

## Cobalt and Zinc and Their Relation with Copper Contents in the Soil

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**Abstract:** The determination of trace elements in food and soil samples by atomic absorption spectrometry was investigated. The main subjective of this study was to evaluation of Effect of climatic factors on copper and its antagonist contents in the soil. In this study, during the seasons, we aimed to recording the rainfall, environmental temperature, soil temperature and humanity. In this study we collected about 72 soil samples (18 samples in each season) from different areas of Ahar city, east Azerbaijan province of Iran. Then samples were sent to the laboratory and the trace elements content of soil samples was measured by atomic absorption method. Results showed that Cu, Zn, and Co were  $2.87 \pm 0.89$ ,  $1.06 \pm 0.308$  and  $1.47 \pm 0.79$ , respectively. In conclusion can be conclude that present study is unique because there was no documented literatures about cu and its antagonist content in the soil of east Azerbaijan area. So, authors suggests that there is more study needs to conclude about this matter.

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### 1. Introduction

Cobalt is a chemical element with symbol Co and atomic number 27. It is found naturally only in chemically combined form (Wells and John, 1990). The free element, produced by reductive smelting, is a hard, lustrous, silver-gray metal. Cobalt-based blue pigments (cobalt blue) have been used since ancient times for jewelry and paints, and to impart a distinctive blue tint to glass, but the color was later thought by alchemists to be due to the known metal bismuth. Miners had long used the name kobold ore (German for goblin ore) for some of the blue-pigment producing minerals; they were named because they were poor in known metals and gave poisonous arsenic-containing fumes upon smelting. In 1735, such ores were found to be reducible to a new metal (the first discovered since ancient times), and this was ultimately named for the kobold. Today, some cobalt is produced specifically from various metallic-lustered ores, for example cobaltite (CoAsS), but the main source of the element is as a by-product of copper and nickel mining. The copper belt in the Democratic Republic of the Congo and Zambia yields most of the cobalt metal mined worldwide.

Cobalt is used in the preparation of magnetic, wear-resistant and high-strength alloys. Cobalt silicate and cobalt(II) aluminate (CoAl<sub>2</sub>O<sub>4</sub>, cobalt blue) give a distinctive deep blue color to glass, smalt, ceramics, inks, paints and varnishes. Cobalt occurs naturally as only one stable isotope, cobalt-59. Cobalt-60 is a commercially important radioisotope, used as a radioactive tracer and in the production of gamma rays.

Cobalt is the active center of coenzymes called cobalamins, the most common example of which is

vitamin B<sub>12</sub>. As such it is an essential trace dietary mineral for all animals. Cobalt in inorganic form is also an active nutrient for bacteria, algae and fungi.

Cobalt is essential to all animals. It is a key constituent of cobalamin, also known as vitamin B<sub>12</sub>, which is the primary biological reservoir of cobalt as an "ultratrace" element. Bacteria in the guts of ruminant animals convert cobalt salts into vitamin B<sub>12</sub>, a compound which can only be produced by bacteria or archaea. The minimum presence of cobalt in soils therefore markedly improves the health of grazing animals, and an uptake of 0.20 mg/kg a day is recommended for them, as they can obtain vitamin B<sub>12</sub> in no other way (Schwarz et al., 2000). In the early 20<sup>th</sup> century during the development for farming of the North Island Volcanic Plateau of New Zealand, cattle suffered from what was termed "bush sickness". It was discovered that the volcanic soils lacked cobalt salts, which was necessary for cattle. The ailment was cured by adding small amounts of cobalt to fertilizers.

Non-ruminant herbivores produce vitamin B<sub>12</sub> from bacteria in their colons which again make the vitamin from simple cobalt salts. However the vitamin cannot be absorbed from the colon, and thus non-ruminants must ingest feces to obtain the nutrient. Animals that do not follow these methods of getting vitamin B<sub>12</sub> from their own gastrointestinal bacteria or that of other animals, must obtain the vitamin pre-made in other animal products in their diet, and they cannot benefit from ingesting simple cobalt salts.

The cobalamin-based proteins use corrin to hold the cobalt. Coenzyme B<sub>12</sub> features a reactive C-Co bond, which participates in its reactions (Voet et al., 1995). In humans, B<sub>12</sub> exists with two types of alkyl

ligand: methyl and adenosyl. MeB<sub>12</sub> promotes methyl (-CH<sub>3</sub>) group transfers. The adenosyl version of B<sub>12</sub> catalyzes rearrangements in which a hydrogen atom is directly transferred between two adjacent atoms with concomitant exchange of the second substituent, X, which may be a carbon atom with substituents, an oxygen atom of an alcohol, or an amine. Methylmalonyl coenzyme A mutase (MUT) converts MML-CoA to Su-CoA, an important step in the extraction of energy from proteins and fats (Smith et al., 1999).

Although far less common than other metalloproteins (e.g. those of zinc and iron), cobaltoproteins are known aside from B<sub>12</sub>. These proteins include methionine aminopeptidase 2 an enzyme that occurs in humans and other mammals which does not use the corrin ring of B<sub>12</sub>, but binds cobalt directly. Another non-corrin cobalt enzyme is nitrile hydratase, an enzyme in bacteria that are able to metabolize nitriles (Kobayashi et al., 1999).

Copper proteins have diverse roles in biological electron transport and oxygen transportation, processes that exploit the easy interconversion of Cu(I) and Cu(II) (Lippard and Berg, 1994). The biological role for copper commenced with the appearance of oxygen in earth's atmosphere (Decker and Terwilliger, 2000). The protein hemocyanin is the oxygen carrier in most mollusks and some arthropods such as the horseshoe crab (*Limulus polyphemus*) (Decker and Terwilliger, 2000). Because hemocyanin is blue, these organisms have blue blood, not the red blood found in organisms that rely on hemoglobin for this purpose. Structurally related to hemocyanin are the laccases and tyrosinases. Instead of reversibly binding oxygen, these proteins hydroxylate substrates, illustrated by their role in the formation of lacquers (Lippard and Berg, 1994).

Copper is also a component of other proteins associated with the processing of oxygen. In cytochrome c oxidase, which is required for aerobic respiration, copper and iron cooperate in the reduction of oxygen. Copper is also found in many superoxide dismutases, proteins that catalyze the decomposition of superoxides, by converting it (by disproportionation) to oxygen and hydrogen peroxide.

Several copper proteins, such as the "blue copper proteins", do not interact directly with substrates, hence they are not enzymes. These proteins relay electrons by the process called electron transfer (Lippard and Berg, 1994).

Zinc is an essential trace element, necessary for plants (Broadley et al., 2007), animals (Prasad, 2008), and microorganisms (Sugarman, 1983). Zinc is found in nearly 100 specific enzymes (other sources say 300), serves as structural ions in transcription factors and is stored and transferred in metallothioneins. It is "typically the second most abundant transition metal in

organisms" after iron and it is the only metal which appears in all enzyme classes (Broadley et al., 2007).

In proteins, Zn ions are often coordinated to the amino acid side chains of aspartic acid, glutamic acid, cysteine and histidine. The theoretical and computational description of this zinc binding in proteins (as well as that of other transition metals) is difficult (Brandt et al., 2009).

There are 2-4 grams of zinc (Rink and Gabriel, 2000) distributed throughout the human body. Most zinc is in the brain, muscle, bones, kidney, and liver, with the highest concentrations in the prostate and parts of the eye (Wapnir and Raul, 1990). Semen is particularly rich in zinc, which is a key factor in prostate gland function and reproductive organ growth (Berdanier et al., 2007).

In humans, zinc plays "ubiquitous biological roles" (Hambidge and Krebs, 2007). It interacts with "a wide range of organic ligands" (Hambidge and Krebs, 2007) and has roles in the metabolism of RNA and DNA, signal transduction, and gene expression. It also regulates apoptosis. A 2006 study estimated that about 10% of human proteins (2800) potentially bind zinc, in addition to hundreds which transport and traffic zinc; a similar *in silico* study in the plant *Arabidopsis thaliana* found 2367 zinc-related proteins (Broadley et al., 2007).

In the brain, zinc is stored in specific synaptic vesicles by glutamatergic neurons (Bitanirwe and Cunningham, 2009) and can "modulate brain excitability" (Hambidge and Krebs, 2007). It plays a key role in synaptic plasticity and so in learning (Nakashima and Dyck, 2009). However it has been called "the brain's dark horse" (Bitanirwe and Cunningham, 2009) since it also can be a neurotoxin, suggesting zinc homeostasis plays a critical role in normal functioning of the brain and central nervous system.

The main subjective of this study was to evaluation of cobalt and Zn and their relation with copper contents in the soil.

## 2. Materials and methods

Present research was descriptive – analytical types of studies. In this study, during the seasons, we aimed to recording the rainfall, environmental temperature, soil temperature and humidity. In this study we collected about 72 soil samples (18 samples in each season) from different areas of Ahar city, east Azerbaijan province of Iran. Then samples were sent to the laboratory and the trace elements content of soil samples was measured by atomic absorption method. Data was analyzed by SPSS software.

## 3. Results

Data related to the Cu content of soil and its antagonists are shown in the table 1.

**Table 1:** trace element content of soil samples in summer

Cu (PPM)	Zn (PPM)	Co (PPM)
2.87±0.89	1.06±0.308	1.47±0.79

Data related to seasonally rainfall, temperature, humidity are showed in table 2.

**Table 2:** the mean value of rainfall, temperature and humidity obtained from weather station in summer

Season	July	August	September
Rainfall (mm)	3.5	1.8	4.5
Environ. Tem. (°C)	22.4	23.1	17.5
Humidity (%)	52	54	65
Soil tem. (°C)	28.3	28.9	24.5

#### 4. Discussion and conclusion

There has been a rapid increase in the levels of environmental pollution over recent decades. Trace elements have an important place among the main pollutants. Accurate determination of trace elements is critical in various fields of science and technology (Tuzen, 2009; Tuzen, 2003). Despite recent rapid advances in technology, separation and preconcentration methods prior to the quantitative determination of trace elements is still often necessary (Soylak and Turkoglu, 1999; Panahi et al., 2010). Direct measurement of trace elements in samples with complex matrixes is often impractical due to either analytical sensitivity limitations or interferences of the matrix. In many techniques the preconcentration step not only increases the concentration of the species of interest, but also eliminates part or all of the interferences (Alfassi and Wai, 1992; Marahel et al., 2011). The copper levels of soil and pastures in most parts of the country are unknown. Copper bioavailability can be low in ruminant diets, especially when molybdenum, sulfur and (or) iron are presented in moderate to high concentrations (Humphries et al., 1983; Suttle et al., 1984; Ward et al., 1993). Therefore determination of copper in the diet or pasture has no diagnostic value in ruminants unless other elements which interact with copper are determined (Underwood and Suttle, 1999).

Narendrula et al., 2012 showed that the level of cobalt observed in Etoile mining area was 20 fold higher than in samples from Penga Penga site in Lubumbashi. These values were 200 fold higher than the contaminated sites from the Greater Sudbury Region in Canada. The levels of cobalt in samples from control sites in DR-Congo were significantly lower than Etoile and Penga Penga mining sites, but similar or higher than the levels detected in contaminated sites from the Sudbury Region. These values were lower than the OMEE guideline limit for cobalt of 50 mg kg<sup>-1</sup>.

Kim et al., 2008 reported a positive but weak interaction between Cu and Zn suggested by regression analysis indicates the toxicity of Cu-Zn mixtures to soil urease is slightly less than additive (antagonistic). They indicated that Copper extractability using CaCl<sub>2</sub> was able to predict urease activity in only one of the tested soils. By contrast, measurements of Cu<sup>2+</sup> activity were predictive of reduced urease activity in both soils (R<sub>2adj</sub> = 0.726, p < 0.0001), indicating that Cu<sup>2+</sup> activity is a more useful predictor of urease inhibition in soils than CaCl<sub>2</sub>-extractable Cu. The present study also highlighted the importance that clay mineral content had on controlling the availability of added metals in soils over time since a greater aging effect on Cu toxicity was found for the fine-textured Hudson than the coarse-textured Arkport soil.

Zn is one of the essential elements for plants and humans, but it is deficient (less than 1.00 mg kg<sup>-1</sup> DTPA extractable Zn) in most calcareous soils and, consequently, in plant and human diets. The critical level for DTPA-extractable Zn is 0.8 mg kg<sup>-1</sup> soil (James and Topper, 1993). Sturgul (2010) reported that the optimum Zn soil test ranges are 3.1 to 20 mg kg<sup>-1</sup> for all soil textures. The need for supplemental Zn applications should be confirmed with plant analysis, in that scalped or severely eroded soils are more apt to be Zn deficient. Also, sands, sandy loams and organic soils are more likely to be Zn deficient than other soil types. Severe soil compaction can also reduce Zn availability. In addition, cool weather during the growing season may also induce Zn deficiency in high demand crops.

The available Fe, Zn, Cu and B in the soil were lower than the critical level, but the available Mn was above the critical level. The soil of this research was calcareous with alkaline pH; therefore, available Zn and B were low. The critical levels of Fe, Zn and B have been determined by many scholars. Rezaei and Malakouti (2001) reported that critical levels of Fe, Zn and B in soils of Iran were 4.8, 1.1 and 1.0 mg kg<sup>-1</sup> soil, respectively. Johnson and Fixen (1990) stated that the critical levels of Fe, Zn, Cu and Mn by the DTPA extraction method and B by the hot water in the soil method were 5.0, 1.5, 0.5, 1.0 and 1.0, respectively. The actual total Fe content of a soil may exceed 50,000 mg kg<sup>-1</sup>; however, the portion available to plants may be less than 5 mg kg<sup>-1</sup> (Hodges, 2010). Page et al. (1982) classified Fe and Zn as: 0-5 mg kg<sup>-1</sup> (very low), 6 to 10 mg kg<sup>-1</sup> (low) and 11 to 16 mg kg<sup>-1</sup> (medium) for Fe, and 0.0 to 0.5 mg kg<sup>-1</sup> (very low), 0.6 to 1.0 mg kg<sup>-1</sup> (low), 1.1 to 3.0 mg kg<sup>-1</sup> (medium) and >3.0 mg kg<sup>-1</sup> (high) for Zn.

Finally, can be conclude that present study is unique because there was no documented literatures about Cu and its antagonist content in the soil of east

Azerbaijan area. So, authors suggests that there is more study needs to conclude about this matter.

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