

Short communication

## Adsorption of trace elements from poultry litter by montmorillonite clay

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### Abstract

Poultry litter (PL) is used as fertilizer on agricultural lands because of its high nutrient content. However, the litter also contains trace elements such as As, Cd, Cu, Pb, and Zn. On land application of PL, these trace elements may be absorbed by crops, leach into groundwater, or enter the aquatic system as run-off. The objective of this research was to study the effect of the addition of montmorillonite clay-mineral (CM) in reducing the release of trace elements from PL. Cd, Cu, and Zn showed significant decreases of 29, 34, and 22%, respectively, in PL aqueous leachate (compared with the control-PL without CM) on mixing with 0.05 g CM but no change in As, Co, and Cr concentrations was observed. Lead showed a significant increase in PL aqueous leachate on mixing with 0.2 g CM but Pb concentration was two orders of magnitude less than in CM aqueous leachate alone. On washing, the settled precipitate (PL + CM) in the centrifuge tubes with water (desorption study) most of the adsorbed metals (Cd 85%, Cu 61%, and Zn 100%) were released. The results of this study show that the addition of CM resulted in significant adsorption of Cd and Cu from PL.

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**Keywords:** Poultry litter; Montmorillonite; Trace elements; Copper; Cadmium; Zinc; Sorption

### 1. Introduction

Maryland is ranked seventh in the nation in poultry production [1]. The Delmarva Peninsula on the Eastern Shore of MD processed approximately 584 million birds in 2002 [2]. Broiler chickens are typically raised for 7 weeks, during which time they produce 12.16 kg of manure per bird [3]. Increased poultry production has resulted in a corresponding increase in the amount of poultry litter (PL) (manure mixed with straw, wood chips, sawdust, or peanut hulls) that must be disposed of. Poultry litter contains all essential plant nutrients (N, P, K, S, Ca, Mg, B, Cu, Fe, Mn, Mo, and Zn) and has been documented as an excellent fertilizer [4,5]. The use of PL improves soil fertility, soil aeration, and increases its water-holding capacity. More than 11.4 million Mg of PL was generated in USA in 1996 and approximately 90% was applied to land as fertilizer [6].

Trace metal salts are often added to poultry feed to increase feed efficiency, egg production, and to prevent diseases [6]. Drinking water and feed spillage also contribute to trace elements in PL [5]. The birds absorb very little of the added metal salts. Studies have shown that when Cu was included in the feed, Cu concentration in the waste was five to six times higher than in waste from birds not receiving Cu; the addition of As to the diet resulted in a seven-fold increase in As in the litter [5]. On average PL contains As, Cd, Cu, Mn, Pb, and Zn 37, 20, 390, 655, 35, and 377 ppm, respectively; this may vary depending on poultry production and management practices [4]. The trace elements (except Mn) are regulated by the United States Environmental Protection Agency (USEPA) for land application because of their potential phytotoxicity. An excess of these elements in the soil can be toxic to plants, may adversely affect organisms that feed on these plants, may result in bioaccumulation in animals and humans [7] and these elements may enter water systems through surface run-off and/or leaching [4,8]. The freshwater criteria for Cu and Zn are 12 and 110 ppm, respectively [9].

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Soils in agricultural areas serve as major sink for trace elements released into the environment from various anthropogenic sources including animal waste addition as fertilizer. Therefore, it is imperative to develop techniques that can treat and stabilize these contaminants in situ in an efficient and cost effective manner [10]. Metal immobilization through precipitation and adsorption decreases trace element concentrations in contaminated soils [11]. In addition to the binding sites on the surface of an immobilizing material, an increase in soil pH also contributes to the immobilization of trace elements by making existing sites more reactive towards metal binding due to decreased proton competition. Alkaline additives can improve the quality of many contaminated soils [12]. Clays are naturally occurring minerals and are widely available, non-toxic, and inexpensive; they are integral components of soil ecosystems. Due to the hydrophilicity of clays, their addition to soils can restore and enhance plant growth especially when the clays have large cation exchange capacities (CEC) [13]. A number of studies have shown that clayey soils retain toxic trace elements [14]. Clays can adsorb heavy metals both by ion exchange reactions and by formation of inner-sphere complexes [15]. The montmorillonite clay-mineral (CM) is composed of units made of two silica tetrahedral sheets with a central alumina octahedral sheet. All the tips of the tetrahedrons point in the same direction and toward the center of the unit. Exchangeable cations occur between the silicate layers; the CEC of montmorillonite is 80–150 milli-equivalents per 100 g [16]. There is little information on the adsorption of trace elements from PL on the addition of clay minerals. The objective of this study was to measure the changes in the concentration of trace elements in PL (aqueous leachate) after mixing with montmorillonite clay-mineral.

## 2. Methods and materials

A representative sample of PL was collected in plastic bags from the university poultry house, air-dried, homogenized, sieved (<4 mm) and stored at 4 °C. The CM (Na-montmorillonite) was obtained from the Clay Minerals Repository, Department of Geology, University of Missouri, Columbia, MO. Poultry litter (1 g) was mixed with montmorillonite (0.0, 0.01, 0.05, and 0.2 g) in polyethylene bottles and 100 ml of ultra-pure water. The amount of CM used was based on preliminary experiments with varying concentrations of CM and were finally dictated mostly by the cost factor, including the cost of spreading in agricultural fields by farmers. The mixtures were shaken in an orbital shaker (Barnstead/Lab-line 4644) at 230 rpm for 31 d, to ensure thorough mixing, centrifuged (IEC Model 2K) at 3000 rpm, and the supernatant filtered (25 µm). All experiments were performed in triplicate. Conductivity, total dissolved solids (TDS) and pH were measured using Horiba U-23 Water Quality Monitor. Total dissolved organic carbon was analyzed using Shimadzu TOC-V Series Analyzer. The filtered supernatant was mixed with nitric acid to bring the pH ≈ 2.5

and an internal standard (10 ppb Yttrium) was added. The trace elements (As, Cd, Co, Cr, Cu, Pb, and Zn) were analyzed using Perkin-Elmer (Elan 6100C) Inductively Coupled Plasma-Mass spectrometer (ICP-MS). For desorption studies, the settled precipitate at the bottom of the centrifuge bottle was mixed thoroughly with 100 ml of ultra-pure water, kept in the shaker for 24 h, centrifuged, filtered, acidified and trace elements analyzed in the filtrate after addition of the internal standard. Statistical analyses was done using ANOVA and LSD mean comparison test ( $P \leq 0.05$ ).

Adsorption and desorption were calculated using the following equations:

$$X = \frac{a - b}{a} \times 100;$$

where  $X$  is initial adsorption (%),  $a$  trace element concentration in PL, and  $b$  is trace element concentration in PL + CM.

$$Y = \frac{a - b - c}{a - b} \times 100;$$

where  $Y$  is desorption (%) and  $c$  is trace element concentration in PL + CM after washing.

$$Z = XY;$$

where  $Z$  is final adsorption (%) after washing.

## 3. Results and discussion

Using multi-element solutions of various concentrations (1, 10, 100 ppb) of trace elements of interest, the equipment standardization was carried out periodically. Little As, Cd, Co, and Cr but significant amounts of Cu, Pb, and Zn were found in the aqueous leachate of CM after 31 d mixing with water (Table 1). On increasing the CM concentrations, the amounts of leached Cu, Pb, and Zn decreased significantly. Swelling of Na-montmorillonite clays (from 10 to 200 Å thickness) with time and subsequent adsorption of cations is well known because of its high CEC [16]. Metal sorption, particularly Zn, on montmorillonite showed that different type of complexes are formed depending on the reaction time; formation of mixed metal solids accounts for the slow continuous sorption reaction at aging times exceeding 20 d [17].

Table 1  
Trace element concentrations (mg/kg) in clay aqueous leachate

Element	0.01 g CM	0.05 g CM	0.2 g CM	LSD
As	0 ± 0	0 ± 0	0.15 ± 0.05	–
Cd	0 ± 0	0 ± 0	0 ± 0	–
Co	0 ± 0	0 ± 0	0.23 ± 0.06	–
Cr	0 ± 0	0 ± 0	0.02 ± 0.03	–
Cu	47.2 ± 12.2 <sup>a</sup>	10.3 ± 5.3 <sup>b</sup>	3.0 ± 0.9 <sup>b</sup>	16.3
Pb	15.5 ± 4.6 <sup>a</sup>	10.1 ± 0.3 <sup>b</sup>	9.3 ± 0.19 <sup>b</sup>	5.3
Zn	43.5 ± 1.8 <sup>a</sup>	29.5 ± 1.2 <sup>b</sup>	21.7 ± 0.5 <sup>c</sup>	2.5

Different superscripts (a and b) indicate significant difference in concentration at  $P \leq 0.05$ .

Table 2

Trace element concentrations (mg/kg) in PL aqueous leachate on the addition of clay

Element	PL	PL + 0.01 g CM	PL + 0.05 g CM	PL + 0.2 g CM	LSD
As	16.4 ± 1.3	17.5 ± 1.5	17.6 ± 4.6	15.3 ± 3.5	5.71
Cd	0.07 ± 0 <sup>a</sup>	0.07 ± 0 <sup>a</sup>	0.05 ± 0 <sup>b</sup>	0.07 ± 0.01 <sup>a</sup>	0.01
Co	0.36 ± 0.02	0.36 ± 0.03	0.28 ± 0.09	0.32 ± 0.08	0.12
Cr	0.7 ± 0.02	0.7 ± 0.02	0.6 ± 0.10	0.8 ± 0.13	0.16
Cu	249.0 ± 16.9 <sup>a</sup>	248.6 ± 14.8 <sup>a</sup>	165.0 ± 17.2 <sup>b</sup>	196.6 ± 25.6 <sup>b</sup>	35.94
Pb	0.03 ± 0.01 <sup>b</sup>	0.03 ± 0.01 <sup>b</sup>	0.05 ± 0.01 <sup>b</sup>	0.13 ± 0.07 <sup>a</sup>	0.06
Zn	77.0 ± 1.9 <sup>a</sup>	73.2 ± 3.3 <sup>a</sup>	60.1 ± 10.1 <sup>b</sup>	75.6 ± 12.0 <sup>a</sup>	15.18

Different superscripts (a and b) indicate significant difference in concentration at  $P \leq 0.05$ .

Table 3

Adsorption and desorption data: trace element concentrations (mg/kg) in PL aqueous leachate on the addition of 0.05 g clay

Element	PL (a)	PL + 0.05 g CM (b) (% initial adsorption, X)	PL + 0.05 g CM (c) (% desorption after washing, Y)	% Final adsorption after washing, Z
Cd	0.07 ± 0	0.05 ± 0 (29)	0.003 ± 0.006 (85)	24.7
Cu	249.0 ± 16.9	165.0 ± 17.2 (34)	33.1 ± 11.5 (61)	20.7
Zn	77.0 ± 1.9	60.1 ± 10.1 (22)	18.7 ± 9.5 (100)	0

No significant change in PL aqueous leachate conductivity (0.17 S/m), salinity (1‰), and total dissolved solids (1.2 g/l) concentration was observed on mixing with CM. Poultry litter aqueous leachate showed the presence of small amounts of Cd, Co, Cr, and Pb and significant amounts of As, Cu, and Zn (Table 2). No change in As, Co, and Cr concentrations was observed on mixing PL with various concentrations of CM (Table 2). Cd, Cu, and Zn showed a significant decrease compared with control (PL without CM) of 29, 34, 22%, respectively, on mixing PL with 0.05 g CM. On mixing PL with CM, an exchange of the divalent cations in the PL with  $\text{Na}^+$  on the clay lattice takes place, and the release of the alkaline metal from the clay may thus slightly increase the pH further reducing the solubility of some metal salts [18]; in this experiment, the pH changed from 8.5 (PL alone) to 8.65 (on mixing PL with 0.2 g CM). Trace elements (As, Co, and Cr) whose concentration did not change on mixing PL with CM appear to be more strongly bound possibly on the organic ligands in PL [19]. Highest reduction in the concentrations of Cd, Cu, and Zn was observed on the addition of 0.05 g CM. In the presence of Cd, Cu is preferentially adsorbed (up to 99%) by bentonite type clays [20]. Partitioning of heavy metals between solid and aqueous phase is controlled by properties such as surface area, pH, ionic strength and concentration of complexing ligands [11].

CM and organic matter are most important groups in contributing to and competing for the sorption of trace elements; this chemi-sorption method is based on valency forces. The functional group  $-\text{Al}-\text{OH}$  produces  $-\text{Al}-\text{O}^-$  upon dissociation and attracts cations forming the complex  $-\text{Al}-\text{O} \cdot n\text{H}_2\text{OM}$  where M denotes cations. The pH regulates the charge and metal adsorption by the surface through competitive processes forming inner-sphere complexes according to Henderson–Hasselbalch equation [21]. The CEC, based on surface charge, controls the adsorption of metals; CEC of montmorillonite is the highest among clays [16,18].

Lead, on the other hand, showed a significant increase on mixing PL with 0.2 g CM; the CM leachate has a very high amount (two orders of magnitude) of Pb compared with PL leachate. The CM is not able to adsorb Pb; poor immobilization of Pb with similar clays has also been reported earlier [22]. Lead has a lower electrostatic attraction because of its lower charge density; presence of organic ligands influences the adsorption of heavy metals on montmorillonite and metal adsorption decreases in the order:  $\text{Cr} > \text{Cu} > \text{Zn} > \text{Cd} \approx \text{Pb}$  [23]. In the present study, Pb released from the CM appears to have been adsorbed by the organic ligands in PL (the amount of dissolved organic carbon in PL leachate was 21 ppm).

On washing the settled precipitate (PL + CM) in the centrifuge tubes with water for desorption studies much of the adsorbed metals (Cd 85%, Cu 61%, and Zn 100%) were released (Table 3). Only Cd (25%) and Cu (21%), from the original amount in PL, were finally retained by the CM supporting interstitial adsorption of Cd and Cu by the CM [24]. The results of this study show that the addition of CM resulted in significant adsorption of only Cd and Cu (and not Zn) from PL. From this study, we can conclude that the addition of 20% CM (0.05 g CM to 1 g PL) to PL in agricultural fields will result in significant retention of Cd and Cu in the soils.

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