# ACCUMULATION OF TRACE METAL ELEMENTS IN SOIL AND IN A VEGETABLE BY FERTILIZER ADDITION

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## ABSTRACT

The practice of fertilization is necessary to reincorporate and provide the soil with additional sources of nutrients in forms that can be assimilated by plants. Fertilizers often contain very small amounts of trace metals as impurities. These can be incorporated into the human diet through the ingestion of food contaminated with these elements.

The soil samples studied came from agricultural soil in the V region, Chile. The characterization carried out indicated a pH and EC expected for a soil with this use, while low values for CEC and MO % were found. The samples were classified as medium P and extremely N-rich soils, and significant increases in these nutrients were found in the SPT and urea treatments, respectively.

The soil was incubated according to two different treatments: with 0.1% of urea, superphosphate (SPT) (5.0 g per pot). After 8 weeks of incubation, wheat seed were planted and harvested after three weeks of growth. Trace metals were determined by Atomic Absorption Spectroscopy (AAS).

Trace metal concentrations followed the trend: Cu < Cr < Zn < Ni for urea treatment; while: Ni < Cu < Zn < Cr for treatment with SPT. The maximum percentage contributed by fertilization was for Cr (59 %). The concentration of metals in root, stem and leaf of the crop were found below the detection limit, except for Zn and Cu in the root. The bioaccumulation factor for Cu and Zn was less than 1 for all treatments, while the translocation index for Zn was also less than 1.

The use of SPT is consistent with a greater contribution of trace metals to the soil compared to urea; consequently, the use of chemical fertilizers could increase the concentration of trace metals in the soil and incorporate them into the vegetables grown in the soil. For this, the use of organic fertilizers such as compost and humus obtained from organic waste raw materials is an increasingly popular alternative in various crops, for which it is necessary to evaluate the trace metal content, as these can accumulate in both the soil and the substrates.

**Keywords:** Fertilizers, metallic trace elements, urea, superphosphate (STP), soil, humus, compost, atomic adsorption spectrophotometry (AAS).

## 1. INTRODUCTION

Modern agriculture like any other branch depends on the technological advancements made in various facets of science to maximize productivity. Many of the inorganic chemicals used in agriculture when not utilized by plants would remain as residues in the soil, water, air, or plant or may get transformed from one form to another [1]. Although the use of fertilizers and plant protection chemicals are the major drivers that increased crop production to achieve self-sufficiency in food production, the human tendency of "if little is good, a lot more will be better" prevailed and lead to indiscriminate use of these inputs over years and resulted in accumulation of these chemicals in soil, water, air as well as in the food chain as residues with serious implications on crop growth as well as human health [2], [3]. Food is the most important route of exposure to these toxic trace elements [4].

Use of inorganic chemicals like fertilizer to rescue dying plants immediately, because it releases nutrients easily into the soil compared to other nutrient sources and absorbed by the plants and also contributes to soil pollution with heavy metals and metalloids like Lead (Pb), Arsenic (As), Cadmium (Cd), Zinc (Zn), Nickel (Ni), Copper (Cu), Iron (Fe), Manganese (Mn), Chromium (Cr), etc. Several studies have shown that the main source of fertilizer derived metals in soils is due to phosphatic fertilizers, manufactured from phosphate that contain various metals as minor constituents in the ores and the overuse of these chemicals has now started affecting the environment in many ways [5]. Excessive utilization of these chemicals generates residues that cause nutrient imbalance and reduction of the yielding capacity of crops [6].

Trace elements or Heavy metals are naturally present in the soil, the amounts present are depending of the parent material from which the soil was formed and these metals are found in the soil in small concentrations. However, these concentrations can increase dramatically due to anthropogenic sources. Additions may come from various sources, e.g. atmospheric deposition (which is higher in industrialized areas) and the use of fertilizers, soil amendments and organic wastes, e.g. biosolids (sewage waste products).

The concept of heavy metal or metallic trace element does not have a standardized definition; this is the name given to metallic elements whose density is greater than (5 $gcm^{-3}$). This term is related to elements that can be polluting and ecotoxic [7], which is why the concept of metallic trace element or trace metal is currently used. Metallic trace elements are present in low concentrations in water or soil [8], and they can be categorized as, possibly essential, and non-essential based on the classification of Kabata-Pendias [9], with respect to their presence in humans. They are found in reduced concentrations in plants and animals and are associated with the essential ones: As, Cu, Co, Ni, Cr, Fe, Zn, Mo and Mn; these are referred to as trace elements or essential micronutrients and are related to metabolic functions, as is the case of enzymes that catalyze Fe, Zn and Cu. On the other hand, non-essential trace metals do not have a biological role, and can be subdivided into non-toxic elements (Ag, Au, Cs) in small concentrations in the environment, and toxic elements (Hg, Cd, Pb) that can mean a series of disorders for people such as cardiomyopathies, effects on the neurological system and damage to the kidney and liver, among others [9]. A feature of special attention for these elements is their accumulation. As they are not biodegradable, their concentration in the environment will not decrease over time, even if they are essential all these elements can be toxic when they exceed certain levels.

The main sources of metals in Chile are mining, industry and agricultural activities. The mining industry and its waste are associated with a large part of the contributions of metal trace elements in nearby localities due to the development of these activities [10]. Atmospheric deposition is a diffuse source of soil contamination, which in some cases is the factor with the highest contribution of heavy metals [11]; reaching the soils through emissions from incineration and burning of fossil fuels [12]. In summary, the introduction of trace metals into the food chain occurs through water sources, atmospheric deposition, and contaminated soils [13].

The concentration of trace metal elements in plants reflects the abundance of these in their growing medium (soil, air and water) and in the nutrient solution that sustains them. Trace elements such as Cu, Fe, Mn, Mo and Zn have key roles in plant metabolism and are part of some enzymes. The absorption of trace metals depends on several factors; however, the adaptability and tolerance of the plant as response mechanisms to environments in chemical imbalance are a matter of constant research.

Trace elements in soil are linked to different fractions: bound to organic matter, precipitates (such as hydroxides, oxides and carbonates), in solution (soluble metal ions and complexes), adsorbed at exchange sites and forming part of the soil structure. The absorption of trace elements from the soil solution to the root depends primarily on their mobility and bioavailability [14]. Bioavailability is understood as the proportion of an element that is available to be absorbed by

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living organisms. Trace metals will be bioavailable when in solution or absorbed at inorganic constituent exchange sites.

On the other hand, bioaccumulation is defined as the increase in the concentration of a chemical compound in living organisms, in contrast to its concentration of that compound in the environment [15]. The absorption of metals and their corresponding bioaccumulation in plants varies according the species The responses of plants to the presence of metals are varied and can range from the exclusion of the metal (excluder species), in which the species limits its transport to the aerial part, to the accumulation of the trace metal in the aerial part, the latter strategy usually appears in plants usually found in contaminated soils [14].

Metal bioconcentration factor (FBC) is used to determine the amount of heavy metals that is absorbed by the plant from the soil. This index reflects the efficiency of the plant to accumulate a certain metal in its biomass [16]. The responses of plants to the presence of metals are varied and can range from the exclusion of the metal (excluder species), in which the species limits its transport to the aerial part, to the accumulation of the trace metal in the aerial part, the latter strategy usually appears in plants usually found in contaminated soils [10].

Another index of interest is the translocation factor (FT) which is a measure of the internal transfer of metals in the plant. This indicator shows the efficiency of the plant in translocating the stored metal from the root to the aerial parts. FT>1 values indicate that the plant is appropriate for use in phyto extraction, while FT<1 values indicate that the species is not effective in the translocation of metals to its aerial part, but has competence for phyto stabilization [17].

Soil fertility refers to the ability of the soil to sustain plant growth and develop optimal crop yields. This characteristic can be enhanced by the use of organic and inorganic fertilizers that feed the soil. The constant use of soils for agriculture results in a depletion of their nutrients, leading to lower yields. In this way, the practice of fertilization is necessary to reincorporate and provide the soil with additional nutrient sources in forms assimilated by plants, achieving a higher yield and better quality of products.

Intensive agricultural activity, such as that carried out mostly in Chile, requires maximizing the amount of production obtained in increasingly less available soils, due to growing urbanization; For this purpose, the use of fertilizers, pesticides and selected seeds is required to achieve greater efficiency. Globally, it is estimated that more than half of the food consumed is produced thanks to the use of mineral fertilizers [18], with the most used being those containing nitrogen, potassium, and phosphates.

In Chile, urea is the main fertilizer used and the most consumed and important in the world [18], whose advantage over other nitrogen fertilizers is its 46% nitrogen content. It is characterized by its high solubility, which increases with temperature, low porosity and high hygroscopic characteristic. On the other hand, triple superphosphate (SPT), commonly used in agricultural practices, stands out for its high phosphorus content and, like urea, can be incorporated into the soil in solid form or dissolved in irrigation water. For this reason, both compounds can be applied to a wide variety of crops periodically.

The excessive use of these chemicals is also one of the causes of eutrophication in water bodies, due to the contribution of nutrients such as nitrogen (in the form of nitrate and ammonium salts), and phosphorus (such as phosphates). The main consequence of this phenomenon in the waters is the decrease in biodiversity and the increase in biomass. The proliferation of algae prevents the penetration of light, making photosynthesis impossible in the depths of the body of water, turning this ecosystem into an anaerobic environment [19]. The effects of the accumulation of heavy metals from agricultural activities are only partially described; on the other hand, the persistence of these elements is of special environmental interest. In the same way, knowledge about the impacts that the bioaccumulation of these compounds could have on vegetables and fruits for direct human consumption is scarce.

The concentrations of trace metals in fertilizers have been the subject of study for decades; Table 1 summarizes the concentrations of these elements in urea and superphosphate, which have been reported in various publications [20]; [21]; [22]; [23].

**Table 1. Concentrations of declared trace metals in urea and superphosphate.**

| Metal (mgkg$^{-1}$) | Cd | Cr | Cu | Ni | Pb | Zn |
|---|---|---|---|---|---|---|
| Urea (a) | 0.008 | - | 0.4 | Nd | nd | Nd |
| Superphosphate (a) | 2.22 | - | 12.5 | Nd | nd | 50 |
| Superphosphate (b) | 23.1 | 232.5 | 42.2 | 60 | 39.4 | 556.6 |
| Urea (c) | <0.01 | - | - | - | 0.4 | - |
| Superphosphate (c) | 8.7 | - | - | - | 3.9 | - |
| Urea (d) | <0.2 | nd | <0.6 | <0.2 | <0.4 | nd |
| Superphosphate (d) | 5.0 | 88.9 | 3.2 | 25.2 | 11.1 | 61.3 |

nd = no detected. (a) Gimeno-García et al., 2001; (b) Pezzarossa et al., 1993; (c) Rodriguez et al., 2014; (d) Raven & Loeppert. (1997).

Trace metals can be incorporated into the human diet through the ingestion of food, this means an accumulation of these contaminants in the soil when their use is prolonged, which is magnified due to the use of excessive amounts and applications [24]. contaminated with these elements, either by direct consumption of vegetables and their respective processed products. Thus, the transfer of metal trace elements constitutes a global food security problem [24].

Chile is a territory that has comparative advantages (climate, sanitary conditions and quality standards) in agricultural production and growing exports in the area, which justifies the application of products that increase the yield of production and improve the quality of crops. Given the background, the need arises to know the impact of chemical fertilization on the increase of heavy metals both in the soil and in harvested vegetables.

The goal of this work was to determine the contribution in the concentration of metals such as Cu, Zn, Pb and Cd to an agricultural soil due to the use of two selected fertilizers, such as Urea and Triple Superphosphate (SPT), and their possible transfer to a vegetable planted in that soil.

## 2. MATERIALS AND METHODS

***2.1 Soil samples.*** The soils studied in this work were obtained from a land for agricultural use in the commune of Limache, V Region, Chile, (33°00'04.4"S 71°15'11.2"W).

***2.2 Material preparation.*** The material used, both for the sampling and for the analysis of the samples in the laboratory, was pre-treated, to avoid and rule out possible contamination. This was made for both polyethylene plastic materials and glassware. It was washed with potable water and Extran® detergent (Merck). A 2% solution of nitric acid (HNO3) Suprapur® (Merck) was added, allowing it to stand for 48 hours. It was subsequently rinsed with distilled water and then with Milli-Q grade deionized water. It was left to dry until use.

### 2.3 Physicochemical Characterization of soils.

***2.3.1 Sample preparation***: The collected samples were sieved to two different fractions, fraction < 2 mm for the physical-chemical characterization and fraction < 63 µm, for the metals determination.

***2.3.2 pH and Electrical Conductivity (EC) determination***: 10.00 ± 0.01 g of each samples were mashed into 50 mL plastic bottles. Then 25 mL of deionized water was added to each flask and subsequently left on an orbital shaker for 2 hours at 150 rpm (Already Enterprise Inc, DSR-2800A model). The pH and electrical conductivity of the suspension were recorded with the previously calibrated multiparameter equipment (HANNA, HI 9813 model) [25].

***2.3.3 Total Organic Carbon (TOC)*** Crucibles were dried at 105.0 ± 0.1 ° C with 3.0 g of sediments samples, then were put into the flask and calcined at 550.0 ± 0.1 ° C for in an oven for 6 hours (Barnstead Internation al, FB 1300 model). The samples were then allowed to cool to room temperature in a desiccator and then be massed. The previous steps were repeated until constant mass [25].

***2.3.4 Soluble Organic Carbon (SOC)***. 0.50 ± 0.01 g of each sample was transferred to a 250 mL Erlenmeyer flask, with a duplicate and two blanks, 10 mL of $K_2Cr_2O_7$ 0.1667 molL$^{-1}$ (Merck p.a.), was added under a hood and with caution 20 mL of concentrated $H_2SO_4$ (Merck p.a.). Samples were allowed to stand for 30 minutes. Later, 180 mL of deionized water and 10 mL of concentrated $H_3PO_4$ (Merck p.a.), was added. Finally, it was titrated with $FeSO_4$ (Merck p. a,), 1.0 $molL^{-1}$ using a platinum electrode (Hanna HI 3831 B) [26].

***2.3.5 Available Phosphorus:*** For the determination of available phosphorus in acidic soils, phosphorus was extracted with a combination of HCl and $NH_4F$ (Bray solution). Then 14 mL of Bray extracting solution was added; it was shaken manually for 1 min and filtered with a syringe filter. Next, 3 mL of the phosphorous standard series, blank, and sample extracts were pipetted into test tubes along with 3 mL of mixed reagent into each tube. It was left to stand for 2 hours until the blue hue developed to its maximum. The absorbance was measured at 880 nm in a spectrophotometer (Shimadzu, Pharmaspec 1700 model) [27].

***2.3. 6 Kjeldahl Nitrogen***: 1.00 ± 0.01 g of samples was mashed into a digestion tube along with a duplicate and two blanks. 1 g of Devarda catalyst (Merck p.a.), 8 mL of concentrated sulfuric acid were added, mixed well and digested for 90 min at 420 ° C. At the end of the time, the tubes were allowed to cool to take them to the distillation equipment, where an Erlenmeyer flask with 25 mL of boric acid-indicator (Merck p.a.) solution was placed at the end of the condenser and in the other the digested sample, which was distilled for 7 minutes. After receiving the final solution in the flask, it was titrated with HCl 0.01 $mol\cdot L^{-1}$ (Merck p.a.) until the color changes of indicator (Digetro VELP® Scientifica, modelo DK 6; Destilador (VELP® Scienfica model UDK 127) [25].

***2.3.7 Cation Exchange Capacity (CEC*)**:** For the determination of the CEC, the method was used by saturation with sodium acetate, washing with ethanol (Merck p.a.), and displacement of the adsorbed Na with ammonium acetate (Merck p.a.). In this way in the obtained extract, the Na displaced by Atomic Absorption Spectroscopy (AAS), (Shimadzu atomic absorption spectrometer; model AA-6800) was measured [25].

### 2.4 Analysis of trace elements in soil and soil modified with fertilizers

***2.4.1 Digestion*:** The digestion of the samples for the determination of metals was carried out by microwaves in tubes covered with Teflon PFA, 250 mg of soil with 1 mL $HNO_3$, 3 mL HCl and 3 mL HF (Tritisol Merck), were added to each tube. This was done for all sites along with one duplicate and ten blanks. Once the tubes were sealed and placed on the microwave oven, the digestion process was started according to the following conditions: Stage 1: 800 W; 80%, 4min, 175°C. Stage 2: 400 W, 80%, 4min, 175°C [28]

***2.4.2 Chemical determination of trace elements.*** Standard solutions for heavy metals were prepared from 1000 $mgL^{-1}$ of each metal (tritisol Merck); samples were analyzed using an atomic absorption spectrophotometer (AAS) (Shimadzu spectrophotometer 6800, ASC-6100).

### 2.4 Analytical method validation and quality control

The experiment was performed in triplicate using the soil sample; calibration curve was obtained to see the linear relationship between absorbance and metal concentration in the dynamic range. The accuracy was measured in relation to coefficient of variation (CV), finding that for all the measurements performed over different days. The recovery was measured using blanks solutions and reference sample soil.

### 2.5 Soil incubation with two types of fertilizers.

***First stage: soil treatment with fertilizer***. Three trays with 1000 g of sifted soil (2 mm) each was installed, three trays with 1000 g of sifted soil (2 mm) each were installed, The doses used are those described according to the manufacturer, the following treatments were assigned, schematized in Figure 1.

***Urea treatment***: the soil was watered three times a week with a prepared solution by diluting 1.0 g of urea in 1000 mL of deionized water, for 4 weeks. The temperature and photoperiod in the chamber culture were 21°C and 12/12 (light/dark hours), respectively ***Triple superphosphate (SPT) treatment***: 20.0 g were incorporated directly into the soil of the fertilizer, previously crushed in mortar, then irrigated with deionized water to its field capacity for 4 weeks.

***Samples control:*** Soil was irrigated with distilled water three times a week at capacity of field, for 8 weeks. After completing the indicated treatments, irrigation was suspended in the three trays for a week.

***Second stage: Cultivation in soil treated with fertilizers***. The soil of each tray was divided, placing 250 g of soil in 4 different pots. To two pots of each treatment, 15 wheat seeds were added, and for 2 weeks, all pots were watered 3 times a week with distilled water (Figure 1).

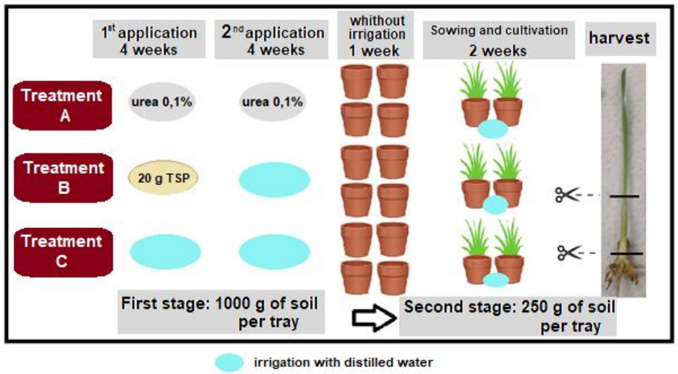

**Figure 1. Soil incubation with fertilizers**

### 2.6 Metal bioconcentration factor (FBC).

This index reflects the efficiency of the plant to accumulate a certain metal in its biomass [16] and is calculated using Equation 1.

$$FBC = (\text{root metal})/(\text{soil metals}) \qquad \text{Eq. 1}$$

FBC>1 values indicate that the species is accumulator, hyper accumulator for FBC>10 values, and is an excluder species when FBC<1.

### 2.7 Translocation factor (FT).

The translocation factor (FT) is a measure of the internal transfer of metals in the plant and is calculated from Equation 2.

$$FT = (\text{metals in part aerial}) / (\text{metals in root}) \qquad \text{Eq. 2}$$

This indicator shows the efficiency of the plant in translocating the stored metal from the root to the aerial parts. FT>1 values indicate that the plant is appropriate for use in phyto extraction, while FT<1 values indicate that the species is not effective in the translocation of metals to its aerial part, but has competence for phyto stabilization [12].

## 3. RESULTS AND DICUSSIONS

### 3.1 Validation of the analytical method.

The calibration curves for the determination of Cd, Cu, Cr, Ni, Pb and Zn are shown in Table 2. The linearity parameter is associated with the value of $R^2$ for all curves a value quite close to unity were observed. Finally, the limits of detection (LOD) and quantification are presented (LOQ) for the six elements

**Table 2. Calibration curves for the trace metals studied.**

| Metal | Slope | $R^2$ | Recovery (%) | LOD ($\mu gkg^{-1}$) | LOQ ($\mu gkg^{-1}$)LC |
|---|---|---|---|---|---|
| Cd | 0.132 | 0.984 | 101.2 ± 5.2 | 0.54 | 1.90 |
| Cr | 0.058 | 0.995 | 98.4 ± 3.6 | 0.25 | 5.40 |
| Cu | 0.086 | 0.992 | 101.6 ± 3.9 | 9.26 | 8.51 |
| Ni | 0.135 | 0.990 | 102.3 ± 3.2 | 0.20 | 5.70 |
| Pb | 0.010 | 0.998 | 101.7 ± 4.0 | 126.6 | 106.3 |
| Zn | 0.281 | 0.998 | 98.9 ± 3.5 | 0.50 | 1.07 |

The validation of analytical methods for determination of trace metals should be considering optimum. The slopes of the curves, the highest sensitivity was observed for Zn followed by Ni and Cd. The coefficient of variation of the samples of known concentration, measured on different days, is less than the 5% allowed for everyone the elements analyzed. The method used for the determination of trace metals in soil and vegetable has good accuracy.

### 3.2 Characterization of physicochemical parameters of an agricultural soil.

#### 3.2.1 Determination of pH, EC, TOC, OM and CEC.

The results of pH, electrical conductivity (EC), organic matter (MO), carbon total organic (TOC %) and cation exchange capacity (CEC), were expressed as the average of the measurements made and the corresponding values are presented in Table 3.

**Table 3. Values of the characterization parameter for the soil sample under study.**

| Parameter | Value |
|---|---|
| pH | $7.13 \pm 0.01$ |
| CE ($dSm^{-1}$) | $0.20 \pm 0.01$ |
| COT (%) | $7.34 \pm 1.90$ |
| OM (%) | $3.92 \pm 0.02$ |
| CEC ($cmol(+)kg^{-1}$) | $1.90 \pm 1.20$ |

According to the reference values for pH and EC, the soil sample studied is classified as neutral and non-saline, pH is inversely related to the mobility of metals in the soil. Most trace metal increase their mobility at more acidic pH, also increasing their concentration in the soil solution, and therefore their bioavailability. Given the characteristics of the soil analyzed, it is expected that the pH, and consequently the mobility of the trace metals, will be strongly influenced by actions inherent to agricultural activity such as irrigation and fertilizer application [29]; [30]. Regarding electrical conductivity, this is directly related to the concentration of dissolved salts, the higher the EC, the higher the concentration of dissolved salts.

The analyzed soil presented EC characteristics that make it suitable for agricultural use, a situation that coincides with the productive activity developed in it at the time of harvesting, in the same way the pH measured was in the optimal range for crops between 6.5 and 7.5 [31]. The results obtained according to the OM and CEC values the soil analyzed presented a very low classification for both. In addition to the important role in soil fertility, OM influences some of its physicochemical properties, such as the decrease in pH when it is found in a higher percentage.

Humic substances, as one of the most relevant fractions of OM, play a transcendental role in the accumulation of trace metals through the formation of stable complexes, which is how the percentage of OM and CEC account for this relationship. In a soil with low levels of OM and CEC, the formation of complexes between organic matter and metals is also low; therefore, the influence of these parameters on the retention of metals in soil colloids is not significant. A greater availability of exchange sites in soil minerals is related to a CEC with higher values, which favors the retention of metallic trace elements [31].

The phosphorus concentration and nitrogen percentage were determined both for the characterization of the soil under study and for the subsequent treatments was carried out. The values determined are presented in Table 4.

**Table 4. Phosphorus concentrations (phosphorous (mgKg-1) and nitrogen (%) determined in the soil sample under study (S-WF) and in the respective treatments performed (S-urea) and (S-SPT).**

| Samples | P ($mgKg^{-1}$) | N (%) |
|---|---|---|
| Soil without fertilizer | $9.9 \pm 2.4$ | $0.29 \pm 0.01$ |
| Soil - Urea | $10.4 \pm 1.5$ | $0.32 \pm 0.02$ |
| Soil - SPT | $19.8 \pm 3.3$ | $0.29 \pm 0.02$ |

According to the reference values indicated, it is possible to evaluate the quality of a soil based on its phosphorus and nitrogen content. Phosphorous, ($mgKg^{-1}$); Low < 5.5 Medium 5.5-11.0 High > 11. Nitrogen (N%): Extremely poor > 0.032; Poor, 0.032 - 0.063; Moderately poor 0.064 - 0.095; Medium 0.096 - 0.126; Moderately rich 0.127 - 0.158; Rich 0.159 - 0.221; Extremely rich > 0.221, [32].

The results obtained show that the unfertilized soil and the one corresponding to the urea treatment sample presented similar phosphorus concentrations, both in the "medium" category. In contrast, the soil fertilized with superphosphate presented considerably higher concentrations, and could be classified as a soil with "high" phosphorus content. On the other hand, the soil studied and its corresponding treatments are classified as "extremely rich" according to their percentage of nitrogen. However, there is an obvious difference in relation to this percentage with respect to soil with urea, the latter being of higher content in the treatments. In summary, phosphorus and nitrogen intake were higher for treatments with PTS and urea, respectively.

### 3.3 Effects of urea and SPT fertilization on wheat seedling growth.

As an additional antecedent, a longer root length was observed in the crop carried out in soil with SPT and urea (Figure 2). In wheat seedlings, the greatest length was observed for soil without fertilizer. Regarding germination, only in the soil with urea did not germinate all the seeds, in addition the latter presented a fairly late germination time compared to the other treatment

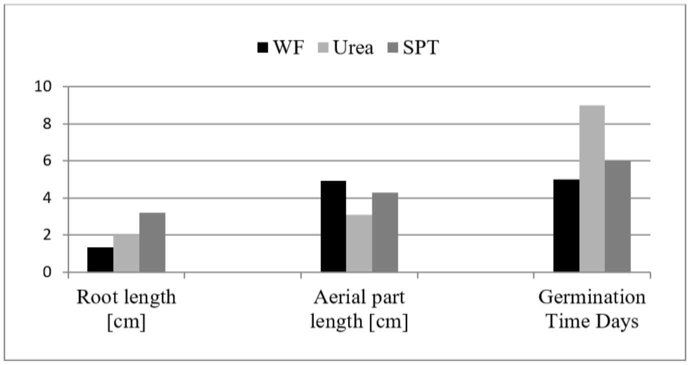

**Figure 2. Fertilization effects in the wheat plant germination (days) and in length (cm) of root and aerial part.**

Both root length and germination time were positively affected with the addition of fertilizer, compared to soil with no fertilizer, while the length of the aerial part of the plant had a slightly negative.

### 3.4 Determination of trace metals in soil and soil modified with fertilizers.

The concentrations of Cu, Cr, Ni and Zn were carried out, in the soil, soil-urea and soil-SPT, (figure 3), while concentrations of Cd and Pb were below the detection limit in all cases.

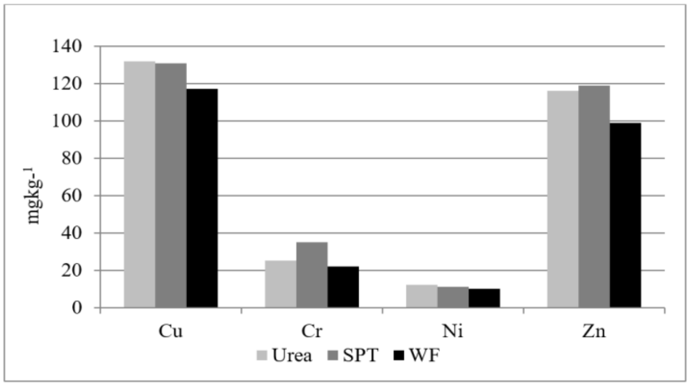

**Figure 3. Comparison of the concentration of Cu, Cr, Ni and Zn in soil with fertilizers (Urea and SPT) and soil without fertilizer (WF).**

In the figure 3, was observed that the highest concentrations of Cu and Ni were found in urea treatment, while for Cr and Zn the highest concentrations were presented in SPT treatment. These results are consistent with the data presented in Table 1 (introduction).

The percentage by which the respective trace metals analyzed increased with respect to the concentration measured in soil without fertilizer (WF). That is shown in Table 5.

**Table 5. Percentages of the corresponding trace metals provided by the fertilizers used with respect to the soil without fertilization.**

| Fertilizers | Metals | | | | |
|---|---|---|---|---|---|
| | Cu | Cr | Ni | Zn | Mean (%) |
| **Urea** | 12.5 | 14.6 | 20.1 | 17.5 | 16.2 |
| **SPT** | 11.2 | 59.4 | 10.2 | 20.4 | 25.3 |

The urea treatment presented a higher Ni contribution to the soil with urea treatment, while for the SPT treatment a significantly higher Cr contribution was observed compared to the rest of the elements. For both types of fertilizers, a similar contribution of Cu and Zn in the soil was observed.

The fertilizer applications considered for this projection correspond to the manufacturers
- Urea: one monthly application at 0.01%.
- SPT: one autumn, winter and spring application of 5.0 g per pot.

**Table 6. Estimation of the annual trace metal intake received by the soil from urea and SPT fertilization.**

| Fertilizer | Metals (kg/ha/year) | | | |
|---|---|---|---|---|
| | Cu | Cr | Ni | Zn |
| **Urea** | 8.53 | 1.88 | 1.19 | 10.06 |
| **SPT** | 3.81 | 3.81 | 0.30 | 5.86 |

The entry of trace metals as a result of agricultural practices shows that Zn is the element that reaches the soil to a greater extent with maximums for fertilizer hands, followed by Cu. On the other hand, the element that has the lowest annual incorporation into the soil as a result of fertilization with urea and/or SPT corresponds to Ni.

Regarding the determination of trace metals in wheat seedlings, it was found that for most of the target trace elements, their concentrations were below the detection limit, with the exception of Cu and Zn that it was possible to determine at root, for the latter in the three sections of the seedling analyzed (leaf, stem and root).

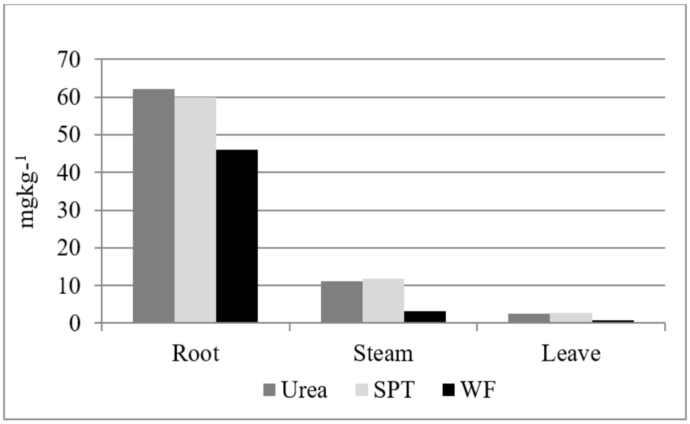

**Figure 4. Variation in Zn concentration in root, stem, and leave of wheat seedlings grown in soil treated with fertilizers (Urea, SPT) and soil without fertilizers (WF).**

For Zn, a significant increase in its concentration in stem and leave is observed for urea and SPT treatments. While urea treatment was the maximum for the root, for leaf and stem this situation is reversed and the maximum is for SPT, despite this it is evident that the difference in concentration between treatments for the three parts analyzed is very small for stem and leave and slightly higher for the root. The percentage in which the concentration of Zn increases with respect to the determination in seedlings without fertilizer is presented in Table 8. For stem and leaf, the concentration of zinc in fertilizer treatments more than doubled the concentrations measured in the unfertilized crop, while for roots it showed an increase of close to 30% for both fertilizers.

**Table 7. Percentages of Zn increase by STP and Urea treatment in different morphological parts of wheat plants**

| Zn (%) increased by fertilizer addition at soil | Root | Steam | Leave |
|---|---|---|---|
| **Urea** | 74.19 | 28.82 | 32.00 |
| **SPT** | 76.67 | 27.11 | 28.57 |

### 3.5 Bioaccumulation (FBC) and translocation (TF) factor.

In view of the background information presented in Table 7, the bioaccumulation factor could only be calculated for Cu and Zn, while the translocation factor was also calculated for the latter element. The values obtained for these indices of importance were calculated based on Equations 1 and 2, are presented in Table 8.

Considering that the values for the bioaccumulation factor for Cu and Zn are less than 1, it would be a plant species that has an exclusionary strategy with respect to these trace metals, that is, when the concentrations in soil are not extremely high, it restricts the entry of the element in question into the plant. As observed for the translocation factor with respect to Zn whose value is less than 1, there is no effectiveness in the translocation of metals to the aerial part of the plant, but it could have potential for the phytostabilization technique.

The concentration of Cu, Cr, Ni and Zn in soil with and without fertilizers in the pots after the wheat harvest was also determined; these concentrations are presented in Table 8

**Table 8. Values determined for indices in plants: bioaccumulation factor (BCF) and translocation factor (TF).**

| Soil- treatment | **FBC**- Zn | **FBC**- Cu | **TF**- Zn |
|---|---|---|---|
| **Urea** | 0.53 | 0.21 | 0.22 |
| **SPT** | 0.51 | 0.25 | 0.24 |
| **WF** | 0.46 | — | 0.02 |

### 3.6 Recommendations regarding the use of chemical fertilizers

Currently there are several ways to calculate the doses of fertilizers and amendments according to the needs of the soil and crops. The incorporation of this information allows more precise decisions to be made regarding the application of fertilization. Even if the application of chemical fertilizers is carried out in accordance with adequate diagnosis and supervision, contamination from the minority constituents of these products will not be avoided. The requirement to maintain high yields due to the intensification of crop production also involves the incorporation of greater amounts of potential pollutants [33].

On the other hand, chemical fertilizers are not the only option available to reincorporate nutrients into the soil and improve its productivity. Organic fertilizers are available in a wide variety not only on the market, but also as waste from agricultural activities. The composition of organic fertilizers such as cow or chicken manure (poultry litter), compost, and worm humus is not free of trace metal elements, as shown in Table 9, which presents the concentration of Cd, Cr, Cu, Ni, Pb, and Zn reported by various authors. Their use entails the reincorporation into the cycle of elements that have already been extracted from the soil, rather than the additional introduction of them, which is a result of the use of chemical fertilizers [34].

**Table 9. Concentration of Cd, Cr, Ni, Pb, and Ni in organic fertilizers**.

| Fertilizers | Metals (mgKg$^{-1}$) | | | | | |
|---|---|---|---|---|---|---|
| | Cd | Cr | Cu | Ni | Pb | Zn |
| Compost[1] | 0.5 | 14.4 | - | 8.71 | 5.41 | 164 |
| Compost[2] | 1.02 | - | 0.46 | 8.11 | 0.26 | - |
| Cow | 0.33 | - | 0.53 | 3.58 | 0.27 | - |
| Poultry litter | 0.34 | - | 0.46 | 1.50 | 0.24 | - |
| Humus[2] | 0.33 | - | 0.49 | 0.34 | 0.29 | - |

(1) Raven y Loeppert (1997) [23]; (2) Dueñas-Rivadeneira et al. (2022)[35]

When comparing the concentrations in Table 9 with those presented in Table 1 (Introduction), it is observed that for the mentioned organic fertilizers, the concentration of trace metals was lower than those reported for the SPT, but higher than that of urea. For this reason, it would be desirable to increase the use of these organic fertilizers, to minimize the increase of metals in agricultural soils and to avoid their possible transmission to agricultural products.

## CONCLUSIONS

The higher concentration of trace metals in the fertilizer is consistent with a greater enrichment of the soil (agricultural) by the element in question. Between the two fertilizers analyzed, SPT leads to a greater contribution of potential contaminants to the soil.

The contribution of trace metals followed the trends: Cu < Cr < Zn < Ni for urea; < Cu < Zn < Cr for the SPT. In terms of trace elements, the greatest contribution of fertilization was Cr.

The use of chemical fertilizers, particularly phosphates such as SPT, produces notable improvements in crops, such as greater root development and increased biomass of their biomass.

The decrease in the concentration of the elements studied in the soil, after the removal of the crop, demonstrates the action bioremediation of the plant used, although this is not an effective species in the translocation of metals to the aerial part of the plant.

The study presented an overview of the transfer of metals to the soil and their cultivation by two selected fertilizers, but it is necessary to extend this analysis to the wide variety of fertilizers existing in the national market. In the same way, it is necessary to study the effect of fertilization, on the concentration of trace metals, of a more diverse variety of crop.

It is advisable to conduct further in-depth studies since, although the results showed levels within the permissible limits of heavy metals, it is important to determine how the metals are bound to chemical species (organic matter and sulfides) to understand their bioavailability.

## CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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## REFERENCES

[1] Rao, S. C., Rama Gayatri, S., Venkateswarlu, B., Jakkula, V. S., Wani, S. P., Kundu, S., Sahrawat, K. L., Rajasekhara R. B. K., Marimuthu, S. and Gopala Krishna, G.,*Int. J. Environ. Sci. Technol*,(2014) DOI 10.1007/s13762-013-0350-9.

[2] Florian, G. and Jerzy, W., *Ecol. Chem. Eng.*, **19**(4-5), 353, (2012).

[3] Intawongse, M., Dean, R. J., *Trends Anal. Chem.*, **25,** 876, (2006).

[4]Liu, C., Shang, Y. and Yin, G., *Tra. Ele. Sci. Guan*., **13**, 41, (2006).

[5]Ukpabi, C. F., Akubugwo, E., Agbafor, K. N., Lebe, N. A., Nwaulari, N. J. and Nneka, E. D., *Am. J. Appl. Chem.*, **2**(4), 228, (2012).

[6] Ramadan, M. A. E. and Al-Ashkar, E. A., *Aust. J.Basic. Appl. Sci*., **1**(3), 300, (2007).

[7] Camacho Barreiro A, Ariosa Roche L. Diccionario de términos ambientales. La Habana: Centro Félix Varela. Diccionario de términos ambientales. La Habana: Centro Félix Varela; .p.45, (1998).

[8] Duffus, J. H. *Pure and Applied Chemistry*, **74**(5), 797, (2007).

[9] Kabata - Pendías A., Mukherjee A. Trace element from soil to human. Springer. New York.Abrol, I. (2007),

[10] Montenegro, G., Fredes, C., Mejías, E., Bonomelli, C., Olivares, L. *Agrociencia*, **43**(4), 427, (2009).

[11] Jomolca-Parra, Y., Lima-Cazorla, L., Manduca-Artiles, M. 2013. *Revista Cubana de Química*, **25** (3), 345, (2013).

[12 [De Gregori, I., Fuentes, E., Rojas, M., Pinochet, H., Potin-Gautier, M. 2003. *Journal of Environmental Monitoring*, **5** (2), 287, (2003).

[13] Muhammad, S.; Ullah, R.; Jadoon, I.A. *Microchemical Journal*, **149**, 103971, (2019)

[14] Méndez, J. P., Ramírez, C. A. G., Gutiérrez, A. D. R., García, F. P. *Agroecosystems*, **10** (1), 29, (2009).

[15] Angelova V., Ivanova, R., Delibaltova, V., Ivanov, K. *Industrial Crops and Products*, **19,** 197, (2004).

[16] Orozco-Corona, D., Consuelo, L., Megchún-García. Valente, J., Hernández, A. Determinación de los factores de bioconcentración, traslocación y riesgos potenciales a la salud en Capsicum annuum L. Tomo II Biotécbnología y Ciencias Agropecuarias. **Pag. 307,** (2022)

[17] IFA, (2022). Recuperado el 8 de diciembre de 2023 de Worldbank.org. https://www.worldbank.org/en/news/podcast/2022/07/22/fertilizer-volatility-and-the-food-crisis.

[18] Odepa. La urea y su comercialización en Chile. Oficina de Estudios y Políticas Agrarias. Ministerio de Agricultura, Santiago, Chile, (2012).

[19] RAPAL. Red de Acción en Plaguicidas y sus Alternativas para América Latina (RAPAL). Contaminación y eutrofización del agua. Impactos del Modelo de Agricultura Industrial. Montevideo, Uruguay, (2010).

[20] Gimeno-García, E., Andreu, V., Boluda, R. *Agraris*, **7**, (2001).

[21] Pezzarossa, B., Petruzzelli, G., Malorgio, F., Tognoni, F. *Communications in Soil Science and Plant Analysis*, **24** (17-18), 2307, (1993).

[22] Rodriguez, J., Alcalá. J.,Hernández, A.,Rodríguez, H., Ruiz, F., García, J., Díaz, P. *Revista Mexicana de Ciencias Agrícolas*, **5** (4), 695, (2014).

[23] Raven, K., Loeppert, R. *J. Environ. Qual*. **26** (2), 551, (1997).

[24] Kang, Y., Pan, W., Zeng, L., Zhang, Q., Luo J. *Sci Total Environ*., **144**, 522, (2015).

[25] Sadzawka A., Carrasco M.,Grez R., Mora M., Flores H., Nesman A. (2006), Métodos de análisis recomendados para suelos de Chile. Instituto de investigación agropecuaria. (INIA, Chile).

[26] Walkley, A. & Black I.A., *Soil Science*, **37** (1): 29, (1934).

[27] Van Reeuwijk, L. P. Procedures for soil analysis. International Soil Reference and Information Centre. Technical paper 9. Wageninger, The Netherlands., (1986).

[28] Copaja S. V..Ferrer D., *J. Chil. Chem. Soc.*, **69**, N°2 (2024)

[29] Aparicio, V. C., Barbacone, A., & Costa, J. L. *Ciencia del suelo*, **32** (1), 94, (2014).

[30]Ginés, I., Mariscal-Sancho, I. Incidencia de los fertilizantes sobre el pH del suelo (2002).

[31] MAPA. Ministerio de agricultura pesca y alimentación, España. Interpretación de análisis de suelos. hoja divulgatoria n°5/93 (1994).

[32] Porta, J., López-Acebedo, M. y Poch, R.M. "Introducción a la Edafología. Uso y protección de suelos": 192-193. Madrid. Ediciones Mundi-Prensa. 2010.

[33]Silviera, M.L.A., Alleonl, L. R .F., Ghilherme, L. R. G. *Scientia Agricola* **60** (4), 793, (2003).

[34] Molina, **M.**, Aburto, F., Calderón, R., Cazanga, M., & Escudey, M. *Soil and Sediment Contamination*, **18** (4), 497, (2009).

[35] Dueñas-Rivadeneira, J., Intriago, F., *La Técnica*, **27**, 26, (2022).