

Contents and main fractions of trace elements in Typic Argiudolls of the Argentinean Pampas

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ABSTRACT

The knowledge of the trace elements in soils of the Pampas remains fragmentary. Agriculture has been intensified in this region increasing the crop demand of micronutrients and increasing the use of fertilizers, which could add measurable quantities of trace elements to soils. We analysed the status of 12 trace elements in three soil fractions of different availability. Typic Argiudolls (soil taxonomy) from six locations of northern Buenos Aires province were sampled. Arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), molybdenum (Mo), nickel (Ni) and zinc (Zn) were extracted with DTPA, with 2N HNO₃ and with HCl-HNO₃-H₂SO₄ and HClO₄. The exceptions were bioavailable boron (B), extracted with hot water, and total B and Cr, determined through instrumental neutron activation analysis. The analysis of the other elements were performed by inductively coupled plasma-atomic emission spectrometry. The total contents were similar or below values found in other soils of the region. Extractable DTPA Zn, Cu and Fe were within the range of variation for the region but Mn data were lower than those found previously in the area. As, B, Co, Cr, Fe, Mo, Pb and Zn predominated in chemical forms which are almost insoluble for plants. Our results broaden the previous information for micronutrients in the Pampean region. For heavy metals, our results corroborate the lack of soil contamination in rural areas of the Pampas.

Keywords: Trace elements, bioavailability, Argiudolls, micronutrients, heavy metals.

INTRODUCTION

There is a great variety of chemical methods to extract trace elements from soils. These methods allow the extraction of total contents, or selective or sequential extractions (Tack and Verloo, 1995). The latter are generally divided into the following fractions: soluble/exchangeable, Fe/Mn oxides bound, organically bound, carbonate and sulfide bound and residual (Shuman, 1985; Sposito *et al.*, 1982). These fractions are not necessarily, closely related to the metal speciation or bioavailability (Tack and Verloo, 1995).

The bioavailable forms are related to several properties and reactions within the soils (Fergusson, 1991; Lee *et al.*, 1997) and chemical extractants developed to represent plant absorption, may extract trace elements from several fractions (Tack and Verloo, 1995). Among the tested extractants, DTPA is one of the commonest

(Fergusson, 1991; Tack and Verloo, 1995), although its effectiveness varies with different trace elements (Pais and Jones, 1997). Another extractant, used in some sequential procedures and as a selective extractant, is nitric acid (Tack and Verloo, 1995). This acid is stronger than DTPA and dissolves the relatively insoluble sulfide bound fraction. In some procedures this acid is used to extract the total contents (Munkholm *et al.*, 1993; Sposito, 1982) although some papers have shown it does not extract all the soil trace metal contents (Sparks *et al.*, 1996). The extraction of the total trace elements is usually performed with a mixture of acids, and this extraction includes the so-called residual fraction of the sequential procedures. This fraction, which is made up of silicates and other structural native minerals, is not considered to be available for plants.

Since the mid 1970s the bioavailable contents of some micronutrients has been determined in soils of the

Argentinean Pampas. However, the knowledge of the trace elements contents is still fragmentary and only an "overall picture" of micronutrient availability has been established: In many areas, soils are deficient or poorly supplied with boron and zinc. In some cases, there are problems with copper but there is a good supply of iron and manganese (Ratto and Fatta, 1990). Knowledge about other trace elements, such as heavy metals is scarce. Lavado *et al.* (1998) have developed the first systematic attempt to determine the baseline level of such elements in several soils of the Pampas.

Agricultural production has been intensified in this region in recent years and yields are now increasing. This process leads to higher crop requirements for micronutrients and to an increase in the use of fertilizers and other inputs. Due to the high soil fertility, fertilizer use has historically been very low, but its application could add measurable quantities of trace elements to soils (Charter *et al.*, 1995; Giuffr  *et al.*, 1997). As is widely known, certain elements have negative effects on biota and human beings (Pais and Jones, 1997). The large crop production of this area is consumed locally but a great deal is also exported. Therefore, it is important to know the status of trace elements in local soils. This information may be useful to establish either present or potential deficiencies of micronutrients or to monitor the eventual accumulation of heavy metals in soils. Our objective was to analyse the status of 12 trace elements from three soil fractions with different solubility.

METHODOLOGY

Six locations of a representative and homogeneous cropland area of northern Buenos Aires province were sampled. The soil in all sites was Typic Argiudoll (Soil Taxonomy); the original grassland was ploughed around 120 years ago. Phosphate fertilizers have been applied in the last 3 years, an annual average of 15 kg P ha⁻¹, mainly diammonium phosphate. In the last 20 years the main crops grown were wheat, soybean or maize. In each location a composite sample from the top soil (0–20 cm) was taken in March 1997. The soils were characterized using the following methods: particle size (pipette method); organic carbon (dry combustion); total nitrogen (Kjeldahl method); pH (1:1 soil:water ratio); cation exchange capacity and exchangeable cations (extraction with ammonium acetate and determination by atomic absorption); available phosphorus (Bray-Kurtz # 1 method).

The following procedures were used for determination of trace elements:

- Bioavailable fraction: As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb and Zn were extracted with DTPA; B was extracted with hot water. The determinations were

performed by inductively coupled plasma-atomic emission spectrometry (ICP-AES);

- HNO₃ extracted fraction: all elements were extracted with 2N HNO₃;
- Total fraction: all elements, except B and Cr, were extracted with HCl–HNO₃–H₂SO₄ and HClO₄. The determinations were performed by ICP-AES. B and Cr were determined through instrumental neutron activation analysis (INAA). Procedures used are fully described by Sparks *et al.* (1996). The data were analysed by ANOVA and the Duncan test.

RESULTS AND DISCUSSION

Table 1 shows the characteristics of a representative sampled soil. As expected from previous soil surveys (Lavado, 1991), the Typic Argiudolls of the studied area has very similar morphological, chemical and physical properties. That similarity in parameters like organic matter or clay content impeded the establishment of significant relations between soil components and trace metals concentration. The average concentrations of the 12 trace elements are shown in Tables 2 and 3. The total contents are similar or below the values found in other non contaminated soils of the region (Lavado *et al.*, 1998). For heavy metals, this shows that present values are, at least, not significantly affected by anthropogenic action. Hot water extractable B and DTPA extractable Zn, Cu and Fe are within the range of data variation previously found in the area (Ratto and Fatta, 1990; Ratto *et al.*, 1997). Conversely, DTPA extractable Mn data were lower than those indicated by the above mentioned authors.

From the data shown in Tables 2 and 3 the difference between HNO₃ extractable and total contents of the studied trace elements can be calculated. HNO₃ is a strong extractant, which extracts metals from all fractions, except the insoluble residual fraction. The differences between extractants show that most B, Fe, Mo and Zn are found in chemical forms almost insoluble for plants (Table 2). For B and Zn, this information is in agree-

Table 1 Soil mean values (0–20 cm depth)

Particle size	
Clay	27.2 %
Silt	58.0 %
Sand	14.8 %
Organic carbon	3.3 %
Total nitrogen	0.3 %
Available phosphorus	13.8 ppm
Cation exchange capacity	23.0 meq 100g ⁻¹
Exchangeable cations	
Ca	17.2 meq 100g ⁻¹
Mg	3.5 meq 100g ⁻¹
K	2.0 meq 100g ⁻¹
Na	0.2 meq 100g ⁻¹
Soil pH	5.9

Table 2 Soil contents of micronutrients (mg kg⁻¹)

Element	Total		HNO ₃ extractable		DTPA extractable	
	Value	Letter	Value	Letter	Value	Letter
Boron	22.33	a	0.55	b	0.46	b
Zinc	55.25	a	2.29	b	1.47	b
Copper	18.50	a	5.73	b	1.38	c
Iron	20900.00	a	549.17	b	70.12	c
Manganese	557.33	a	483.13	b	9.73	c
Molybdenum	1.80	a	0.10	b	0.01	c

Different letters mean significant differences between treatments at ($P < 0.05$) Duncan test.

ment with previous research, which showed that they are the commonest micronutrients deficiency in the Pampas. There are few data about the level of soil Mo in the studied area. Mo plant requirements are very low, but this micronutrient is critical for Leguminosae (Pais and Benton Jones, 1997). This might be important for soybean, the main crop in this area. Consequently, it will be necessary to study this micronutrient even further. For Fe, our data have shown a very high concentration in the residual fraction. This would be difficult to explain because iron in soils appears mainly as crystallized oxides (Pais and Benton Jones, 1997). Furthermore, DTPA extractable Fe is also very high. Accordingly, there are no records of iron deficiencies in the area. Mn and Cu exhibited different behavior. Mn showed a predominance of the HNO₃ extracted fraction. Soil Mn is mainly located as oxides and bound to the organic matter (Shuman, 1985) and this could be the reason for this behavior. For copper, the bioavailable and nitric acid extracted fractions are an important proportion of the total content. There is, then, a potential supply of these two micronutrients for plants, in agreement with known information: deficiencies of Mn are not known and deficiencies of Cu are uncommon.

Table 3 shows values of the remaining trace elements. None of the elements studied here approach "dangerous" concentrations (Pais and Benton Jones, 1997). The average concentrations in the analysed soils is within the range of normal variation of non-contaminated soils of the world and does not reach the maximum registered levels (Frink, 1996). There are, however, some differences among them. Almost all Cr in soils is in insoluble form, in agreement with the fact that the native minerals of chromium are practically inert (Pais and Benton Jones, 1997). Most As, Co and Pb are also in insoluble forms. For Pb, the data are in accordance with the classic findings of Karamanos *et al.* (1975) who found that use of HNO₃ distinguishes between the native and the added form of Pb, because this acid extracts the latter selectively. The DTPA extractable lead and its relative proportion to total lead is low (Singh *et al.*, 1998). The prevalence of the residual fraction (the difference between the HNO₃ and total extraction) for those four

Table 3 Soil contents of other trace metals (mg Kg⁻¹)

Element	Total		HNO ₃ extractable		DTPA extractable	
	Value	Letter	Value	Letter	Value	Letter
Arsenic	0.68	a	0.10	b	0.07	b
Cadmium	0.62	a	0.21	b	0.18	b
Cobalt	35.78	a	5.42	b	0.14	c
Chromium	24.33	a	0.14	b	0.01	c
Nickel	6.67	a	2.13	b	0.49	c
Lead	15.50	a	5.31	b	0.67	c

Different letters mean significant differences between treatments at ($P < 0.05$) Duncan test.

elements indicates lower levels of antropogenic contamination (Tack and Verloo, 1995). On the other hand, an important proportion of Cd and Ni was extracted by DTPA suggesting that they are in fractions relatively bioavailable. Nevertheless, as stated, the absolute values of them are low (Singh *et al.*, 1998) and far from threshold data of contaminated soils (Frink, 1996).

In short, this simple soil fractionation procedure, confirms and broadens the previous information on micronutrients in the Pampean region. This information was based mainly on the comparison of soil concentrations with deficiencies thresholds from other countries. For heavy metals, our results corroborate the lack of soil contamination in rural areas of the Pampas.

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