Evaluation of *Cu* and *Zn* Content in Soils and their Interaction with Some Physicochemical Soil Properties

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Abstract. The content of metals in soils depends on the combined effect of several factors, which include the properties of the metals themselves and their concentrations in the soil, environmental conditions and soil components. Topsoil samples from different plots of a rural area, which combines reforestation (forests soils) with agriculture (pasture and cultivation soils) and livestock in the Galicia region, NW Spain, were analyzed for total Cu and Zn, pH, organic matter content, and particle size distribution. The geological substrate of the study area is mainly biotitic schist. The aims of this study were to investigate the total Cu and Zn concentrations in the topsoil samples, and to examine the relationship of these metals with the mentioned physicochemical properties using a correlation analysis. Soils were characterized by conventional analytical methods. Total Cu and Zn contents were determined by atomic absorption spectrophotometry after wet digestion with a hot mixture of nitro-perchloric-hydrofluoric acids. The results showed that the soils have on average moderately acid pH, considerable organic fraction and clay loam texture. The total Cu and Zn concentrations were low (mean about 25 mg kg^{-1} and 78 mg kg^{-1} respectively), which reveals that these topsoils are not contaminated. The statistical analysis showed positive correlations between the sum of the clay and silt contents, and the total Cu and Zn concentrations. There are no significant correlations between total Cu and Zn, and organic matter content.

1. Introduction

Soils are dynamic systems and their genesis depends on the parent material, climate, organisms, position in the landscape, which determines the hydrological regime and time. The content of metals in natural soils is determined by the parent material and soil properties, such as pH, organic matter content, and clay content, since metals occur naturally in the earth's crust, but the elemental content of a soil can be increased due to anthropogenic activities [1]. Metals can be transferred from soil to the other environmental compartments, such as groundwater or crops, and can affect human health through the water supply and food chain [2]. Analysis of metal concentrations in soils is critical for policy making orientated at reducing metal inputs to soil and maintaining or even improving soil functions. It is widely accepted that determining the total content of heavy metals in a soil is not sufficient to understand their ecological availability as contaminants or to estimate potential risks. However, the total content is generally used as an initial indicator of reference in order to compare the metal levels with the legal limits [3].

The aims of the study were (1) to determine the total Cu and Zn concentrations in surface soils, and (2) to establish relationships between heavy metals (Cu and Zn) and some selected physicochemical soil properties. The linear correlation coefficients between heavy metals and soil properties were calculated. Organic matter content, pH, clay, silt and sand percentages were the analyzed soil properties. The study soils are located in a rural area of Galicia region (NW Spain) that combines reforestation (forest soils) with agriculture (pastures and cultivation soils) and livestock.

2. Material and Methods

2.1. Study Area

The study area is part of a rural area that combines reforestation (forest soils with pine and eucalyptus) with agriculture (pastures and cultivation soils) and livestock in the Galicia region (NW Spain). Pastures and cultivation soils are exposed to liming materials as well as the application of organic and inorganic fertilizers, which could be a source of Cu and Zn for agricultural soils [4, 5]. Cu and Zn are present in numerous agrochemicals and in slurries (especially pig slurry). The study area is located upstream of a reservoir, the only source of drinking water for the city of A Coruña and its metropolitan area. In addition, this reservoir is under special protection because of its outstanding natural value. Therefore, the Cu and Zn concentrations in the soils located upstream of the reservoir may be determinant for the health of this ecosystem. The geological substrate of the study area is dominated by biotitic schists from the Órdenes Complex [6], which are formed by easily alterable minerals such as calcium plagioclase, amphiboles and biotite. The predominant soil types are Umbrisols and Cambisols [7]. Mean annual rainfall is about 1100 mm and mean annual temperature is 13 ºC. Detailed information about climate, hydrological regimes, and metal transport in this area was provided in previous studies [8, 9, 10, 11].

2.2. Field and analytical methodology

The samples come from forests soils, pastures and cultivation soils. A set of six soil samples for each land use was taken. Each soil sample consists of about 4-6 subsamples collected from the top 20 cm layer of the sampling plot. Soil samples were air-dried, mixed and passed through a 2 mm nylon sieve to remove gravel-sized materials and large plant roots. Special care was taken to avoid metal contamination. All the material was pre-cleaned with 0.01 M HNO_3 and rinsed with double-distilled water.

According to [12], the following parameters were determined: soil pH in a 1:2.5 soil to water or KCl ratio; total organic carbon content by oxidation with a mixture of $K_2Cr_2O_7$ and H_2SO_4 and titration with Mohr Salt; nitrogen content by Kjeldahl method; particle size distribution was determined after the oxidation of the organic matter with hydrogen peroxide, separating the fraction > 50 mm by sieving, and the fraction < 50 mm by the Robinson pipette method. This yielded the size fractions > 50 µm (sand), 50 mm –2 µm (silt), and < 2 µm (clay).

Total Cu and Zn contents of the soil samples were determined by atomic absorption spectrophotometry after wet digestion with a hot mixture of nitro-perchloric-hydrofluoric acids (5 mL aqua regia and 1 mL of 40% HF) under high-pressure conditions. The accuracy and analytical precision in the determination of the total Cu and Zn contents were examined by analyzing a reference material (NCS ZC 73004) and duplicate samples in each analytical set.

2.3. Statistical analysis

An analysis of the variance (ANOVA) and a post-hot test (Tukey) were performed to check significant differences between land uses, both in terms of physicochemical properties and Cu and Zn contents. Pearson correlation coefficients were calculated to assess the relationship between the total metals and the soil physicochemical properties.

3. Results and discussions

3.1 Topsoil characteristics

Table 1 lists the general properties of the studied soils under different land uses, and the results of the total Cu and Zn concentrations. All soils are characterized by moderately acid pH and high content of organic matter. Despite this, the mean pH value was significantly higher ($p < 0.05$) in the agricultural soils (mean pH-H_20 of 6.0 for pastures and 5.8 for cultivation soils) than in the forests soils (mean pH-H_20: 5.1). These differences could be due, on the one hand, the liming of the agricultural soils, since as a corrective measure liming increases the soil pH and, on the other hand, possible acidifying effect of the vegetation supported by the forest soils.

Mean organic matter content ranges from 4.3% to 14.3%. Forest soils are the soils with the highest organic matter content and with relatively high C/N ratio (20), which promotes organic matter accumulation. In contrast, pastures and cultivation soils are characterized by a higher decomposition rate (C/N ratio: 13 and 10 respectively), with organic matter degradation being favored. No significant differences in particle size distribution values were observed among land uses, their texture being on average clay loam.

Table 1. Means and ranges (in parentheses) of the general properties and total Cu and Zn concentration of the soils studied. Different letters within the rows correspond to statistically significant differences ($p < 0.05$) among the land uses.

	Forest	Pasture	Cultivation
pH-H_20	5.1^b (4.7 - 5.3)	6.0^a (5.4 - 6.4)	5.8^a (5.1 - 6.4)
pH-KCl	4.2^b (4.0 - 4.4)	5.1^a (4.5 - 5.5)	4.6^a (4.0 - 4.9)
Organic matter (%)	14.3^a (8.5 - 19.3)	9^{ab} (3.1-12.3)	4.3^b (2.8 - 5.5)
C/N	20 (11 - 29)	13 (8- 22)	10 (3 - 15)
Clay (%)	26.38 (22.05 - 36.41)	24.02 (20.68 - 29.27)	21.70 (19.38 - 26.04)
Silt (%)	41.55 (30.99 - 46.65)	47.55 (42.46 - 51.46)	45.31 (41.0 - 49.80)
Sand (%)	32.07 (29.73 - 34.00)	28.43 (24.76 - 32.11)	32.99 (28.16 - 38.00)
Cu (mg kg^{-1})	23.7 17.3 - 29	24.8 (22.4 - 28.3)	27.0 (20.7-31.9)
Zn (mg kg^{-1})	60.8 (55.9 - 63.8)	83.2 (60.3 - 104.5)	90.2 (69.6 -102.8)

3.2 Total Cu and Zn

The content of Cu (mean 25.1 mg kg^{-1}) ranges from 17.3 to 31.9 mg kg^{-1} for forest and cultivation soils, respectively, but no statistically significant differences were detected among the three land-use types. The concentration of Zn (mean 78.1 mg kg^{-1}) ranges from 55.9 to 104.5 mg kg^{-1} for forest and pasture soils, respectively. In contrast to Cu, Zn presented significant differences among land uses, which were higher ($p < 0.05$) in cultivation (mean 90.2 mg kg^{-1}) and pasture soils (mean 83.2 mg kg^{-1}) than in forest soils (60.8 mg kg^{-1}). Overall mean Cu and Zn concentrations were low, which is consistent with the concentration of these metals in the C-horizon of the soils in the study area [13]. When compared with metal concentrations in surface horizons of natural soils in the surrounding area [14], Cu and Zn concentrations were also low (table 2). The observed concentrations indicate that the study soils are not contaminated by Cu and Zn since none exceeded the generic reference levels established for soils in Galicia for the protection of natural ecosystems [15, 16] that are 50 mg kg^{-1} for Cu and 200 mg kg^{-1} for Zn (table 2).

Table 2. Concentration of Cu and Zn in the soil samples of this study compared with the C-horizon, surface horizons of natural soils in the surrounding area, and generic reference levels established for soils in Galicia for the protection of natural ecosystems (mg kg^{-1}).

	Cu	Zn
This study	25.1 (17.3-31.9)	78.1 (55.9-104.5)
Mean of the C-horizon	20	300
Surface horizons of natural soils	26 (3-89)	58 (22-132)
Generic reference levels	50	200

3.3 Relationship between metals and the selected properties of the soil

From the correlation analysis between metals and the three analyzed soil properties the key role of the finest fractions of the soil was evident. Thus, Cu and Zn showed significant and positive correlations ($p < 0.01$) with the sum of the clay and silt ($r = 0.68$, and 0.77), and significant and inverse with the sand fraction content ($r = -0.68$, and -0.77, respectively). These results coincide with several studies that have been reported by other authors previously and were related to the higher surface area of the finer particles, which increases the adsorption capacity of metals [17, 18]. On the other hand, for pH significant positive correlations were only observed with Zn ($r = 0.68$, $p < 0.01$). Despite the high content of organic matter in these soils and the general tendency of metals, especially Cu, to associate with the organic matter [19], no significant correlations between the total metals and organic matter content were observed. These results indicate that the retention of Cu and Zn in the soils of this study depends more on the mineral fraction than on the organic fraction, which is in agreement with the findings of [20, 21].

4. Conclusions

Overall mean Cu and Zn concentrations were low, and none of the analyzed samples reached the generic reference levels established for soils in Galicia for the protection of natural ecosystems, which suggests little influence from agricultural and forestry activities on the input of metals in these soils. Positive correlations with the silt and clay content but not with organic matter content have been observed for total Cu and Zn concentrations in this study, which indicates that the fine mineral fractions are an important sink for Cu and Zn in these soils. The pH only showed significant and positive correlations with Zn.

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