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Cu and Zn in soils under concentrated feeding animal operations. Córdoba. Argentina

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Abstract: ***The Colacha stream basin (Córdoba, Argentina) is an agro-ecosystem where intensive livestock production exists. Protein complexes supplied to animals incorporate heavy metals into the environment through faeces and urine. In order to determine the presence and behavior of heavy metals (Cu and Zn) in soils located under concentrated animal feed operation (CAFOs), three soil profiles were surveyed according to livestock activities a) medium cow CAFO b) small pig CAFO c) natural soil (reference). The results were treated with multivariate descriptive statistics techniques. The soil profiles under CAFOs, presented maximum Cu and Zn values of 34.37 ppm and 43.31 ppm, respectively. These values are in the range of the average concentration of soils worldwide, although they showed a notorious increase compared to the background regional soil values (Cu = 7.31 ppm and Zn = 11.67 ppm) that is, an increment of 470% and 370% respectively. The results and multivariate statistical analysis indicate that Cu and Zn in available state and complexed with organic matter (OM) are controlled by pH and OM values. In the most disturbed soil profile (medium CAFO) there is more OM and total Cu and Zn values are most clearly associated with it. The results show the impact of livestock on soil, which could be a source of pollutants wherein eventually would trigger their migration to the water table.***

Keywords: heavy metals, soil profile, livestock activities**.**

1. Introduction

The accumulation of heavy metals from agricultural activities, in soils, sediments and water, may involve a potential risk to human health due to their transfer into the food chain. As was stated by [1], heavy metals constitute an ill-defined group of inorganic chemical hazards, and those most commonly found at contaminated sites are lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu), mercury (Hg), and nickel (Ni). Soils are the major sink for heavy metals released into the environment by anthropogenic activities and unlike organic contaminants which are oxidized to carbon oxide by microbial action, most metals do not undergo microbial or chemical degradation, and their total concentration in soils persists for a long time after their introduction [1]. Trying to increase crop yields, agricultural activities incorporate tons of fertilizers and pesticides to soils. To grow and complete the lifecycle, plants must acquire not only macronutrients (N, P, K, S, Ca, and Mg), but also essential micronutrients. Some soils are deficient in the heavy metals (such as Co, Cu, Fe, Mn, Mo, Ni, and Zn) that are essential for healthy plant growth and crops may be supplied with these as an addition to the soil or as a foliar spray [1]. Also, several common pesticides used quite extensively in agriculture contain substantial concentrations of metals (Cu, Hg, Mn, Pb, or Zn.) [2].

Livestock activities, through animal nutrition and disease control, incorporate contaminants to soil through faeces [3], situation that is magnified in feedlot systems [4]. Until recently, the major emphasis on effluents from concentrated animal feed operation (CAFOs) has been on regulating the major inorganic compounds, nitrates and heavy metals. Excreta disposal constitutes a potential risk for soil and groundwater contamination with nitrates, chlorides, heavy metals, hormones, among others [5] y [6]. In the past decade, with the recognition that pharmaceuticals are reaching the environment even after treatment in a sewage water treatment plant (SWTP), attention has turned to the pollutants released from CAFOs that could have an effect on the environment. For example antibiotics are now being studied in different sites of the world [6]. Most of the compounds are released in concentrations several orders lower than their lowest observable effect. However, even very small amount of sulphonamides and tetracycline reaching the soil induce antibiotic resistant genes (ARGs) in soil bacteria, thus the study of ARGs is a new way of evaluating the affects of antibiotics in the environment. [6] y [7]. The application of biosolids (e.g., livestock manures) in rural areas to land leads to the accumulation of heavy metals such as As, Cd, Cr, Cu, Pb, Hg, Ni, Se, Mo, Zn, Tl, Sb, and so forth, in the soil [8]. Although most manures are seen as valuable fertilizers, in the pig, cow and poultry industry, the Cu and Zn added to diets as growth promoters may also have the potential to cause metal contamination of the soil [9, 10]. The manures produced from animals on such diets contain high concentrations of As, Cu, and Zn and, if recurrently applied to restricted areas of land, can cause considerable accumulation of these metals in the soil in the long run. According to a study in the argentine pampean region [5] the food and faeces in cow breeding showed, respectively, similar percentages of Ca (2.4-2.6) Mg (1.4-1.9), Na (1.0-1.6), K (1.2-1.4), N (2.4-1.7) and P (0.7-0.7) and differ especially in OM (91- 51) and heavy metals percentages.

2. Study Area

In the Argentine Republic, millions of hectares are dedicated to agricultural practices existing therefore a strong necessity to study the contamination processes from different perspectives. Different tracers have been used to identify groundwater contamination in agricultural areas where livestock sites were identified, for example, nitrates and Nitrogen isotopes [11, 12], caffeine [13], invertebrate groundwater communities [14] and antibiotic resistance and genetic patterns of *Escherichia coli* [7].

In this work, the study area (150 km^2) comprises the northern part of the La Colacha stream basin, located at the south of Cordoba, Argentina (Figure 1). It is a rural piedmont area where land uses are especially devoted to agriculture and livestock. The direct seeding of soybean with use of pesticides and fertilizers is a common practice. Some farms dedicated to concentrated feeding animal operations were recognized. It is therefore essential to establish the dynamics, functioning and mobility of different chemical elements that enter the soil in this region. Thus, the objective of this study is to determine the presence and behavior of the heavy metals Cu and Zn in soils located under livestock activities comparing with a natural soil, taken as a reference.

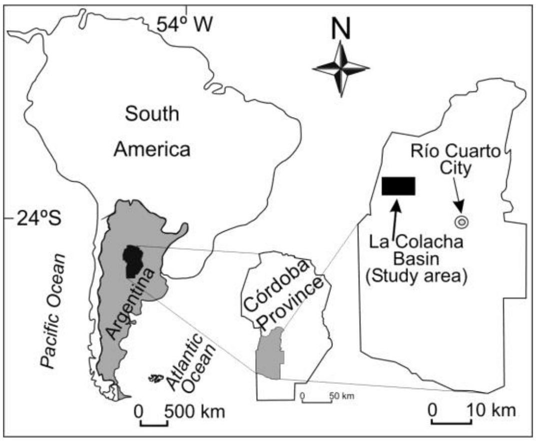

Figure 1. Location of study area

3. Materials and methods

To define the basic geological-geomorphological-pedological characteristics of the basin under research, a field survey was carried on. Moreover, a land use survey (irrigation practices, agrochemicals uses, feed lots location and so on) was made to define the sampling sites. Three soil profiles were selected and described. Two soil profiles were located under livestock activities a) cow medium CAFO (approximately 500 animal units) b) pig small CAFO (less than 100 animal units) and c) a natural soil located beneath a small natural relict forest, used as reference. The soil description and sampling was carried out according to the number 18 Soil Survey Handbook [15]. In the Laboratory of the Geology Department (National University of Rio Cuarto, Argentina) the following variables were measured: organic carbon (OC) and organic matter (OM) with the Walkley and Black modified method [16]; pH (soil-water ratio 1: 2.5) using the potentiometric method; exchangeable bases (CEC) by the ammonium acetate method, determining calcium and magnesium by titration and sodium and potassium by flame photometry [17]. Samples of the three soil profiles were taken and identified at field according to the observed horizons. In the laboratory they were treated in mortar and finally sieved. After that, 500 g of each horizon were extracted and sent to the LIQA Laboratory located in Villa María city (Córdoba, Argentina). Zn and Cu complexed with organic matter (O-Zn and O-Cu) were measured using the atomic absorption method, after digestion with sulfuric acid. Available Zn and Cu, that is, in solution and exchange sites (A-Zn and A-Cu), were determined using SISS method (by means of atomic absorption and EDTA 0.05 M, pH = 7.00). The results were treated with descriptive statistical techniques (multivariate analysis) using [18].

4. Results and Discussion

Climate on the region is of the subhumid type and it is characterized by a rainfall concentration (80% from the total) on spring and summer seasons. La Colacha is mostly a piedmont basin although the upper basin is located in Los Chañares hills (small prolongation of the Comechingones Mountains, in the Pampean Mountains range) where the igneous -metamorphic bedrock outcrops. Except at the small mountain area (upper basin), the area has a moderate undulating relief, covered by very fine sand- silty loess and loessoid sediments from the Holocene and Late Pleistocene and alluvial and colluvial fine holocene sediments [19].

The representative soil of this piedmont area has evolved from the aforesaid loess type sediments. The typical profile is a shallow sandy loam soil (solum 0.40 m), that shows low development, some to excessively drained, with moderate permeability. The soil is characterized by a low pedogenetic evolution being dominant the typical Hapludolls, with little illuviation features and poor clay enrichment in the Bw horizon [19].

Soil profiles S88 and S86 which, as was indicated, are located under livestock activity, have some compaction degree and an evident lack of vegetation cover (Figure 2). Morphological descriptions of S88 and S86 soil profiles match with the regional soil (typical Hapludoll, coarse silty, illitic, thermal), [20]. The soil properties are described in Table 1.

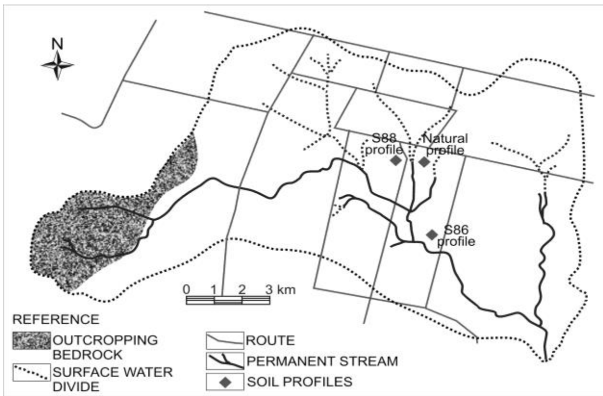

Figure 2. Location of soil profiles

In the S88 and S86 profiles, the pH of the horizons shows an increase in relation to the natural soil. The content of OM presents an increment in S88 in relation to the natural soil in the Ap and Bw horizons, an aspect related to bovine excreta accumulation whereas there is a considerably decrease in the C horizon.

The lowest OM values in S86 soil profile could be due to the OM loss as a consequence of a marked decrease in the livestock activity in recent years in this small CAFO along with the sheet hydric erosion processes observed elsewhere in the area [20]. This is a difference between OM in both soil profiles taking into account that in S88 soil, the excreta supply is more significant in recent years and the topography allows greater OM accumulation (Figure 3).

Table 1: Description of the three soil profiles selected

	Natural profile			*S88 profile*			*S86 profile*		
Horizons	***Ap***	***Bw***	***C***	***Ap***	***Bw***	***C***	***Ap***	***Bw***	***C***
Depth [cm]	0-8	15-27	>40	0-8	15-27	>40	0-8	15-27	>40
pH	6.44	7.30	7.60	7.64	7.88	9.66	7.97	7.52	8.63
MO%	4.74	2.08	1.39	4.81	4.46	0.68	3.89	1.37	1.14
Na^+	0.40	0.39	0.42	3.53	3.76	4.44	0.71	0.55	0.97
K^+	2.5	2.3	2.8	5.35	3.00	3.22	8.28	8.13	4.25
Ca^{+2}	9.2	12.8	12.8	8.70	7.70	14.0	6.00	4.00	10.50
Mg^{+2}	0.2	3.6	3.2	11.50	13.30	19.0	14.00	7.60	13.50

Figure 3. a) Concentration of the livestock faeces and urine. b) Compaction of Ap horizon

The Na^+, K^+ and Mg^{+2} values are greater than the natural soil values, while Ca^{+2} values show a small decrease. These cation concentrations may be justified in both profiles if the supplied food to animals (protein, magnesium oxides, ClNa salt, etc.) together with the excreta composition [5] are taken into account.

The Zn and Cu concentrations in each horizon of the soil profiles are exhibited in the Table 2.

Table 2: Concentration of the Zn and Cu in soil profiles

	Natural profile			*S88 profile*			*S86 profile*		
Horizons	Ap	Bw	C	Ap	Bw	C	Ap	Bw	C
Horizons	A	Bw	C	A	Bw	C	A	Bw	C
Depth [cm]	0-8	15-27	>40	0-8	15-27	>100	0-8	15-27	>40
O-Zn	9	11	--	11	20	--	17	16	--
A-Zn	2.6	0.4	0.5	33	13	0.5	5.4	5.3	0.5
Zn Total	12	11.5	0.5	43	33	0.5	22	21	0.5
O-Cu	5.9	4.5	--	9.6	4.8	--	32	4.6	--
A-Cu	1.4	1.5	0.5	6.2	2.1	1.3	2.0	2.2	1.5
Cu Total	7.3	6.0	0.5	16	6.9	1.3	34	6.8	1.5
Zn and Cu concentration in ppm. O = organic; A = Available									

The soil profiles under livestock activity showed maximum Cu and Zn total values of 34 and 43 ppm respectively, which are within the low range of average concentrations cited for different soils in the world (for Cu = 2 to 250 ppm [21] and Zn = 10 to 300 ppm [22]. However, Cu and Zn values in S86 and S88 profiles increased 470% and 370% respectively with regard to the natural soil profile.

Taking into account the values along depth, it was observed that A-Zn and A-Cu decrease and pH increase in deepest horizons. This situation is possible considering that a lower pH would increase metal concentrations in solution (available form). Furthermore, it was observed a decrease of OM in the deepest horizon and the major O-Zn and O-Cu values were associated to Ap and Bw horizons. In these farming systems, the OM present in the Ap horizon is heavily dominated by particulate or labile organic matter, while in the Bw horizon OM is associated with the mineral phase [7].

A-Cu values deviate very few from natural background values and have more uniformity in all three horizons compared to Zn concentrations. However, comparing to natural backgrounds, O-Cu showed an important increase in the Ap horizon in the S86 soil profile, with a sharp decline towards the Bw horizon, which might be related to the high capacity of Cu to be complexed with more labile OM and then the low migration ability.

The multivariate statistical analysis (cluster R type) of S88 soil profile shows two major groups (Figure 4). Group A links Na^+, Mg^{+2}, Ca^{+2} and pH, indicating the dependence of these ions in solution in relation to pH. Group B gathers OM, Zn, K^+, Cu and CEC, presenting a high correlation between OM and Zn, demonstrating their ability to be complexed. Taking into account the animal food composition, the nucleus K^+-Cu reveals the direct impact that livestock produces on the soil profile. Finally CEC linking with Zn, Cu and K^+ elements could be showing that intensive farming is creating a competition of such elements in the exchangeable sites, while OM contributes mainly to the total cation exchange capacity.

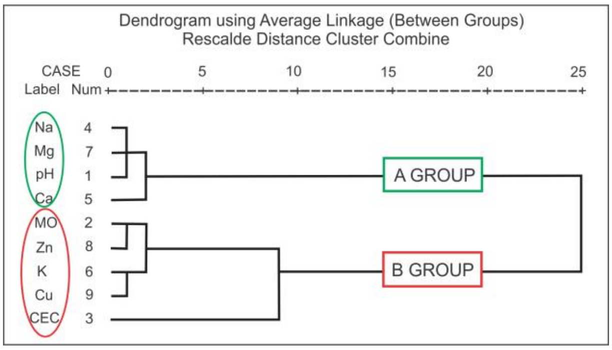

Figure 4. Cluster R mode, S88 profile

The cluster analysis of S86 profile presents two groups (Figure 5). Group A associates K^+, Zn and Cu which together explain the impact of livestock on the soil. Group B represent those elements and properties involved in the most important intrinsic characteristics of the soil, linking major cations (Na^+ and Ca^{+2}) to pH and the subgroup CEC plus OM.

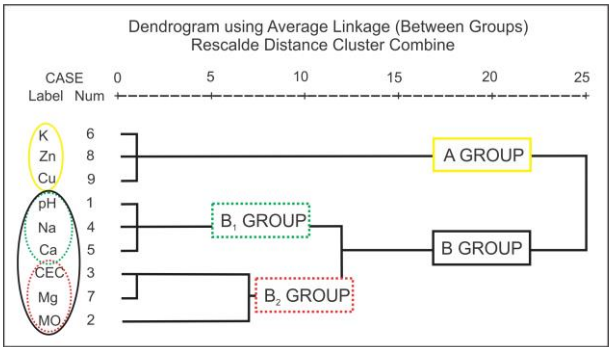

Figure 5. Cluster R mode, S86 profile

5. Conclusion

The conceptual model and multivariate statistical analysis show that the natural and the disturbed soil profiles presented Cu and Zn values in the low range of the average concentrations found in worldwide soils. However, although they are low, in the soil profiles under livestock activities, the total metal values increased greatly in relation to the natural background values in this region (470% and 370% for Cu and Zn, respectively). The results indicate that Cu and Zn values (available and complexed with organic matter) are controlled by pH and the organic matter quantities. In the most disturbed soil profile (more animals) there is more organic matter and total Zn and Cu values are most clearly associated with it, as was showed by statistical analysis.

The results show the impact of livestock on soil making it a possible pollution source which could facilitate the arrival of metals into groundwater (unconfined aquifer), a situation that must be monitored. In addition, more soil profiles must be studied to better understand the pollution scenario.

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