MEDWIN PUBLISHERS
Committed to Create Value for Researchers

Journal of Ecology and Natural Resources
ISSN: 2578-4994

The Effect of Compost and Apatite on Pb Distribution in the Pb-Contaminated Soil

Ho CL and Kuo SL*

Department of Technology and Management, Open University of Kaohsiung, Taiwan

***Corresponding author:** Shu-Lung Kuo, Department of Technology and Management, Open University of Kaohsiung, Taiwan, Tel: +886 7 8150815; Email: singsuey@ms28.hinet.net

Research Article

Volume 6 Issue 2

Received Date: June 01, 2022

Published Date: June 10, 2022

DOI: 10.23880/jenr-16000285

Abstract

There are various techniques for rehabilitating soils contaminated by heavy metals, such as physical treatment, chemical treatment, and phytoremediation. Pb-contaminated soils are mostly treated with soil mixing, soil dressing, or soil washing. In this study, hydroxyapatite powder and organic compost of different mix ratios were added to two kinds of high-concentration synthesized Pb-contaminated soils (1000 mg/kg), which were processed with sequential extraction schemes after different incubation periods in order to examine the distribution of Pb forms in them. The form distributions analyzed included the exchangeable form Pb (PbE), Fe-Mn oxidation form Pb (PbFe-Mn), organic bonded form Pb (PbO), and residual form Pb (PbR). The findings indicated that after stabilization for one month, the alkaline Tk series soil was less susceptible to Pb contamination when no hydroxyapatite and compost was applied, which made it more difficult for Pb in the soil to interact with cations and trigger exchange reactions. Next, the PbR concentrations of the two soils tested were higher after hydroxyapatite was added. This result suggested that hydroxyapatite helped to stabilize the Pb in the soil samples and prevented it from precipitating, thereby controlling the Pb concentration at a certain level to avoid contamination. Lastly, when hydroxyapatite and compost of different mix ratios were applied to the two kinds of Pb-contaminated soils, we found that the PbE concentration of the Tk series soil declined as the concentration of compost increased, suggesting that increasing the compost concentration raised the pH value of the soil and enhanced its fertility. On the other hand, the PbE concentration of the Lp series soil increased as the compost concentration rose, indicating that an increase in compost concentration hampered plants from absorbing soluble nutrients in the soil, thereby making it easier for Pb to precipitate via cation exchange and resulting in Pb contamination.

Keywords: Pb-contaminated soil; Apatite; Hydroxyapatite; Rehabilitating Soils

Introduction

Generally speaking, soils have the capacity to accommodate contaminants. As contaminants enter soils via air or water, some parts of them are degraded via chemical or biochemical reactions, with only a small part of them reentering the atmosphere or water via the soils. Once soil is contaminated and the contaminants have exceeded its capacity, the soil's remediation and rehabilitation will become relatively difficult [1,2]. Besides, crops will absorb contaminants in the soil, inflicting damage to humans via the food chain; contaminants will also jeopardize drinking water and underground water sources as they move inside the soil. In addition, heavy metals can accumulate to a high level in soils, with high toxicity and low mobility. They will not degrade and disappear due to biological effects. Thus, they may hinder the growth of crops and reduce yields. Crops may also accumulate heavy metals, whereby the quality of agricultural products will be deteriorated. Humans and animals will be poisoned if they consume said agricultural products [3-5].

The geochemical forms of heavy metals in soils can directly affect their solubility and potential mobility in soils [6,7]. When industrial wastewater containing Pb is discharged into the environment, Pb will enter the human body via the food chain involving microorganisms, crops, and fish and shellfish. Pb deposited in soils will be dissolved in water and eventually concentrated and accumulated in organisms. When a person's blood lead level exceeds 120 μg/100 mL, he/she will suffer from lead poisoning. Symptoms of lead poisoning include chronic nephritis, gout, lead encephalopathy, spasticity, petechiae, and anemia [8,9]. Thus, problems derived from lead pollution cannot be ignored. Such problems include a decrease in the number of bacterial, fungal, and actinomycete populations in heavy metal-contaminated soils, mineralization and nitrification of organic nitrogen, and nitrogen fixation in rhizobia, whereby crop yields will decline [10,11]. The use of compost can provide soil microbial populations with energy needed for their growth, while facilitating the activity of soil microbial populations and maintaining a balanced ecosystem. A relevant study [12,13] has pointed out that adding phosphate rock to lead-contaminated soils can effectively stabilize lead and reduce its solubility in soils. Moreover, the results of the experiment on the use of phosphate rock show that when more phosphate rock is added to lead-contaminated soils, less amount of lead is extracted from said soils. There is a significant decrease in lead content as the duration of adding phosphate rock to lead-contaminated soils increases [14,15]. This phenomenon is called ageing. With the results of the experiment on adding phosphate rock to contaminated soils of different lead contents, it can be estimated that adding 10 g of phosphate rock to 100 g of soil with a lead content of 2250 mg/kg will help to reduce the lead content to its natural level [1,16].

In this study, hydroxyapatite powder and organic compost of different mix ratios were added to two kinds of high-concentration synthesized Pb-contaminated test soils (1000 mg/kg), which were processed with sequential extraction schemes after different incubation periods, in order to examine the distribution of Pb forms in them. Four forms: Pb_E, $Pb_{Fe\text{-}Mn}$, Pb_O, and Pb_R were analyzed to examine the Pb stabilization and precipitation mechanisms of individual soils.

Materials and methods

Sources of test soil samples

This study selects Taiwanese soils with two different categories of properties as the sampling soil sample.

(1)Taikang series soil (Tk series soil): The sample soil was obtained from Gangshan District, Kaohsiung City. It developed from alluvial parent rock and is characterized by a reddish hue and rich iron and aluminum oxides. Since it is acidic, it is suitable for sugarcane plantation.

(2)Lopei series soil (Lp series soil): The sample soil was obtained from Neipu Township in Pingtung County, Taiwan. It is a kind of oxidized diluvium soil containing abundant iron and aluminum oxides and is characterized by fine texture. Its high iron and aluminum oxide content makes it an ideal catalyst carrier. This kind of soil is ideal for planting pineapples.

Analysis of the chemical composition of the two test soil samples

An analysis of the chemical composition of the test soil samples can help in examining their chemical content, including free elements and elements that appear in crystal form. From the data obtained, researchers can estimate the proportion of each chemical element when it forms oxide. The procedure for the analysis is as follows: Place 0.1 g of soil from each of the two test soil samples in a polytetrafluoroethylene cup. Add 1.5 ml of aqua regia and 2.5 ml of hydrofluoric acid (HF) to the cups, respectively, and then heat the soil inside the cups at 110°C for 2 h. After the soil cools down, add 25 ml of boric acid to the soil and heat the soil again (without exceeding the boiling point) for 10 to 15 min so that sediments can be completely depleted. Run the soil solution through filters and add deionized water until the total volume reaches 100 ml, and then test the chemical composition of the two soil samples with inductively coupled plasma atomic emission spectroscopy (ICP-OES).

Preparation of Pb concentrations in test soil samples

The Tk series soil and Lp series soil were air-dried, ground, sifted with a 10-mesh (≦2 mm) filter, and stored inside PE buckets. The processed soils were then mixed with $PbNO_3$ to create two kinds of 1000 mg/kg Pb-contaminated soil samples (Merck, $Pb(NO_3)_2$, 99.9%). After the samples were dried, the same amount of deionized water was added and mixed properly with the two kinds of samples before they were put aside and dried again. The entire preparation involved two times of wetting and drying of the samples, which underwent a month of incubation for a subsequent study.

Stabilizing lead in the soil samples with hydroxyapatite and compost

100 g of each kind of the two Pb-contaminated soils (1000 mg/kg) were placed in 250 mL conical flasks. Each

sample was mixed with 10 g hydroxyapatite and 0%, 1%, 2%, 3%, and 5% compost before being processed in an isothermal shaker at 25°C for 30 d. The samples were then air-dried for subsequent analysis.

Extraction for analyzing various Pb distributions in the test soil samples

1 g of Pb-contaminated soil (1000 mg/kg) from each test soil sample was mixed with 40 mL of 0.11M CH_3COOH. Deionized water was added to the samples to make the total volume of each reach 50 mL. The mixtures were then shaken for 16 h at room temperature (rt) and processed with a centrifuge for 30 min, after which the supernatants were extracted and analyzed for the oxidation form concentrations of the soils. The subnatants were mixed with 40 mL of 0.1 M NH_2OH HCl before deionized water was added so that the total volume of each mixture reached 50 mL. The mixtures were then shaken for 16 h at rt and processed with a centrifuge for 30 min, after which the supernatants were extracted and analyzed for the $Pb_{Fe\text{-}Mn}$ form concentrations of the soils. The subnatants were mixed with 10 mL of 0.1M H_2O_2 and shaken for 1 h in a water bath at 85°C. The mixtures then had 50 mL of 1M $CH_3COOHNH_4$ added before being shaken for 16 h at rt and processed with a centrifuge for 30 min. The supernatants were extracted and analyzed for the Pb_0 form concentrations of the soils. Lastly, the subnatants were mixed with 10 mL of 0.1M aqua regia and deionized water, so the total volume of each sample reached 50 mL. The mixtures were shaken for 16 h at rt and processed with a centrifuge for 30 min. The supernatants were extracted and analyzed for the Pb_R form concentrations of the soils.

Results and Discussion

Analysis of oxides of different elements in the composition of two test soil samples

Table 1 shows the results of the analyses of the elemental compositions of the two kinds of soil samples. In terms of texture, the Tk series soil's particle size was around 0.063-0.004 mm, with silt taking up 53.4% of the composition and clay taking up 44.2%. In contrast, the Lp series soil had smaller particle size than the Tk series soil; it was low in sand content, which only took up 14.6%, but had high clay content, which took up 53.0%. In terms of pH, the Tk series soil's pH value was 8.25, meaning that it was a kind of strong alkaline soil because the parent material of the Tk series soil was high in calcium carbonate; its substratum contained a significant amount of lime concretion particles, which resulted in high pH value [17]. Conversely, the parent material of the Lp series soil was rich in iron and aluminum oxides, which rendered the soil acidic (pH = 4.21). As for specific surface areas, that of the Lp series soil (179.13 m^2/g) was significantly larger than the Tk series soil (24.51 m^2/g), indicating that the texture of the Lp series soil was finer than that of the Tk series soil. The degree of rock weathering of the Lp series soil was more complete than the Tk series soil, which was corroborated by the Lp series soil having higher clay content than the Tk series soil [18]. In further examining the soils' cation exchange capacity (CEC), we found that the CEC of the Tk series soil (14.43 cmole/kg) was higher than that of the Lp series soil (11.96 cmole/kg), suggesting that Tk series soil particles were lined up more densely than the Lp series soil particles. Also, the Tk series soil had higher organic matter content than the Lp series soil, indicating that the Tk series soil had higher Pb adhesion capacity than the Lp series soil.

soil	Water content %	pH	CO_3^{2-} %	CEC cmole/kg	Specific surface area (m^2/g)	Particle Size (%)			texture	organic matter content %
						sand	silt	clay		
Tk series soil		8.23		14.43	24.51	2.4	53.4	44.2	SiC	1.61
Lp series soil	3.33	4.21	0.63	11.96	179.13	14.6	32.4	53.0	clay	1.28

Table 1: Results of an Analysis on the Basic Properties of the Tk and Lp series soil

Pb distribution in test soil samples without hydroxyapatite and compost being added

Pb-contaminated Tk series and Lp series soils without hydroxyapatite and compost being added were incubated for a month and three months, respectively, and then analyzed for their Pb distribution. The analysis results are shown in Table 2. Table 2 indicates that after a month of incubation, the Pb_E concentration of the Lp series soil was higher than that of the Tk series soil, meaning that Pb in the Lp series soil precipitated after interacting with cations, causing Pb contamination. Similarly, after a month of incubation, the highest Pb concentration was observed in the $Pb_{Fe\text{-}Mn}$ of the Tk series soil, suggesting that the Pb contamination is less likely to occur in the alkaline Tk series soil, as Pb in the soil is less likely to interact with cations and trigger exchange reactions [19].

Compost concentration	Incubation period	Test soils	Pb_E	PbFe-Mn	Pb_O	Pb_R
			----mg/kg----			
0%	One month	Tk series soil	116 ±1.7	597 ±2.6	123 ±5.6	70 ±1.7
		Lp series soil	532±7.0	209 ±7.5	57 ±1.2	76±1.2
	Three months	Tk series soil	115±5.0	634±10.3	165±9.0	186±6.0
		Lp series soil	510±6.0	237±6.6	56±2.0	132±1.2

Table 2: Distribution of Pb forms in the soil samples without hydroxyapatite and compost being added.

Moreover, Table 2 shows that the resulting Pb_E concentrations of soil samples after three months of incubation were lower than those after only a month, meaning that longer incubation periods make it more difficult for Pb to precipitate via exchange reactions with cations, thereby making it less likely to cause Pb contamination. On the other hand, $Pb_{Fe\text{-}Mn}$ concentrations of the two soil samples increased after three months of incubation when compared to those after a month of incubation. This result suggests that the longer the incubation period, the less likely the occurrence of Pb contamination, since increasing iron and manganese concentration over time made it more difficult for Pb to precipitate via exchange reactions with cations [5,11].

Furthermore, Table 2 indicates that regardless of the organic forms of the two soil samples, there were no significant differences between the Pb_0 concentrations after one month and three months of incubation. However, the Pb_0 concentration of the Tk series soil was remarkably higher than that of the Lp series soil, meaning that it was easier for Pb to form hydroxides or phosphate precipitation that stayed in the structure of the Tk series soil. This result reflects the findings of the aforementioned experiment on Pb_E concentration.

Distribution of Pb forms in the soil samples when only hydroxyapatite was added

Table 3 shows the distribution of Pb forms in the two soil samples with hydroxyapatite being added and incubated for one month and three months, respectively. The results indicate that the Pb_R concentration was the highest compared to the other Pb form concentrations. Also, the Pb_R concentrations were remarkably higher after hydroxyapatite was added to the two samples. This finding suggests that hydroxyapatite helped to stabilize Pb in the soil samples, making it more difficult to precipitate and prevent Pb contamination by controlling the Pb concentration [20]. Moreover, in examining how incubation time influences the distribution of Pb forms in the soil samples, Table 2 shows that the Pb_E concentrations of the two samples after three months of incubation were lower than when the samples were only incubated for one month. This result demonstrates the same trend as that observed in Table 1: i.e., the longer the incubation period, the less likely the precipitation of Pb via exchange reactions with cations, leading to Pb contamination. The above analysis shows that hydroxyapatite can effectively immobilize Pb in the soil samples, decreasing the amount of Pb precipitated.

Compost concentration	Incubation period	Test soils	Pb_E	PbFe-Mn	Pb_O	Pb_R
			----mg/kg----			
0%	One month	Tk series soil	48 ±6.5	491 ±12	12 ±0.6	327 ±15.5
		Lp series soil	57 ±13.5	80 ±13.5	84 ±15.5	576 ±5.1
	Three months	Tk series soil	37 ±1.2	221 ±27.5	44 ±4.2	559 ±6.2
		Lp series soil	31 ±7.4	61 ±6.2	97 ±2.6	629 ±10.1

Table 3: Distribution of Pb forms in incubated soil samples with hydroxyapatite being added.

Distribution of Pb forms in the soil samples when both hydroxyapatite and compost were added

Table 4 presents the distribution of Pb forms in the two soil samples with hydroxyapatite and compost of different ratios being added and incubated for one and three months, respectively. The results show that after three months of incubation, the Pb_E concentration of the Tk series soil decreased (36→29→26) as the amount of compost increased. This result indicated that increasing compost concentration helped to raise the pH value of the soil and improve its fertility, while increasing the soluble nutrients in the soil that can be absorbed by plants [12,20]. In contrast, the Pb_E

concentration of the Lp series soil increased (25→31→35) as the compost concentration increased. This result signifies that an increase in compost concentration caused the soluble nutrients in the soil to decline (which can be corroborated by the finding in Table 2, where the Pb_E concentration of the Lp series soil was generally higher than that of the Tk series soil, making it easier for Pb in the Lp series soil to precipitate via exchange reactions with cations and causing Pb contamination). Also, an analysis of Pb_R shows that after a month and three months of incubation, the concentration of Pb_R was noticeably higher than that of the other three Pb forms because hydroxyapatite formed highly stable pyromorphite with Pb in the soil samples. Pyromorphite can enhance soil fertility and lower the availability of Pb in the soil, causing Pb precipitation to decline [12,19]. Moreover, Table 4 shows that the Pb_R concentrations of the two soil samples declined as the amount of compost increased, probably because the more compost added, the more the organic acid to precipitate part of the Pb_R, causing its concentration to drop [21,22]. This finding was contrary to the results in Tables 2 and 3 (which present the analysis results of soil samples when compost was not added). The above findings show that the amount of compost added influences the degree of precipitation of the Pb_R concentration, and that the amount of compost added was directly proportional to the amount of Pb_R precipitated.

Compost concentration	Incubation period	Test soils	Pb_E	PbFe-Mn	Pb_O	Pb_R
			----mg/kg----			
1%	One month	Tk series soil	27±1.0	46±2.0	346±11.5	452±21.5
		Lp series soil	52±2.1	92±5.5	117±4.2	565±6.0
	Three months	Tk series soil	36±1.2	42±2.6	117±9.0	680±16.7
		Lp series soil	25±4.6	75±4.0	330±20.1	394±27.0
3%	One month	Tk series soil	26±0.6	44±2.5	370±18.2	438±1.2
		Lp series soil	42±8.0	188±22.3	138±1.2	458±9.0
	Three months	Tk series soil	29±1.7	53±6.8	135±17.0	657±6.1
		Lp series soil	31±3.5	94±5.6	350±3.0	363±8.1
5%	One month	Tk series soil	27±3.0	41±5.0	373 ±8.5	437±2.1
		Lp series soil	35±12.0	242±8.0	149±6.8	399±12.2
	Three months	Tk series soil	26±5.3	42±5.6	157±13.0	65 ±16.6
		Lp series soil	35±0.6	98±8.0	372±15.4	331±26.9

Table 4: Distribution of Pb forms in incubated soil samples with hydroxyapatite and compost being added.

Conclusion

In this study, hydroxyapatite and compost of different mix ratios were added to high-concentration Pb-contaminated soil samples (1000 mg/kg), which were incubated for a month and three months, respectively, and had their distribution of four Pb forms analyzed via sequential extraction. Analyses of the basic properties of the two kinds of soils revealed that the Tk series soil had high pH as its parent material was high in calcium carbonate and its substratum contained a significant amount of lime concretion particles. In contrast, the Lp series soil was acidic because its parent material was high in iron and aluminum oxides. This study found that, after incubating the Tk series and Lp series soil samples for a month without hydroxyapatite or compost being added, the Pb_E concentration of the Lp series soil was higher than that of the Tk series soil, suggesting that the Lp series soil is more susceptible to Pb contamination because Pb in the soil is more likely to precipitate via exchange reactions with cations. Moreover, after three months of incubation, the Pb_E concentrations of both soil samples dropped below the level resulting from a month of incubation. This result indicates that the longer the incubation period, the less likely the occurrence of Pb contamination, since Pb is less likely to precipitate via exchange reactions with cations. Next, after incubating the two Pb-contaminated soil samples with hydroxyapatite being added for one month and three months, respectively, concentrations of Pb_R in both samples became the highest among the four Pb forms. The Pb_R concentrations in soils with hydroxyapatite being added were also significantly higher than those in soils without the substance being added. This result suggests that hydroxyapatite helped to stabilize Pb in the soils so that it did not precipitate so easily, thus controlling the Pb concentration below the contamination level. Finally, when it comes to soil samples with hydroxyapatite and compost of different mix ratios being added, Pb_R concentrations of both samples were found to be noticeably higher than those of the other three Pb forms after one month and three months of incubation because hydroxyapatite and Pb in the soils formed pyromorphite, a highly stable mineral that helps to enhance soil fertility and lower the availability of Pb in soil, causing the amount of Pb precipitated to decline. We hope that the research findings can be widely applied to contaminated soil treatment, serving as a reference especially for soil remediation and rehabilitation at soil treatment sites.

References

1. Beiyuan J, Awad YM, Beckers F, Tsang DCW, Ok YS, et al. (2017) Mobility and phytoavailability of As and Pb in a contaminated soil using pine sawdust biochar under systematic change of redox conditions. Chemosphere 178: 110-118.
2. Bilondi MP, Toufigh MM, Toufigh V (2018) Using calcium carbide residue as an alkaline activator for glass powder-clay geopolymer. Constr Build Mater 183: 417-428.
3. Dong D, Derry LA, Lion LW (2003) Pb scavenging from a freshwater lake by Mn oxides in heterogeneous surface coating materials. Water Res 37(7): 1662-1666.
4. Wang Y, Feng X, Villalobos M, Tan W, Liu F (2012) Sorption behavior of heavy metals on birnessite: relationship with its Mn average oxidation state and implications for types of sorption sites. Chem Geol 292-293: 25-34.
5. Tóth G, Hermann T, Silva MRD, Montanarella L (2016) Heavy metals in agricultural soils of the European Union with implications for food safety. Environ Int 88: 299-309.
6. Meynet P, Hale SE, Davenport RJ, Cornelissen G, Breedveld GD, et al. (2012) Effect of activated carbon amendment on bacterial community structure and function in a PAH impacted urban soil. Environ Sci Technol 46(9): 5057-5066.
7. Bucher R, Diederich P, Escadeillas G, Cyr M (2017) Service life of metakaolin-based concrete exposed to carbonation. Cem Concr Res 99: 18-29.
8. Clarke CE, Kielar F, Talbot HM, Johnson KL (2010) Oxidative decolorization of acid azo dyes by a Mn oxide containing waste. Environ Sci Technol 44(3): 1116-1122.
9. Zhao FJ, Ma YB, Zhu YG, Tang Z, McGrath SP (2015) Soil contamination in China: current status and mitigation strategies. Environ Sci Technol 49(2): 750-759.
10. Rajapaksha AU, Chen SS, Tsang DCW, Zhang M, Vithanage M, et al. (2016) Engineered/designer biochar for contaminant re- moval/immobilization from soil and water: potential and implication of biochar modification. Chemosphere 148: 276-291.
11. Gu F, Peng Z, Zhang Y, Tang H, Ye L, et al. (2018) Facile route for preparing refractory materials from ferronickel slag with addition of Magnesia. ACS Sustain Chem Eng 6: 4880-4889.
12. Pan SY, Shah KJ, Chen YH, Wang MH, Chiang PC (2017) Deployment of ac- celerated carbonation using alkaline solid wastes for carbon mineralization and uti- lization toward a circular economy. ACS Sustain Chem Eng 5(8): 6429-6437.
13. Huang Y, Deng MH, Wu SF, Jan JPG, Li TQ, et al. (2018) A modified receptor model for source apportionment of heavy metal pollution in soil. J Hazard Mater 354: 161-169.
14. Fang SE, Tsang DCW, Zhou FS, Zhang WH, Qiu RL (2016) Stabilization of cationic and anionic metal species in contaminated soils using sludge-derived biochar. Chemosphere 149: 263-271.
15. Zeng H, Yin C, Qiao T, Yu Y, Zhang J, et al. (2018) As(V) removal from water using a novel magnetic particle adsorbent prepared with iron-containing water treatment residuals. ACS Sustain Chem Eng 6(11): 11734-11742.
16. Wang L, Yeung TLK, Tsang DCW, Lau AYT, Poon CS (2017) Recycling con- taminated sediment into eco-friendly paving blocks by a combination of binary ce- ment and carbon dioxide curing. J Clean Prod 164: 1279-1288.
17. Liao CJ, Chung TL, Chen WL, Kuo SL (2007) Treatment of pentachlorophenol contaminated soil using nano scale zero-valent iron with hydrogen peroxide. Journal of Molecular Catalysis A: Chemical 265(1-2): 189-194.
18. Kuo SL, Wu EMY (2014) Adsorption cadmium and aniline of organoclay by HDTMA and CDTEA intercalating. Indian Chemical Society 91: 1757-1763.
19. Wang L, Cho DW, Tsang DCW, Cao X, Hou D, et al. (2019) Green remediation of As and Pb contaminated soil using cement-free clay-based stabilization/solidification. Environmental International 126: 336-345.
20. Liu LW, Li W, Song WP, Guo MX (2018) Remediation techniques for heavy metal-contaminated soils: principles and applicability. Sci Total Environ 633: 206-219.
21. McCann CM, Gray ND, Tourney J, Davenport RJ, Wade M, et al. (2015) Remediation of a historically Pb contaminated soil using a model natural Mn oxide waste. Chemosphere

138: 211-217.

22. Hettiarachchi GM, Pierzynski GM, Ransom MD (2000) In situ stabilization of soil lead using phosphorus and manganese oxide. Environ Sci Technol 34(21): 4614-4619.