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TOTAL CONTENT AND AVAILABILITY OF MICRONUTRIENTS IN SOILS AND LIVESTOCK MANURE

Contenido total y disponibilidad de micronutrientes en suelos y excretas bovinas

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Key words: trace metals, cattle manure, sequential extraction, organic fertilization

ABSTRACT

The use of feedlot cattle manure appears as an important source of certain trace metals in soils that can be mobilized by water modifying the surface and groundwater quality. The current study is focused on assessing the availability of copper (Cu), zinc (Zn), cobalt (Co) and molybdenum (Mo) in manure from confined beef cattle systems and different soils of the Chaco-pampean plain, using a sequential extraction scheme. Soils and bovine manure coming from intensive (IS) and extensive (ES) beef cattle systems were collected. Total contents of Cu, Zn, Co and Mo were determined after microwave assisted acid digestion. Availability was evaluated through sequential extraction, including water-soluble and exchangeable fraction (EXCH), organic matter bound fraction (OM), inorganic precipitated fraction (INOR), and residual fraction (RES). Total Cu and Zn contents found in manure coming from IS were higher than the concentration of the aforementioned trace elements determined in all soils and manure analyzed from ES. EXCH-Cu only appears in IS cattle manure samples, while EXCH-Zn found in IS manure samples were higher than the soils samples analyzed. The higher levels of total and availability forms of Cu and Zn determined in IS manure compared to soils samples, require considering when this organic amendment is applied as fertilizer. These results indicate that the reuse of intensive cattle manure as fertilizer in agricultural areas could provide available forms of metals in soils and could contribute to reduce the environmental impact caused by the accumulation of excreta in pen soils during long periods in farms.

Palabras clave: elementos traza, estiércol bovino, extracción secuencial, fertilización orgánica

RESUMEN

El uso de excretas provenientes de sistemas intensivos de engorde bovino aparece como una fuente importante de ciertos metales traza en suelos, los cuales pueden ser movilizados por escorrentía y lixiviado, modificando la calidad de cursos de agua superficial y subterránea. Este trabajo propone evaluar la disponibilidad de cobre (Cu), zinc (Zn), cobalto (Co) y molibdeno (Mo) en excretas provenientes de sistemas intensivos de engorde bovino y en diferentes suelos de la llanura Chaco-pampeana, utilizando un procedimiento de extracción secuencial. Se recolectaron muestras de suelos y excretas provenientes de sistemas intensivos (SI) y extensivos (SE) de producción de ganado vacuno. Los contenidos totales de Cu, Zn, Co y Mo se determinaron mediante digestión ácida asistida por microondas. La disponibilidad fue evaluada mediante un esquema de extracción secuencial que incluyó una fracción soluble en agua e intercambiable (INT), una fracción unida a materia orgánica (MO), una fracción inorgánica (INOR) y una fracción residual (RES). Los resultados obtenidos mostraron mayores contenidos totales y de la fracción intercambiable de Cu y Zn en excretas provenientes de SI respecto de las muestras de suelos y excretas provenientes de SE. Estos resultados indicarían que el uso de las excretas de sistemas intensivos de engorde bovino incrementaría las formas más disponibles de metales en suelos, de modo tal que su empleo como enmiendas orgánicas puede contribuir a reducir el impacto ambiental que origina su acumulación en suelos de corrales.

INTRODUCTION

Population growth and global demand for agricultural products have promoted an important increase in livestock production (FAO 2002). In Argentina, traditional beef cattle systems, mainly grazing or extensive were modified to intensive production units, where animals are fed with diets based on concentrated foods. For instance, 1.47 million heads of cattle were fattened in beef cattle intensive systems in 2017 (MAGyP 2017).

Concentrated foods contain a high nutrient load to achieve efficient production rates, but in general beef cattle retain less than 20 % of the consumed nutrients (Hou et al. 2016). The excreta levels daily eliminated by a bovine are around 5 to 6 % of their body weight. For example, a steer of 400 kg live weight generate between 20-25 kg of manure per day. Considering an 80-85 % moisture, an average of 3 kg of solid residue is daily produced per animal (Steinfeld et al. 2006).

The production and storage of these wastes are responsible for most environmental problems associated with intensive beef cattle production systems (De Vries et al. 2015). Major forms of pollution associated with manure management in intensive livestock production include eutrophication of surface water, leaching of nitrates and pathogens, nutrients and trace metals accumulation in soils, release of ammonia, methane and other gases (FAO 2005).

Most of the environmental problems associated with land application of manure have centered on surface and/or groundwater pollution with nitrogen or phosphorus. However, the high levels of trace elements observed in manure of confined beef cattle condition a potential danger of soil pollution (Sungur et al. 2016). Trace metals accumulation in soil through manure application may cause phytotoxicity and zootoxicity problems; or may leave soils by leaching surface-water runoff, causing water and sediment contamination. In previous studies in our lab, it was determined that trace elements, mainly Cu and Zn, are eliminated in beef cattle manure in high levels and repeated land application resulted in elevated concentrations of these metals in soils. Metal accumulation appeared to be directly proportional to the age of emplacement of the establishment (Moscuzza and Fernández-Cirelli 2009).

In order to mitigate the environmental effect, cattle manure has been used in biogas production or organic fertilization. Livestock manure has been traditionally used as an organic fertilizer in farmlands, employed to improve soil quality and recover phosphorus, carbon, and nitrogen, essential nutrients for plants growth (Zhao et al. 2014). It has been reported that the addition of animal manure or compost increases organic matter content and improves the soil aggregates stability, porosity, water retention and infiltration capacity (Sager 2007).

In the Chaco-pampean plain, a wide agricultural region located in the center of Argentina where most intensive beef cattle production units are located, many soils present low levels of micronutrients such as Cu and Zn, and deficiencies have been reported in grazing cattle (Lavado et al. 2004, Lavado 2006). Therefore, the use of manure from intensive beef cattle production systems as a source of organic fertilizer could represent an environmentally friendly way of disposing these organic wastes and supplement soils and forages destined to grazing cattle in an area naturally deficient in these micronutrients.

Several factors including metals adsorption in soils, metals distribution between the different geochemical fractions and availability, should be considered when manure is applied as fertilizer in crop soils (Torri and Lavado 2008, Achiba et al. 2010).

Within this context, it will be of interest to predict potential changes of the mobility and availability of trace elements arising from feedlot manure application and the inorganic compositions of the target soils from various organic fertilizers. Therefore, in the present study the availability of copper, zinc, cobalt and molybdenum will be studied in manure from confined beef cattle systems and different soils samples from the Chaco-pampean plain, by using a sequential extraction scheme.

MATERIALS AND METHODS

Soil samples from different regions of the Chaco-pampean plain in Argentina were collected. Five sampling sites were selected taking into account the differences in edaphoclimatic conditions between agro-ecological zones. These sites were located in different departments of the Buenos Aires province (**Fig. 1**):

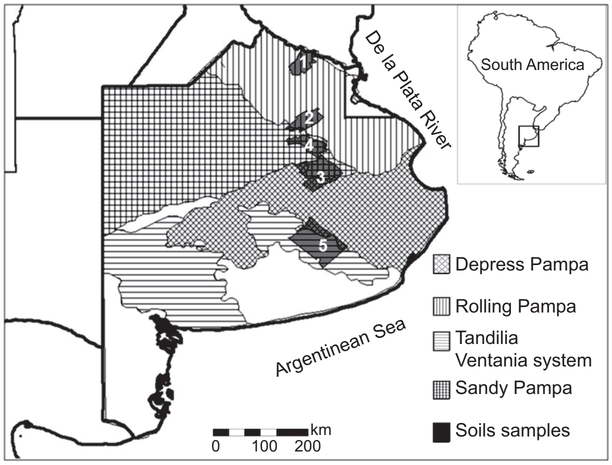

Fig. 1. Different agro-ecological zones of the Buenos Aires province and soil samples, adapted from Secretaría de Agricultura, Ganadería, Pesca y Alimentos (1995)

- Site 1, Baradero (33º 48’ 57” S-59º 32’ 03” W)
- Site 2, Navarro (34º 58’ 19” S-59º 08’ 22” W)
- Site 3, Las Flores (35º 51’ 54” S-58º 54’ 43” W)
- Site 4, Roque Pérez (35º 21’ 30” S- 9º 30’ 49” W)
- Site 5, Tandil (37º 19’ 55” S-59º 02’ 25” W)

Baradero is located in the “rolling Pampa”. Las Flores and Roque Pérez departments are part of the northwest of Buenos Aires province, denominated “sandy Pampa”. The Navarro department is in the north border of the “depressed Pampa”. The transition zone with the rolling Pampa and Tandil belongs to an area denominated “Tandilia system”, a zone of hills. Soil samples (0-10 cm depth) were obtained by an auger blade in uniform environments with minimal anthropic disturbance due to tillage (sampling land surface: 2-3 ha). About 20 aliquots were collected following a zig-zag pattern, ensuring equidistance between sampling points. Samples were mixed to obtain a final sample of 1 kg, stored in polyethylene double bags and labeled. Samples were air dried and sieved (2 mm) before analysis. Characteristics of Buenos Aires province soils, provided by the Soil Institute of INTA, were used to characterize the sampled environments (INTA 1988).

Also, homogeneous samples of bovine manure from three beef cattle intensive systems (IS) and from a cattle extensive system (ES) was collected. In each system, 30 manure subsamples (0.5 kg) were obtained with a steel plain shovel avoiding soil incorporation. Subsamples were mixed and the final sample (1 kg) was preserved at 4 ºC in a double plastic bag, air dried and sieved (2 mm) before analysis.

Soil samples were characterized by measuring extractable phosphorus (Bray-Kurtz method), pH (1:2.5 soil water ratio), organic carbon (OC; Walkley-Black method), and total Kjeldahl nitrogen (TKN; Microkjeldahl method). Moreover, electrical conductivity (EC), cation content (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} by the atomic absorption method), cation exchange capacity (CEC; steam-distillation method) and clay content (Bouyoucous method) were determined. Detailed description of these methods can be found in Sparks (1996). All manure samples were characterized using similar methods and techniques.

The total content of Cu, Zn, Co and Mo was determined in soils and manure samples by microwave assisted acid digestion (Microwave 3000, Anton Paar, Austria) using the method 3051A (USEPA 1996). Four fractions of these elements were obtained from all samples by the sequential extraction procedure of McGrath and Cegarra (1992): water-soluble and exchangeable fraction (EXCH), organic matter bound fraction (OM), inorganic precipitate fraction (INORG) and residual fraction (RES). Soil and manure samples (3 g) were placed into a 50 mL centrifuge tube; 30 ml of $CaCl_2$ 0.1 M (EXCH), NaOH 0.5 M (OM), Na_2EDTA 0.05 M (INOR) reagents were sequentially added and each one shaken for 16 h. The residual fraction (RES) was calculated as the difference between total content of the metal previously determined and the addition of the extracted fractions (EXCH + OM + INOR). At the end of each extraction, soil suspensions were centrifuged at 3600 rpm for 45 min and filtered through Wathman filter paper grade 42. Because NaOH and Na$_2$EDTA reagents also extracted organic matter, the supernatant was digested in aqua regia (HNO$_3$/HCl, 1:3) prior to metal quantification.

Contents of Cu, Zn, Co and Mo were analyzed in all extracts by atomic emission spectrometry (ICP-OES Optima 3000 DV, Perkin Elmer) using an external calibration with quality control standard 21 (atomic spectroscopy standard, Perkin Elmer Pure 100 mg/L).

RESULTS AND DISCUSSION

Physical and chemical characteristics of soil and manure samples

According to geo-referenced site information of physical and chemical characteristics, soil sample of site 1 correlated with Atucha (At) series (Soil Chart INTA, number 3360-35, Baradero). Taxonomically, these soils are classified as Abruptic Argiudolls and Typic Argiudolls (SSS 2014). Soil samples corresponding to site 2 correlated with Navarro (Na) series (Soil Chart INTA, number 3560-17, Tomás Jofré) and are classified as Argiaquic Argialbolls (SSS 2014). Soil samples corresponding to site 3 corresponded to Tronconi (Tri) series (Soil Chart INTA, number 3560-35, Juan Blaquier) and are classified as Natric Duraquolls. Soil samples corresponding to site 4 matched with Pueblitos series (Pu) (Soil Chart INTA, number 3560-29, Roque Pérez). Taxonomically, these soils are classified as Typic Argiaquolls and Argiaquic Argialbolls (SSS 2014). Soil samples corresponding to site 5 resembled Tandil (Ta) series (Soil Chart INTA, number 3760-23 and are classified as Typic Argiudolls).

The characteristics of the soil samples from the selected departments are shown in **table I**. Results are consistent with the typical characteristics of soils in these agro-ecological areas (Salazar and Moscatelli 1989). Additionally, a north-south gradient of clay and sand content was observed. Soils from north of the Buenos Aires province (Baradero and Navarro) presented higher levels of clay in comparison with the southern departments. In case of sand, south soils showed the highest levels (Las Flores and Roque Pérez). These obtained gradients are typical in soils from the Pampean Region. All soils samples were slightly acidic except the sample from Roque Pérez and showed low values of EC. Samples from Las Flores, Roque Pérez and Tandil had the highest levels of OC and TKN. Soil from Navarro presented the highest phosphorus content. Also, the variability observed in CEC values is related to the size and type of clay, and OC % of each soil sample.

TABLE I. PHYSICAL AND CHEMICAL CHARACTERISTICS OF THE SAMPLED SOILS (0-10 CM)

Locality	Baradero	Navarro	Las Flores	Roque Pérez	Tandil
Clay (%)	27.5	20.0	15.0	15.0	15.0
Silt (%)	53.5	56.2	43.9	42.1	51.7
Sand (%)	19.0	23.8	38.1	42.9	33.3
Soil texture	Clay silt	Silt	Silt	Silt	Silt
pH[a]	6.9	6.4	6.9	8.1	6.5
EC (dS/m)	0.2	0.3	0.1	0.3	0.1
Ext. P (mg/kg)	4.3	54.2	35.7	5.1	33.3
OC (%)	1.3	1.8	2.6	2.1	2.8
TNK (%)	0.1	0.2	0.2	0.2	0.2
Ca (cmol$_c$/Kg)	7.6	13.6	14.6	11.9	16.9
Mg (cmol$_c$/Kg)	1.4	1.9	2.0	1.4	2.2
Na (cmol$_c$/Kg)	0.4	0.3	0.3	0.3	0.2
K (cmol$_c$/Kg)	0.9	1.5	1.4	1.0	1.5
CEC (cmol$_c$/Kg)	13.0	21.0	23.6	15.2	26.0

[a] pH measured potenciometrically in a 1:2.5 soil water ratio, ECV: electrical conductivity measured, Ext. P: extractable phosphorus by the Bray-Kurtz method, OC: organic carbon measured by the Walkley-Black method, TKN: total Kjeldahl nitrogen measured by the Microkjeldahl method, cation content (Ca, Mg, Na, K) measured by the atomic absorption method, CEC: cation exchange capacity measured by the steam-distillation Method. Detailed description of these methods can be found in Sparks (1996)

Manure samples from IS showed higher levels of total organic carbon (22.5-31.6 %), total Kjeldahl nitrogen (1.6- .8 %), and extractable phosphorus (139.7-144 mg/kg) in comparison to soil samples. In contrast with soil samples values, manure showed a slightly alkaline pH and higher EC (**Table II**).

TABLE II. PHYSICAL AND CHEMICAL CHARACTERISTICS FROM CATTLE MANURE SAMPLES COMING FROM INTENSIVE PRODUCTION SYSTEMS (IS)

	IS-1	IS-2	IS-3
pH^a	7.8	7.6	8.7
ECV (dS/m)	0.6	2.2	1.4
Ext. P (mg/kg)	139.6	143.1	143.9
OC (%)	29.6	22.5	31.6
TKN (%)	1.6	1.6	1.8

^{a}pH measured potenciometrically in a 1:2.5 soil water ratio, ECV: electrical conductivity measured, Ext. P: extractable phosphorus by the Bray-Kurtz method, OC: organic carbon measured by the Walkley-Black method, TKN: total Kjeldahl nitrogen measured by the Microkjeldahl method. Detailed description of these methods can be found in Sparks (1996)

For NTK %, OC %, pH and EC (dS/m) values, results obtained in the present work were in agreement with nutrient composition of beef cattle manure found in published researches. Total Kjeldahl nitrogen ranged 0.93-2.43 %; total organic carbon 5-16 %, pH 7.5-8.6 and EC 1.76-9.06 dS/m. However, extractable phosphorus content in mg/kg was lower than values reported in bibliography (720-3100 mg/kg) (Eghball and Power 1994, Hernández et al. 2002, Irshad et al. 2013, Magrí and Teira-Esmatges 2015). Nutrient content in feedlot manure will differ considerably depending on the type of animal, its food ration and the method of collection and storage. Feedlot manure was a traditional source of nutrients (primarily NTK and P) and organic matter. Land application improves the overall soil quality and reduces soil and water losses. Total salt concentrations can be used to estimate EC. Manure may contain high levels of soluble salts (Reynolds et al. 2002). Calcium carbonate ($CaCO_3$) is commonly added to cattle diets as a source of calcium, and the recommended level is 7 g/kg of ration (Klemesrud et al. 1998). Much of the $CaCO_3$ is excreted and the pH of manure can be increased (become more basic) as a result (Eghball 1999). These facts could explain the higher EC and slightly alkaline pH obtained in manure samples analyzed in our work.

Concentration of heavy metals in soil and manure samples

Total concentrations of Cu, Zn, Co and Mo in soils are shown in **table III**. Levels of Cu ranged from 6 to 15 mg/kg; and Zn ranged from 9 to 60 mg/kg. In the case of Co and Mo, levels ranged from non-detectable in some soils samples to values of 6.5 and 4.1 mg/kg, respectively. These contents are in accordance with the average concentrations found in pampas soils (Lavado et al. 2004), and within the range expected for uncontaminated soils (Cu: 1-50 mg/kg; Zn: 1-900 mg/kg; Mo: 0.1-40 mg/kg; Co: 2-40 mg/kg) (Adriano 2001).

Trace element contents in manure samples from intensive and extensive production systems are shown in **table IV**. Levels of total Cu and Zn were higher in IS manure compared to ES manure and soils, but they did not exceed the maximum limit in sediments and sludge to apply in agriculture according to Law 24.051 (Cu: 100 mg/kg; Zn: 500 mg/kg) (HWAL 1992). The total Cu content in manure reported in previous studies varied from 6.7 to 71.1 mg/kg. For total Zn, values ranged from 63 to 332.6 mg/kg (Nicholson et al. 1999, Sager 2007, Benke et al. 2008, Miller et al. 2018). The main source of trace elements is the mineral core used for livestock feed which conditions the trace element content in manure (Miller et al. 1991). Total levels of Co and Mo in manure from IS were similar or lower to those obtained in soils and ES manure. Since cattle requirements of these elements are low, the amount added to food is not significant (Bolan et al. 2003). The total content of Co in cattle manure is reported to be about 2.2 to 3.6 mg/kg (Bolan et al. 2004, Larney et al. 2008) and Sheppard and Sanipelli (2012) found total values of Mo of 3.91 mg/kg.

These results underline the importance of excreta reuse as organic fertilizer to prevent trace elements accumulation and potential pollution. Manure addition is being recognized as a major source of metal input to soils. Several studies analyzed the long-term influence of cattle manure application in total and available concentration of metals in soil. An increase in total Cu and Zn content in manure-amended soils compared to unamended soils after repeated application of manures was observed, and the effect was noticeable in soils up to 0-15-30 cm depth (control soil: 20.6 and 17.3 mg/kg Cu, manure irrigated soil: 34.0-22.7 mg/kg Cu, respectively; total Zn increased from 72.2 mg/kg in the control treatment to 187.5 mg/kg in manure amendment soils). However, no significant increase in total soil Co was detected after 25 yrs. of continuous annual manure application. This

TABLE III. TOTAL CONTENTS AND SEQUENTIAL FRACTIONS OF Cu, Zn, Co and Mo IN SOILS (mg/kg)

	Soils				
	Baradero	Navarro	Las Flores	Roque Pérez	Tandil
EXCH-Cu	nd	nd	nd	nd	nd
OM-Cu	3.78 (26.32 %)	0.03 (0.24 %)	4.70 (43.08 %)	0.91 (14.7 %)	3.22 (36.43 %)
INOR-Cu	1.72 (11.98 %)	2.49 (19.82 %)	1.70 (15.58 %)	0.46 (7.43 %)	1.20 (13.57 %)
RES-Cu	8.86 (61.70 %)	10.04 (79.94 %)	4.51 (41.34 %)	4.82 (77.87 %)	4.42 (50 %)
Total Cu	14.36	12.56	10.91	6.19	8.84
EXCH-Zn	11.68 (27.58 %)	0.74 (1.25 %)	2.01 (2.11%)	1.29(3.78%)	0.29 (0.61%)
OM-Zn	0.86 (2.03 %)	3.72 (6.26 %)	3.91 (4.11 %)	1.12(3.28%)	3.74 (7.84%)
INOR-Zn	4.08 (9.63 %)	10.41 (17.53 %)	1.47 (20.48 %)	3.56(10.42%)	4.82 (10.1 %)
RES-Zn	25.73 (60.76 %)	44.53 (74.97 %)	6.69 (73.29 %)	28.18(82.52%)	38.88 (81.46%)
Total Zn	42.35	59.40	9.08	34.15	47,73
EXCH-Co	nd	nd	nd	nd	nd
OM-Co	0.09 (1.53 %)	0.38 (7.29 %)	0.50 (11.74 %)	nd	0.43 (6.57 %)
INOR-Co	0.18 (3.07 %)	0.33 (6.33 %)	0.28 (6.57 %)	nd	0.34 (5.20 %)
RES-Co	5.60 (95.40 %)	4.50 (86.37 %)	3.48 (81.69 %)	nd	5.77 (88.23 %)
Total Co	5.87	5.21	4.26	nd	6.54
EXCH-Mo	nd	nd	nd	nd	nd
OM-Mo	nd	0.52 (14.77 %)	0.23 (7.08 %)	nd	0.49 (10.4 %)
INOR-Mo	nd	0.49 (13.92 %)	0.27 (8.31 %)	nd	0.38 (8.07 %)
RES-Mo	3.99 (99.75 %)	2.51 (71.31 %)	2.76 (84.92 %)	nd	3.84 (81.53 %)
Total Mo	3.99	3.52	3.25	nd	4.71

EXCH: water-soluble and exchangeable fraction extracted with $CaCl_2$ 0.1 M, nd: not detected, OM: organic matter bound fraction extracted with NaOH 0.5 M, INORG: inorganic precipitate fraction extracted with Na_2 EDTA 0.05 M, RES: residual fraction calculated as total (EXCH + OM+ INOR)
In brackets: distribution of Cu, Zn, Co and Mo as a percentage of total content

could be attributed to the fact that the amount of Co applied over the years was probably low compared to the natural content of Co in these soils (Benke et al. 2008, Miller et al. 2018). Different results were found by Tlustoš et al. (2016), who reported that long-term farmyard manure application did not significantly change the pseudo-total and potentially mobilizable element contents. Zhao et al. (2014) investigated the risk of heavy metal contamination from cattle manure fertilization. The heavy metals analyzed (Cu, Zn, Mn, Fe, Pb, Cd, and Cr) were gradually enriched in soils during long term application of manures and incorporation of chemical fertilizers, except for Zn. The total Zn decreased to 1.8-13.8 % after application of manure and total Cu concentrations in the soil significantly increased up to 10.6 - 26.7 % in all manure treatments applied. These observations indicate that long term applications of manures could modified the initial status of trace metals in soils.

Potential availability of trace metals in soils samples

Results of sequential extractions in soils are shown in **table III**. Cu was mainly found as Cu-RES in most of the soil samples, except for Las Flores where it was uniformly distributed between Cu-OM and Cu-RES. Roque Pérez, Baradero and Tandil soil samples showed a similar distribution between Cu-OM and Cu-INOR, while in Navarro soil, a higher content of Cu-INOR was found. In the five soil samples, Cu-EXCH was below the detection limit of the analytic technique used (≤ 0.01 mg Cu/kg). According to these results, the extracted soil samples did not present available forms of Cu but showed high percentages of the other fractions. The largest proportion of Cu was specifically adsorbed to organic matter and, to a lesser extent, precipitated with primary or secondary minerals or in residual fractions (Torri et al. 2011). The exchangeable fractions may indicate that the most available form for plant uptake of this metal is Cu^{2+}. This species was below the analytical detection limit in three representative pristine soils (< 0.5 mg Cu/kg) of the Pampas region. However, no Cu deficiencies were reported in these soils or in the rest of the Pampas region in recent years (Sainz-Rozas et al. 2003, Melgar 2006). In general, as organic matter increases, Cu availability decreases. Although binding with organic matter reduces fixation by soil minerals and leaching, availability of Cu to plants is also reduced. Krishnamurti and Naidu (2002) found a

TABLE IV. TOTAL CONCENTRATION AND DISTRIBUTION OF Cu, Zn, Co AND Mo (mg/kg) IN MANURE COMING FROM INTENSIVE AND EXTENSIVE CONFINED LIVESTOCK SYSTEMS AMONG DIFFERENT SEQUENTIAL FRACTION

	ES	IS-I	IS-II	IS-III
EXCH-Cu	0.11 (0.66 %)	1.94 (3.28 %)	1.54 (6.86 %)	1.67 (6.67 %)
OM-Cu	2.19 (13.19 %)	22.85 (38.60 %)	11.49 (51.16 %)	5.68 (22.70 %)
INOR-Cu	5.1 (30.72 %)	7.74 (13.07 %)	3.17 (14.11 %)	11.32 (45.24 %)
RES-Cu	9.2 (55.42 %)	26.67 (45.05 %)	6.23 (27.74 %)	6.35 (25.38 %)
Total Cu	16.6	59.20	22.46	25.02
EXCH-Zn	1.42 (2.17 %)	4.24 (1.98 %)	7.07 (4.35 %)	8.31 (9.52 %)
OM-Zn	8.28 (12.66 %)	54.02 (25.22 %)	41.33 (25.44 %)	13.34 (15.28 %)
INOR-Zn	8.45 (12.92 %)	19.32 (9.02 %)	35.44 (21.82 %)	22.39 (25.64 %)
RES-Zn	47.25 (72.25 %)	136.62 (63.78 %)	78.6 (48.39 %)	43.27 (49.56 %)
Total Zn	65.40	214.20	162.44	87.31
EXCH-Co	0.07 (4.79 %)	0.09 (6.29 %)	0.17 (11.33 %)	0.15 (8.93 %)
OM-Co	0.1 (6.85 %)	0.1 (6.99 %)	0.1 (6.67 %)	0.16 (9.52 %)
INOR-Co	nd	nd	0.27 (18 %)	0.1 (5.95 %)
RES-Co	1.29 (88.36 %)	1.24 (86.71 %)	0.81 (54 %)	0.73 (43.45 %)
Total Co	1.46	1.43	1.50	1.68
EXCH-Mo	0.07 (1.44 %)	0.3 (20.00 %)	0.78 (22.10 %)	0.7 (18.92 %)
OM-Mo	0.45 (9.24 %)	0.81 (54.00 %)	0.25 (7.08 %)	0.5 (13.51 %)
INOR-Mo	1.43 (29.36 %)	0.32 (21.33 %)	0.48 (13.60 %)	0.34 (9.19 %)
RES-Mo	2,99 (61.40 %)	0.37 (24.67 %)	2.02 (57.22 %)	2.16 (58.38 %)
Total Mo	4.87	1.50	3.53	3.70

ES: cattle manure coming from extensive production system, IS: cattle manure coming from intensive production system, EXCH: water-soluble and exchangeable fraction extracted with $CaCl_2$ 0.1 M, nd: not detected, OM: organic matter bound fraction extracted with NaOH 0.5 M, INORG: inorganic precipitate fraction extracted with Na_2 EDTA 0.05 M, RES: residual fraction calculated as total (EXCH + OM+ INOR)
In brackets: distribution of Cu, Zn, Co and Mo as a percentage of total content

significantly correlation with fulvic complex Cu ($R^2 = 0.944$, $P < 0.0001$). Fulvic complex Cu was found to explain 89.2 % of the variation in phytoavailable Cu. These facts indicate that Cu deficiencies in soils could be determined not only by the concentration in the solution phase but influenced by diffusion process from the solid-phase.

In the case of Zn in soil through samples, the main source was founded as Zn-RES, reaching fraction values close to 80 %. Moreover, the Zn-INOR fraction was higher than Zn-OM in all soil samples. This result is typical for Zn found in non-contaminated soils, where it is mostly present as unreactive forms included in the crystal lattices of minerals (Shuman 1999). Unlike other metals, the Zn-EXCH fraction was observed in all soil samples. These results indicate the presence of easily available forms of Zn from the soil.

Co and Mo were uniformly distributed between OM and INOR fractions, but the highest proportion was found as Co-RES and Mo-RES. It is important to emphasize that the residual fraction is related to the unavailable forms of trace elements, because they are incorporated inside crystalline lattice and clays structures of soil (Soriano-Disla et al. 2010). Factors like acidic character and the increase in iron and aluminum solubility decreases Mo availability since they react with Mo making it unavailable. Co deficiency in soil is affected mainly by Mn and Fe oxide content in soils and the organic fraction. Transformation of Co was concomitant with the changes of Mn, therefore, controlled by the changes of redox potential and pH (Han and Banin 2000, Li et al. 2004). All these factors need to be considered when Mo and Co deficiencies are evaluated in soils.

Maity et al. (2017) found a positive correlation between fine and very fine sand, silt and clay and total carbon with metal concentrations in sediments. In our work, soil samples in areas located to the northwest of Buenos Aires had a higher percentage of clay and a lower percentage of sand, in agreement with the higher total contents of Cu and Zn. Likewise, factors like pH, CEC and $CaCO_3$ were found to have less impact in metal concentrations. Luo et al. (2012)

determined significantly negative correlation coefficients between $CaCl_2$ extractable metals (Pb, Zn) and soil pH and EC. This fact could explain the low availability determined for Cu y Zn in the soils samples (with exception of Site 1) analyzed in our work considering the pH values (6.4-8.0). $CaCl_2$ mainly extracted metals in soil solution and exchangeable metals weakly adsorbed to negatively charged soil constituents. A positive correlation between EXCH-Zn and clay content was found in the present work, which explains their high percentages in different fractions of Site 1.

Heavy metals of the soil matrix are complexed over the negatively charged surfaces of colloidal organic matter and clay particles through an electrostatic attraction (Alloway 1990, Adriano 2001). Sungur et al. (2015) determined positive correlations between clay contents and metals of especially less available fractions (OM and RES), indicating that metals were held over negative surfaces of clay particles and between clay layers. Clay adsorption was a dominant process over metal binding into the soil matrix. In our research, Cu was recovered in OM and RES fraction in soil samples coming from Site 1, which showed highest percentages of clay (27.5 %).

Potential availability of trace metals in manure samples

The distribution of Cu, Zn, Co and Mo fractions obtained by sequential extraction of manure samples coming from IS and ES are shown in **table IV**. The Cu, Zn and Co distribution among the studied sequential fractions showed a similar behavior. Cu content in IS samples was similarly distributed in all fractions, observing a predominance of Cu-OM (22.7-51.2 %). Cu-EXCH appeared in higher percentages in IS samples manure than in ES manure and was not detected in soils samples. Zn was highly obtained as RES (48.4-63.8 %), although Zn-OM and Zn-INOR had also a high recovery percentage with other treatments (Zn-OM: 15.3-25.4 %; Zn-INOR: 9.0-21.8 %). Mo showed a similar behavior, being recovered in high percentages as Mo-RES, although major values of Mo-OM and Mo-INORG were detected (54-21.33 %). The low contents of Co determined in feedlot manure were found mainly as RES fraction (64 %-86.71 %).

Values of Cu-OM and Zn-OM from IS manure were considerably higher than those found in soil and ES manure (Cu-OM: 13.19 %; Zn-OM: 12.66 %). This can be attributed to the higher total organic carbon content of IS manure and the metal-complexation with organic C-based ligands.

In general, the metal distribution between EXCH, OM and INORG fractions was higher in manure samples from IS compared to ES and soils (**Table III**). The distribution of trace metals among these fractions varies widely according to the chemical properties of individual metals and the characteristics of manures, which are a function of the animal feed and the manure treatment process (Bolan et al. 2004). L'Herroux et al. (1997) fractionated metals in swine manure and observed that most of Cu (66.5 %) was in organic-bound, Cd (76.7 %) and Zn (67.2 %) in oxide-bound (call it "weakly bound to specific, mainly inorganic, sites"), and Mn (69.2 %) in carbonate-bound forms. The carbonate-bound fraction was mainly related to reducing conditions (i.e., low redox potential) in the manure slurry. Co and Zn were mainly founded in the "hydroxides" fraction (75 %). Slurry analysis showed that under reducing conditions and at pH around 5, the metals studied in pig slurry were in available forms, except for part of the iron, which remained in the residual fraction.

Sungur et al. (2016) applied a sequential extraction of Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn in accordance with the Community Bureau of Reference (BCR) scheme, to manure samples collected from three farms. It is important to emphasize that unlike the sequential extraction procedure employed in our work, the BCR exchangeable fraction, which includes metals adsorbed on essential components such as clays, carbonates and humic acids, is extracted with acetic acid. The reducible fraction includes metals bound to Fe and Mn oxides. The oxidizable fraction contains metals that may be complexed or peptised by the natural organic substances. For cow manure samples, these authors detected that Cd (64 %), Mn (52 %), and Zn (52 %) were bound primarily to acid-soluble and reducible fractions, which were in easily available forms. Likewise, it was also found that Pb, Co, Ni, Cu, and Cr were in less available fractions (oxidizable and residual [40.92-48.26 % for Co, 43.44-45.68 % for Cu, respectively]). In general, this behavior was observed in duck and goat manure. These results are consistent with those obtained from IS cattle manure samples analyzed in our research. For cattle manure, higher percentages of trace metals among acid-soluble, reducible, and oxidizable fractions (considered by the authors as mobile fractions) were obtained. Also, the ability and susceptibility of metals to be released from manure samples is highly related to the extractant employed in the sequential scheme (acidic environment, ion exchange mechanism, etc.).

Cattle manure from intensive production systems showed a higher value of the exchangeable fraction for all metals in comparison to that from extensive systems and soils. These results suggest a major contribution of labile forms and other available fractions (like bound to organic matter and carbonates) of trace elements to the soil when manure from IS is applied as organic fertilizer. The speciation of trace elements is substantially significant to understand the availability of heavy metals, and the chemical forms content of heavy metals in manure may be traced before being applied in agricultural areas.

Metals introduced to soils undergo several reactions that include adsorption, complexation, precipitation, and reduction, which control their leaching and runoff losses and availability (Bolan et al. 2004). In the case of manure addition, these reactions are evidenced by the presence of a high amount of organic carbon (dissolved organic carbon [DOC]), soluble salt concentration (salinity), and acidification caused by the mineralization of organic nitrogen. Addition of organic amendments such us manure by-products has shown increases in the organic matter cation exchange capacity in soil. Zhao et al. (2014) observed an increase of the different fractions of Cu in soils amended with farmyard manure, indicating that organic matter fixed most of the Cu and the concentration increased with the application of organic matter. Benke et al. (2008) also documented that a portion of the soil EDTA-extractable Cu reverted to less soluble forms throughout the soil profile related to organic matter retention of metal by complexation.

The addition of DOC promotes the formation of soluble aqueous metal-organic complexes and, to a lesser extent, metal-inorganic complexes, and it is expected to dominate the chemistry of metal solutions in manure-amended soils (Lwin et al. 2018). Such wastes of plant and animal origin contain large amounts of DOC, and the addition of certain organic manures increases the pH and EC, thereby enhancing the solubilization of soil organic matter (Jackson et al. 1999, Jackson and Miller 2000). EDTA-extractable Zn significantly increased with long-term manure applications over the years at surface and subsurface depths probably favored the formation of soluble DOC-Zn complexes (Tlustoš et al. 2016). Though organic Zn was easily decomposed, there was a significant increase in the relative amount of carbon-bound and organic-bound Zn after manure application. The change of Zn distribution may be related to the effect of pH (Illera et al. 2000).

Such increase in DOC may enhance microbial activity, but lowering the reduced redox potential in the soil. Although sthe oluble organic metal fraction is not readily bioavailable to plants, it is relatively mobile, and it has been shown that the application of metal-rich biosolids and animal manure enhances the leaching of metals in soils (Hsu and Lo 2001). The lower pH and higher OC content due to manure applications may cause increased Zn solubility and its downward movement (Benke et al. 2008). It is important to emphasize that application of cattle manure as an organic amendment could induce changes in soils properties (such as pH, redox potential organic matter content) and modify the availability and soil fraction distribution of the metals added.

CONCLUSIONS

It has been found that the exchangeable fraction content of trace elements in manure from intensive beef cattle production systems was higher than that observed in extensive cattle manure and soils. Results indicate that micronutrients, mainly Cu and Zn, could be easily available in manure samples from intensive production systems. This difference is even more evident in the case of Cu, which was not detected in soils as Cu-EXCH. The higher levels of total and available forms of Cu and Zn determined in IS manure compared to untreated soil samples, indicates that a careful analysis is required when this organic amendment is applied as fertilizer. In any case, the reuse of intensive cattle manure as fertilizer in agricultural areas could reduce the environmental impact of metals accumulation in pen soils and decrease the potential risk of pollution.

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