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Short Communication

Characterization of Heavy Metals in Livestock Manures

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Abstract

The use of animal waste for soil amendment is a viable option for waste management. For safe and sustainable management of waste, it is important to assess its chemical speciations. Therefore, an experiment was carried out to compare changes in heavy metals (HM) [cadmium (Cd), mercury (Hg), nickel (Ni), and lead (Pb)] fractions in five types of livestock manures, namely cow, goat, sheep, chicken, and ostrich. The metals were stepwise fractionated into exchangeable, adsorbed, organically bound, carbonate-precipitated, and residual forms by extracting with 0.5 M KNO_3, de-ionized water, 0.5 M NaOH, 0.05 M Na_2 EDTA, and 4 M HNO_3, respectively. Extractability of HM was found to be highly dependent upon the type of waste as well as extracting agent. Manures differed for the release of HM as chicken > ostrich > sheep > cow > goat. Extractions released HM in the order of Ni > Pb > Cd > Hg. For all metals, extracting agents differed in the order HNO_3 > EDTA > NaOH > KNO_3 > H_2O, irrespective of the kind of manure. Carbon content in the poultry manure (both ostrich and chicken) was less than other animals. Poultry manure released more P than goat, sheep, and cow. Chicken manure got the highest pH (9.5) whereas cow manure had the lowest pH value (8.4). Among manures, EC was measured as goat > cow > sheep > ostrich > chicken.

Keywords: livestock manures, heavy metal fractions, extracting agents

Introduction

Organic waste is produced wherever there is human habitation. In industrialized countries the production of organic waste is relatively increasing each year. The main forms of organic waste are household food waste, agricultural waste, and human and animal waste. The management of livestock manure with consideration for environmental quality should be an important goal when recycling farm wastes as soil amendments [1, 2]. Livestock manures contain a considerable amount of heavy metals [1]. Increasing interest in the recycling of manure as soil amendments has now raised concern about possible metal contamination from its use [1, 3]. Heavy metals are the most widely known pollutants that ultimately transfer to the aquatic system [4]. This concern has potential for substantially restricting manure use in the future, if no precaution is taken to reduce heavy metal content. The large amounts of poultry waste produced annually are dispersed intensively over relatively small areas of land, resulting in accumulations that pose potential environmental risks to the surface and groundwater [5]. It is essential to assess the actual composition of metals to reduce the risk of offsite contamination and ensure a safe agro-ecosystem.

Several methods have been developed to predict phytoavailability of metals, which have largely been applied for

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plants and soil. Phyto-availability often has been defined through one-step soil extracting procedures. The amount of heavy metals extracted by such methods gives an idea of the size of a pool that might be depleted by a plant during the growth period; however, the extent of extracting methods depends on the soil tested. The determination of total heavy metal content of soil samples is not sufficient to evaluate the possible mobility and, consequently, the bioavailability of toxic metals to a living organism. The application of sequential extraction procedures allows the determination of chemical forms in which the elements appear to be associated in the sample. It can help to assess how strongly they are retained in soil and how easily they may be released into soil solution. Different sequential extraction techniques, such as the five-step procedure of Tessier et al. [6], are commonly applied to evaluate the actual and potential mobility of metals in the environment. These heavy metal pools may be selectively affected by plant uptake, and change in their proportions may give an idea on the mechanism responsible for heavy metal uptake in comparison with chemical pool in the soil.

Speciation of heavy metals in soils determines the availability for metals for plant uptake and potential for contamination of groundwater following the application of composts to agricultural lands [7]. Conceptually, sequential fractionation categorizes metals associated with chemically homogeneous fractions that ultimately affect metal availability. Sequential extraction (or fractionation) procedures have been developed predominantly to determine the amounts and proportions of metals present in different forms in soil or sediment samples [6]. However, such procedures have also been used quite widely to fractionate metals in animal waste, poultry waste, tannery sludge, and waste-treated soils [8-11]. Trace metals in soils and bio-waste exist in different forms, including:

i) water-soluble
ii) exchangeable
iii) linked to organic substances
iv) occluded or co-precipitated with oxides, carbonates and phosphates, or other secondary minerals
v) ions in the crystalline lattices of the primary minerals [12, 13].

The first three chemical forms are considered to be balanced among themselves; this equilibrium is influenced by pH and the concentrations of metals and ligands. The metals present in these forms are considered to be the most available forms of plant nutrition, with each successive form representing less availability [12].

Determination of total metal concentrations in soils or manures is considered to be of limited use in assessing potential environmental impacts, since it may indicate the overall level of metals in the material but provides no information on the chemical nature or potential mobility and bioavailability of a particular element [14]. Contaminating effects of heavy metals in soils depends on their chemical associations. Therefore, determining the chemical form of a metal in soils is important to evaluate its mobility and bioavailability.

Fractionation procedures are often criticizes because of their complexity and difficulty in interpretation, arising from potential problems such as lack of specificity of extractants and sorption of metals during extraction [15]. Yet the use of sequential extraction techniques to fractionate metals in solid materials and to evaluate their potential effects has become widely used and well recognized [6].

Metal fractionation in poultry and animal waste can provide useful information to predict their bio-availability and the potential for contamination of soils and waters. Most research on metal contamination in soils has been done in relation to municipal sewage sludge application and, to date, very little work has been done in relation to metal input from animal waste and poultry manure by products [16]. Research reports on the speciation of metals in poultry and other animal manures are particularly quite lacking. Therefore, an experiment was conducted to compare heavy metal fractions among five types of livestock manures.

Experimental Procedures

Five types of manures (cow, goat, sheep, chicken and ostrich) were collected locally. The manures were air dried, crushed and sieved (< 250 micron) to ensure homogeneity. For carbon content manure samples were weighed up to 50g into porcelain crucibles and ashed at 550ºC for 2 h. On removal from the oven, samples were placed in glass desiccators and allowed to cool for 30 min. before the initial oven-dry weight was recorded to calculate percent loss in weight. This indicated the loss of carbon. The pH and electrical conductivity (EC) were measured in 1:5 sample-H_2O suspensions by EC meter and pH meter, respectively. Phosphorus was extracted with water and determined by blue color method via spectrophotometer at 710 nm [17].

Metal Fractionation

Modified versions of a sequential extraction procedure [8] were employed to fractionate the solid-phase chemical forms of the metals. The modified extraction procedure, developed on the basis of studies with model-heavy metal compounds, is believed to give data concerning the forms of heavy metals. Sequential extractions were carried out in triplicate using 0.5 g of each manure sample in 50 mL centrifuge tubes. The trace elements (metal is substituted for trace elements or heavy metals for brevity throughout the text) were fractionated into exchangeable, adsorbed, organically bound, carbonate precipitated and residual forms by sequential extractions with 25 mL of the following reagents: 0.5 M KNO_3, 16 hours; de-ionized water, 2 hours (extracted three times and combined); 0.5 M NaOH, 16 hours; 0.05 M Na_2 EDTA, 6 hours, and 4 M HNO_3 16 hours at 80ºC, respectively. The schematic fractionation procedure is given in Fig. 1. During each extraction, the sample suspension was centrifuged at 5,000 rpm for 15 min. and the resulting supernatant solution was decanted and filtered by a 0.22-µm filter. The content of metals [nickel (Ni), lead

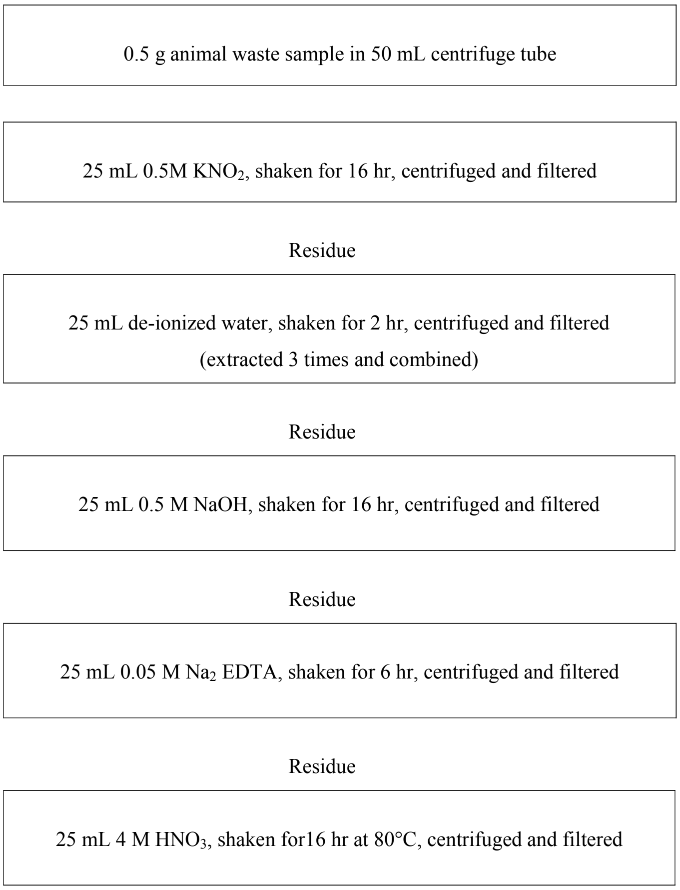

Fig. 1. Schematic diagram of sequential fractionation of trace elements.

(Pb), cadmium, (Cd), and mercury (Hg)] in the filtered solution was determined with an atomic absorption spectrophotometer using standards with the extractant to form the background matrix. A complete weight balance system was used to determine the amounts of metal obtained by each extraction. Taking into account the volume of water carried over in the next extraction, each metal fraction was corrected for the aqueous phase elements in lieu of washing the sample with deionized water after centrifugation, as suggested by Stover et al. [8]. Manures' effects on metal fractions were analyzed by the analysis of variance using Statview software [18]. A probability level of < 0.05 was considered significant and means were compared by least significant difference (LSD-test).

Results and Discussion

Investigation of metals fractions in animal manures can provide useful information to predict their bio-availability and the potential for contamination of soils and waters. Therefore, this experiment was carried out to compare changes in metals (Ni, Pb, Cd, and Hg] fractions in five types of animal manures, namely cow, goat, sheep, poultry, and ostrich. The metals were stepwise fractionated into exchangeable, adsorbed, organically bound, carbonate-precipitated, and residual forms by extracting with 0.5 M KNO_3, de-ionized water, 0.5 M NaOH, 0.05 M Na_2 EDTA, and 4 M HNO_3, respectively. Heavy metals extracted by various chemicals methods were given in Figs. 2 and 3. During the extraction process, the amounts of metals remained highly dependent on extraction methods. The metal fractions extracted by reagents varied in the order HNO_3 > EDTA > NaOH > KNO_3 > H_2O. Concentration of Cd was varied according to animal waste. Regardless of extractant, manure samples differed for Cd as ostrich > chicken > sheep > cow > goat. Mercury differed among manures as sheep > chicken > ostrich > cow > goat. Regardless of extractant, manure samples differed for Ni as sheep > chicken > ostrich > goat > cow (Fig. 2). Lead differed among manures as chicken > sheep > ostrich > goat > cow. Higher content of trace elements in poultry litter (PL) have been associated to their addition in the poultry feed for disease prevention and enhanced feed efficiency. Therefore, high concentrations of these elements in PL enhanced trace elements in PL-amended soils [19]. Bolan et al. [2] reported that the concentration of metals can vary considerably among animal manures. Additional variation is associated with the age of the animal type of ration, housing type, and waste management practice. Increases in metal concentrations in animal feed have often resulted in concentrations in the manure by-products in the effluent. The type of bedding material in animal waste units may influence the litter dry matter and other chemical properties [20]. Pare et al. [21]

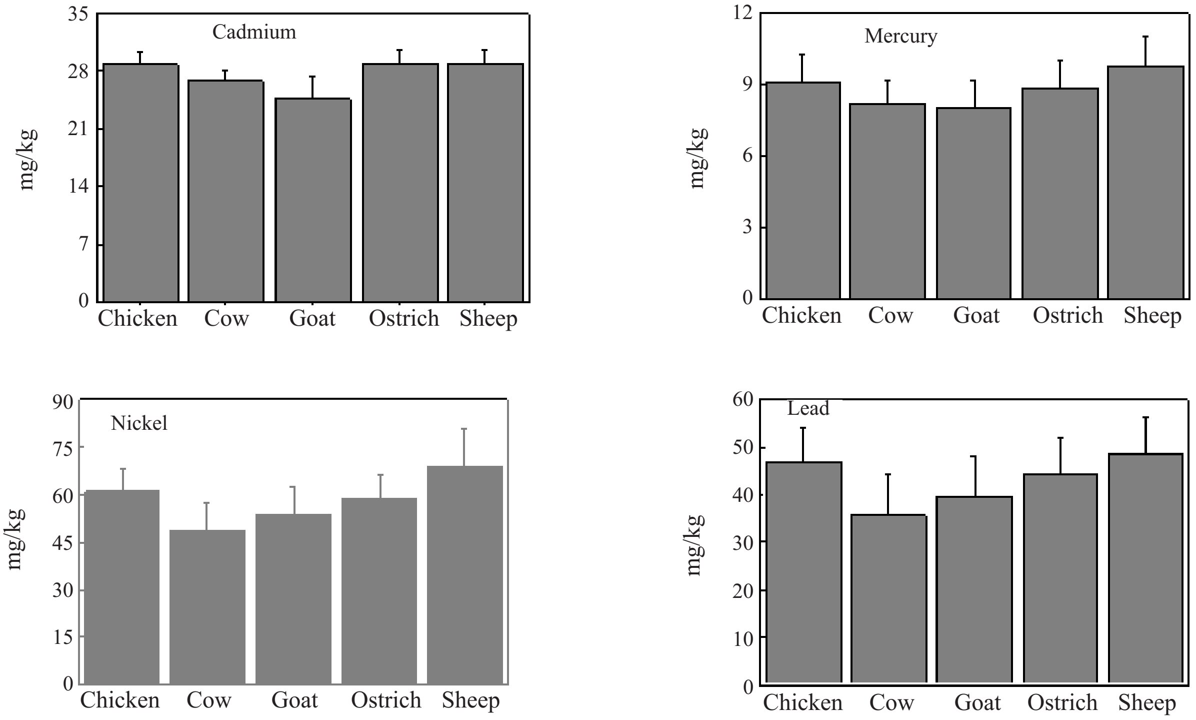

Fig. 2. Comparing trace element concentrations in livestock manures.

reported increases in the total concentration of some residual heavy metals, ranging from 26 to 145% increases after 41 days to composting of biosolid and municipal solid wastes; concentrations of some other metals remained constant or decreased during composting. Sequential extraction of metals indicated a decline in soluble component and an increased in residual, organically bound forms [21].

Irrespective of the manure, elements were varied in the order of Ni > Pb > Cd > Hg (Fig. 2). Metal differences in manures may reflect the variability in the total amount of element in a particular waste. The variations in the heavy metals could be related to the chemical properties of the individual metal and the characteristics of the manures, which are a function of the animal type, feed, and farm practices.

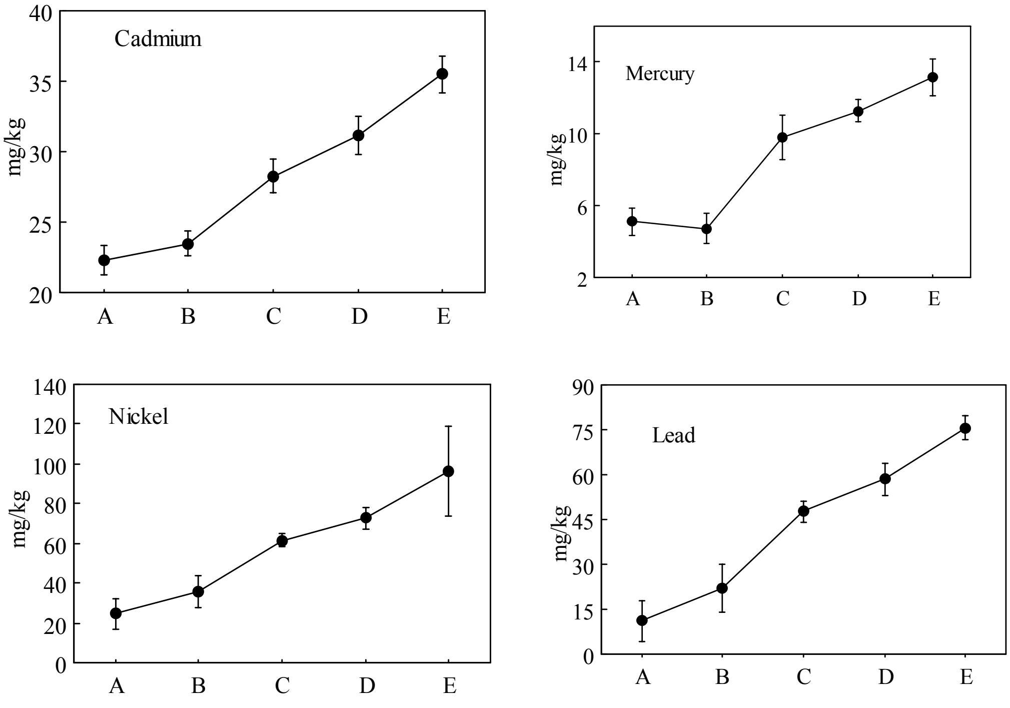

Fig. 3. Trace element concentrations in livestock manures as affected by different extraction methods.
A – KNO_3, B – H_2O, C – NaOH, D – Na_2EDTA, E – HNO_3

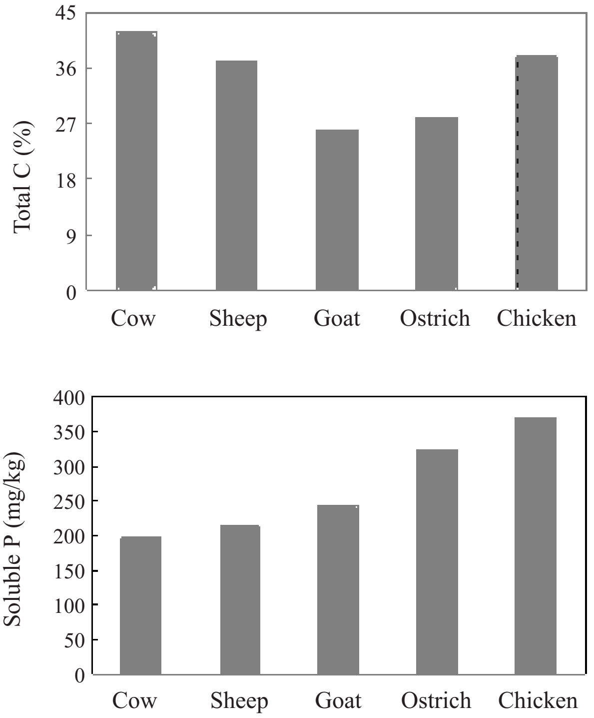

Fig. 4. Total carbon and water-soluble P in livestock manures.

Carbon content in poultry manure (both ostrich and chicken) was less than other animals (Fig. 4). Poultry manure released higher content of water-soluble P than goat, sheep, and cow. pH in the chicken manure was highest (9.5), whereas lowest pH was found in cow (8.4). Among manures, EC was ordered as goat > cow > sheep > ostrich > chicken (Fig. 5).

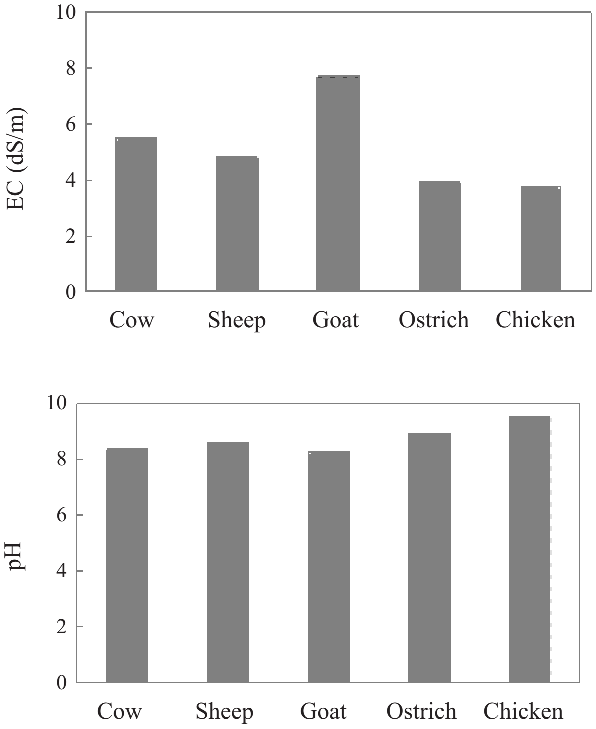

Fig. 5. Electrical conductivity (EC) and pH of livestock manures.

Faridullah et al. [22] reported substantial impact of ashing on the fractions of the trace elements in chicken and duck litter. They related the inhibited solubility of the metals in the incinerated samples to the formation of insoluble metals complexes in the presence of inorganic elements and enhanced alkaline pH of the ash. Trace elements precipitation is highly pH-dependent and increases with pH for many trace elements. Lindsay [23] also reported that trace elements form soluble precipitates with phosphate, sulfides, and other anions. The metal content of manure by-product depends primarily on the amount used in the feed and health remedies. Increases in metal concentration in animal feed often have resulted in corresponding increases in their concentrations in manure by-products [24]. The differences in metal distribution among fractions could have implications on the mobility and/or bioavailability of these metals when poultry or duck litter is applied to the soils. Heavy metals, when in high enough concentrations, have the potential to be both phytotoxic and zootoxic [9]. Since metal phytotoxicity in soils is determined by the fraction of the metals that is bioavailable, the lower concentrations of soluble and exchangeable elements formed in particular manure may produce less concern about potential toxic effects of associated metals in the agro-ecosystem.

The extractability of elements varied considerably depending on type of livestock and extraction methods. The principal metal forms in manure and manure-treated soil are soluble, exchangeable, absorbed, organic bound, oxide bound, and precipitated [25, 26]. Our previous studies indicated the metals in the animal waste in the stable organically bound, carbonate, and residual forms and the extractions were relatively varied for heavy metals [27]. Ure [28] reported that the EDTA method extracted elements in all the non-silicated bound soils. Pueyo et al. [29] recommended the 0.01 M $CaCl_2$ extraction method because of its feasibility for elemental analysis. The available pool of metal also is the most labile form in the soil environment and has greater leaching potential than the other forms [29].

Conclusions

We have concluded that the extractability of heavy metals was the function of animal waste and the extraction reagent used. Manures differed for the release of HM as chicken > ostrich > sheep > cow > goat. Except water, extractions released HM in the order of Ni > Pb> Cd > Hg. The amount of extracted metals varied in the order HNO_3 > EDTA > NaOH > KNO_3 > H_2O, irrespective of the type of manure. Carbon content in poultry manure (both ostrich and chicken) was less than other animals. Poultry manure released more P than goat, sheep, and cow. pH of chicken manure was highest (9.5), and the lowest pH was found in cow (8.4). Among manures, EC was ordered as goat > cow > sheep > ostrich > chicken. It is suggested that manure may cautiously be examined for metal content before its application to an agricultural field.

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