the field. A trial and error experiment showed that this conditions was obtained by an addition of about 1600 g dry soil for each layer.

Topsoil sample was treated and mixed toughly with lime and or zeolite before being put on top on the subsoil in the columns. The topsoil treatment were : (1) topsoil without any treatment (control), (2) topsoil with heavy metal additions, (3) topsoil's with heavy meals and lime additions, (4) topsoil with heavy metal and zeolite additions, (5) topsoil with heavy metal and lime as well as zeolite additions. The amount of lime (CaCO3) added was equivalent to 8 ton ha- 1 and zeolite was 1%. Subsoil sample was left untreated. All treatment was conducted in duplicates.

The soil columns were then moisten with water by an addition of I 00 ml of water and then incubated for 1 week to allow the soil sample and the treatment materials to reach equilibrium. The standard solutions containing 50 mg/l of each metal was given at 50 ml to each column by pouring it into the columns to cover the whole surface of topsoil. The column was then leached with 250 ml water every other day starting week after the heavy metal additions.

Observations

All columns were analyzed at the end of each leaching time (30 or 60 days). Each column was sampled at 4 column layers, 2 layers for the topsoil i.e. 0-10 cm (L-1) and 10-20 cm (L-2) and 2 layer for the subsoil i.e. 20-30 cm (L-3) and 30-40 cm (1-4). Soil sample for each column layer was mixed toughly, analyzed, and assumed to have one for soluble heavy metals or other soil properties. Soil analyses included the DTPA-extractable heavy metals (Pb, Cd, Cu, and Zn) and the soil pH. Analyses of the initial conditions of soil properties included the soil textural classes, pH, CEC, organic C, total N, and exchangeable cations (Ca, Mg, K, Na, Al, and H).

RESULT AND DISCUSSION

Change in Soil pH

It is documented that soil reaction 9 pH 0 is one of the most important soil properties that affect the immobilization of heavy metals in soil system. The changes in soil pH as affected by lime and or zeolite treatment in soil columns leached with water for 30 or 60 days have defined.

The soil treated with heavy metal alone or heavy metal + zeolite showed no pH deference in all column layers from that of the control after 30 days of water leaching. In contrasts, the lime treatment apparently increased the soil pH about I unit in columns layer 1 (L-1) and 2 (1-2). This pH pattern did not change within 60 days of water leaching, showing that the influence of lime in enhancing the soil pH was retained long enough in the soil columns.

The increased in soil pH was associated with the neutralization of H+ ion by C)32- and or HCO3- ions produced HCO3- or neutral compounds and, thereby, decreased the soil acidity. Because the increase in soil pH in inversely correlated with heavy metal solubility's (Salam, 1995; Lindsay, 1979), the pattern is useful for enhancing the immobilization of heavy metals in soil system to retard heavy metal movements by percolating water in soil profiles.

The pact that soil pH in column layer 3 (1-3) of the lime-treated columns was higher compared to that of the same layer in the columns not treated with lime showed that this was also affected by lime treatment in the topsoil through water leaching during 30 or 60 days ion of C03 2- and HCO3- produced by lime reaction in soil may have leached trough to columns layer 3 and combined with H+ ion and, thereby, neutralized parts of the soil acidity. This fact also showed that lime treatment of topsoil might influence the subsoil properties that may affect the heavy metals immobilization.

Solubility and Translocation of Cu and Zn

Cooper and Zn two of the heavy metal elements that are essential for plants. Required in small amounts, these plant nutrients may be toxic to plants if their solubility in soil is high. These elements may also be toxic to other living thing such animal and human beings if they contaminate to ground water used for drinking water as result of heavy metals leaching through soil profiles. The solubility and translocation of Cu and Zn in soil columns affected by lime and or zeolite treatment.

Part of the Cu added to the columns through the standard solution were retained by soil particles in columns layer 1 (based on a simple calculation the standard solution should have increased the Cu solubility as high as 4 mg kg-Leif no Cu immobilization occurred). It also clearly shows that the lime treatment increased the immobilization of Cu, in accordance with some previous report (Salam, 1995; Salam and Marwah, 1994). On the contrary, the zeolite treatment caused no effect on the immobilization of the element as apparently shown by the overlapping of the lines for the column treated with copper alone and the column treated with copper+zeolite and also of the lines between column layer I and 2 for the column treated with copper+lime and the column treated with copper+lime+zeolite. This observation shows that, different from lime, zeolite did not reduce the solubility of Cu in this soil.

Careful comparison on Cu translocation after 30 and 60 days of leaching showed that part of Cu from column layers 1 and 2 in column treated with copper only moved to column layer 3 and 4, and partly probably out of the columns system. Part of Cu in column treated with copper+lime also moved more significantly to the sublayers or out of the column system. No significant Cu movement occurred in column treated with copper+zeolite.

The above observation showed that the treatment retarded the translocation of Cu even trough it caused no decrease in the Cu solubility. On the contrary, even trough lime treatment decreased the Cu solubility, it could not retard the Cu translocation. The significant translocation of Cu in column treated with copper+lime+zeolite showed that lime might have decreased the bonding energy between zeolite and the element.

Zinc showed different movement pattern from Cu, particularly because the water used for the leaching experiment contained detectable Zn by flame AAS (0.47 ppm). Due to this impurity the part of the added Zn that may have been immobilized by soil particles in he control soil could not be estimated. On the contrary, the solubility of Zn significantly increased higher than that was added through the standard solution (4 mg kg-1), obviously as a result of Zen accumulation introduced by the leaching water.

The lime treatment decreased the Zn solubility in columns layers I and 2, in accordance with the hypothesis and the previous reports (Salam and Maswah, 1994; Fahad, 1987) as a result of the increase in soil pH caused by lime reaction in soil. Different from its influence to Cu, the zeolite treatment and its interaction with lime decreased the solubility of Zn even though the effect was lower than that of the lime treatment.

Careful observation on the changes in Zn solubility after 30 and 60 days of leaching showed that there was a significant translocation of Zn in column treated with Zn alone. For example, in column layer 4 (L-4) the solubility of Zn at 60 days was about twice that of at 30 days. There was also Zn translocation in the lime-treated columns but it did not change the Zn solubility in column layers 1 and 2, showing that the effect of lime in reducing Zn solubility lasted long.

Translocation of Zn in the Zn++zeolite-treted colonial occurred more significantly. Zinc solubility in the top layers decreased while that in sub layers increased drastically as a result of water leaching to subsoil. A significant leaching of Zn was also observed in the Zn+zeolite+lime also showed that Zn was leached out from column layers 3 and 4, indicating that this element is fairly mobile in the soil columns.

Solubility and Translocation of Cd and Pb.

Cadmium and Pb are two of the heavy metals potential to be pollutants in the environment and are not essential for plant. The distribution of Pb and Cd in the soil columns are affected by lime and/or zeolite treatment after a 30 or 60 days of water leaching.

The solubility of Cd in the soil is relatively low. The major part of the Cd added through the standard solution was immobilized in column layer 1. However, its solubility was greatly affected by lime and/or zeolite treatment. Lime and its interaction with zeolite significantly decreased the solubility of Cd at 30 days of leaching. Conversely, zeolites alone shifted part of Cd to lower energy bonding, thereby, its showed higher solubility in DTPA.

Most of Cd was held in column layer 1 (0-10 cm) where the Cd standard solution was poured. However, Cd translocation occurred during water leaching, as seen from the pattern of Cd distribution in soil column after 60 days even through there was no Cd accumulation in column layer 2-4. Cadmium solubility in column treated with Cd alone was lower compared to those in the other columns, indicating that Cd in this column was held weakly and easily leached by percolating water and, thereby, its solubility quickly leased with leaching time. In contrast, Cd solubility in the lime-treated column was higher because the bonding between Cd and soil particles was stronger and, thereby, depressed the leaching of this metal. In addition, the solubility of Cd in the zeolite-treated columns was also lower than that of in the lime-treated columns as a result of a weaker bonding of Cd on the soil or zeolite particles.

The major part of the Pb added to the soil columns was also immobilized by soils. Different from Cd, lime and/or zeolite treatment effectively decreased the solubility of Pb in columns layer 1. However, Pb translocation seemed to occur in every treatment. Translocation of Pb significantly occurred in columns treated with Pb alone or white Pb+zeolite as a result of a weaker bonding between Pb and soil particles.

CONCLUSIONS

Most of the Pb, Cd, and Cu added into the soil columns through the standard solution were immobilized in topsoil. Generally, Pb, Cd, Cu. and Zn moved in the soil columns, driven by water leaching for 60 days ; the translation was apparently shown by Zn. Lime effectively reduced the heavy metal (Pb, Cd, Cu, and Zn) solubility and retarded their movements due to the lime role in enhancing the topsoil pH.

Zeolite and its interaction with the lime showed no consistent effects on heavy metals solubility and movements. Zeolite reduced the solubility of Pb and Zn but did not affect the solubility of Cu and even increased the solubility of Cd in the topsoil. Pb and Zn movements in the zeolite-treated were fairly fast.

ACKNOWLEDGMENT

This study was partially supported by the University of Lampung Research Institute (through DPP/SPP research Grant) and the Directorate General of Higher Education (DGHE) Department of Culture and Education RI through the competitive Grant (Hibah Bersaing) Project FY 1995/1996 (HB IV/1). The support is gratefully acknowledged.

LITERATURE CITED

1. Affandi, RTM Sutamihardja, and D. Sopandie. 1993. Pemanfaatan Limbah Lumpur Perusahaan Air Minum (PAM) dan zeolite alam sebagai media tanam. Seminar Nasional Penanganan Limbah Industri dan Limbah Oragnik, Bogor, 17 Nov. 1993
2. Alloway BJ 1990. Heavy Metals in Soils. John Wiley & Sons, Inc, New York.
3. Fahad, AA 19877, Movement of manegenese-54 in calcareous soils as affected by leaching solution, lime content, sanilization, and sterilization, Soil Sci.Soc.Am.J 51:1487-1492
4. Helling, CSC. Chester, and RB Corey, 1964. Contribution of organic matter and clay to soil cation-exchange capacity as affected by the pH of the saturating solutions. Soil Sci.Soc.Amer.Proc. 28:517-520
5. Kabata-Pendias, A H pendias 1992. Trace elements in soils and Plants, 2nd ed. CRC Press. London.
6. Lagerwerff, J.V. 1982, Lead mercury, and cadmium as environmental contaminant pp. 593-636 In JJ Mortvedt. PM Giordano, and W.L Lindsay (Eds). Micronutrients inagriculture SSSA, Inc. Madison
7. Linsay WL 1979. Chemical Equilibria in Soils. John Wiley & Sons, New York
8. Salam, AK 1993. Residu Kadminium dalam tanah 15 tahun setelah tanah diperlakukan dengan limbah industri dan kapur. Seminar Nasional Penanganan Limbah Industri Tektil dan Limbah Organik, Bogor, 17 Nov. 1993.
9. Salam, AK and N. Maswah 1994. Pengaruh P dan pH terhadap besi ddan mangan tersedia pada Ultisol masam dari Lampung. Pp 135-142. In a Djausal, M. Utomo dan Yohanes (Eds.) Pros. Semigitasi Bahaya Gempa dan Hasil Penelitian. Universitas Lampung, Bandarlampung.
10. Salam AKA 1995. Imbilisasi Logam Berat di Dalam Tanah Selama 1 Tahun. Jurnal Ilmiah Ilmu-ilmu Pert. 3(l):20-27

11. Salam AK, S Djuniwati, JT Harahap and Suwarto 1997. Imobilisasi logam berat asal limbah industri di dalam tanah tropika: 1. Sifat kimia limbah industri, J. Ilmiah Ilmu Pertanian (In rev.)
12. tyler, LD and MB Mcbride 1982. Mobility and extractability of Cadmium, copper, nickel and zinc in organic and mineral soil columns Soil Sci. 134:198-205
13. Welch, JE and LJ Lund 1989. Zinc movement in sewage-sludge treated soils as influenced by soil properties, irrigation water quality and soil moisture level. Soil Sci. 147:208-214
14. Zelazny LW, and FG Calhoun 1982. Palygorskite (attapulgite) sepiolite talc, pyrophyllite and zeolites, pp 435-470. In JB Dixon and SB Week (Eds). Mineral in soil environments. SSSA, Inc. Madison

Table 1. Selected properties of soil[1].

	Sampling Depth (cm)	
Soil Properties	0-20	20-40
Texture (%)	clay	clay
Sand	20.0	16.0
Silt	32.4	18.4
Clay	47.6	65.6
pH H_2O (1:2)	5.93	5.85
pH KCl (1:2)	4.92	4.95
Organic C (%)	1.17	0.85
Total N (%)	0.23	0.15
C/N	5.07	5.92
Exchangeable Cations ($cmol_c kg^{-1}$)		
Ca	4.96	4.01
Mg	0.84	0.20
K	0.64	0.31
Na	0.20	0.19
H	0.10	0.20
Al	nd[2]	nd
CEC ($cmol_c kg^{-1}$)	7.34	5.48

[1]Avg. of 3 replicates; [2]Not detectable

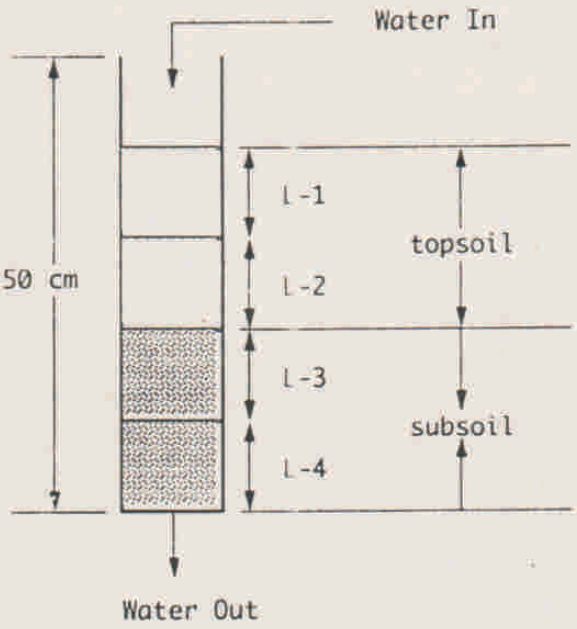

Figure 1. Topsoil and subsoil arrangement in an experimental column (L-1 0–10, L-2 10–20, L-3 20–30, dan L-4 30–40 cm).

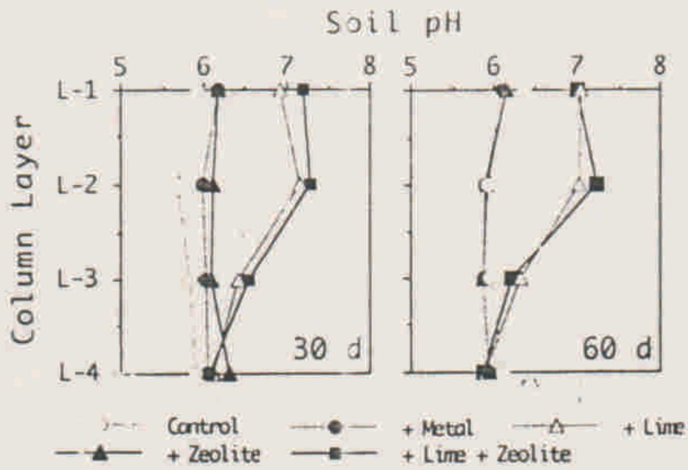

Figure 2. Soil reaction (pH) along the soil column as affected by lime and/ or zeolite treatment after 30 and 60 days of leaching (L-1 0–10, L-2 10–20, L-3 20–30, dan L-4 30–40 cm).

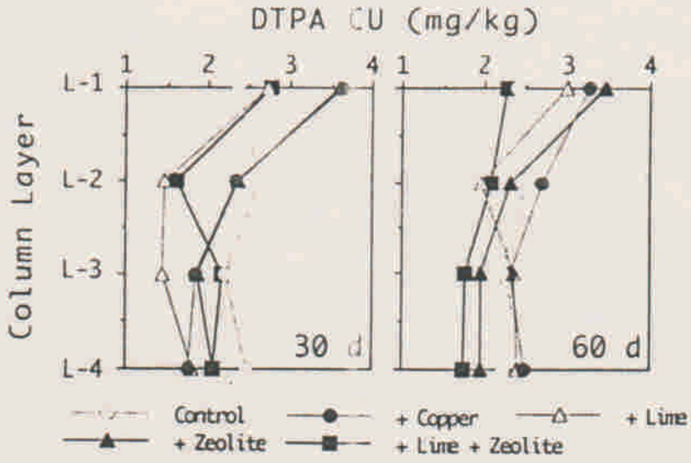

Figure 3. Copper solubility along the soil column as affected by lime and/ or zeolite treatment after 30 and 60 days of leaching (L-1 0–10, L-2 10–20, L-3 20–30, dan L-4 30–40 cm).

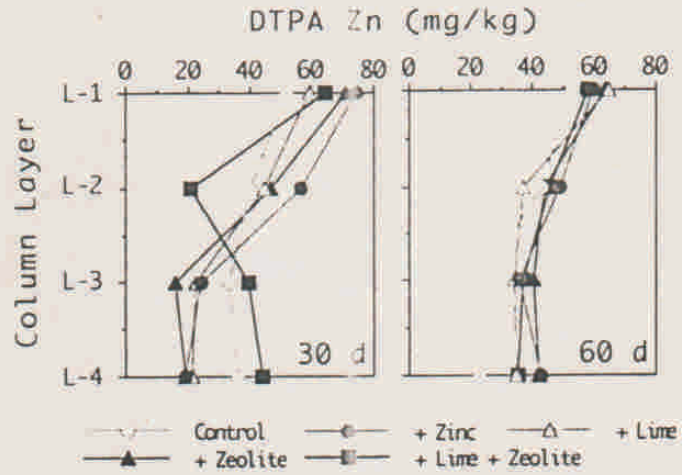

Figure 4. Zinc solubility along the soil column as affected by lime and/ or zeolite treatment after 30 and 60 days of leaching (L-1 0–10, L-2 10–20, L-3 20–30, dan L-4 30–40 cm).

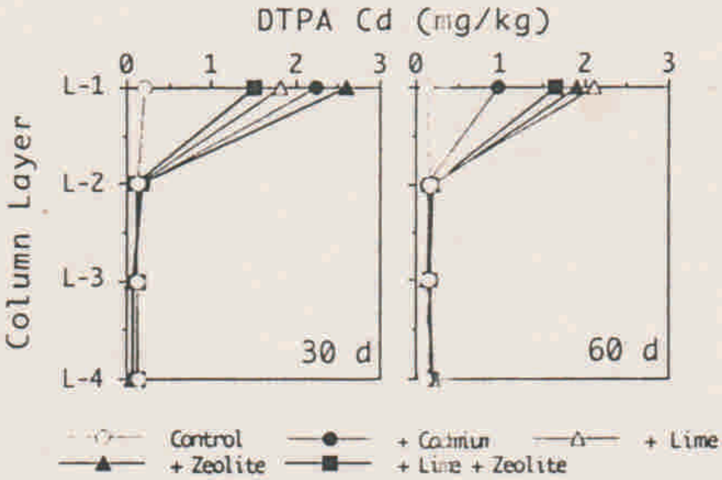

Figure 5. Cadmium solubility along the soil column as affected by lime and/ or zeolite treatment after 30 and 60 days of leaching (L-1 0–10, L-2 10–20, L-3 20–30, dan L-4 30–40 cm).

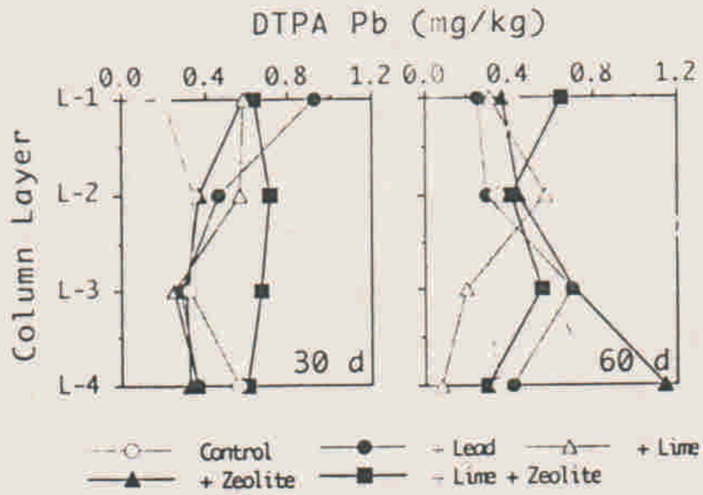

Figure 6. Lead solubility along the soil column as affected by lime and/ or zeolite treatment after 30 and 60 days of leaching (L-1 0–10, L-2 10–20, L-3 20–30, dan L-4 30–40 cm).