

Evaluation of soil elements such as Cu, Fe and Mo and their relation with Ahar climateKarim Amininia^{1*}, Amirparviz Rezaeisaber², Ali Rezaie²

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Abstract: Micronutrient problems are expected to increase in the future because of the increase in cropping intensity, the use of high-yielding varieties and the more extensive use of nitrogen, phosphorus and potassium fertilizers. The main subjective of this study was to evaluation of Fe and Mo and their relation with copper 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, Fe and Mo were 2.73 ± 0.79 , 7.42 ± 0.92 and 2.21 ± 0.97 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

The most important role of the molybdenum in living organisms is as a metal heteroatom at the active site in certain enzymes. In nitrogen fixation in certain bacteria, the nitrogenase enzyme, which is involved in the terminal step of reducing molecular nitrogen, usually contains molybdenum in the active site (though replacement of Mo with iron or vanadium is also known). The structure of the catalytic center of the enzyme is similar to that in iron-sulfur proteins: it incorporates a Fe_4S_3 and multiple MoFe_3S_3 clusters (Santos et al., 2008).

In 2008, evidence was reported that a scarcity of molybdenum in the Earth's early oceans was a limiting factor for nearly two billion years in the further evolution of eukaryotic life (which includes all plants and animals) as eukaryotes cannot fix nitrogen, and must therefore acquire most of their oxidized nitrogen suitable for making organic nitrogen compounds, or the organics themselves (like proteins) from prokaryotic bacteria (Scott et al., 2008). The scarcity of molybdenum resulted from the relative lack of oxygen in the early ocean. Most molybdenum compounds have low solubility in water, but the molybdate ion MoO_4^{2-} is soluble and forms when molybdenum-containing minerals are in contact with oxygen and water. Once oxygen made by early life appeared in seawater, it helped dissolve molybdenum into soluble molybdate from minerals on the sea bottom, making it available for the first time to nitrogen-fixing bacteria, and allowing them to

provide more fixed usable nitrogen compounds for higher forms of life (Mendel and Bittner, 2006).

The molybdenum cofactor (pictured) is composed of a molybdenum-free organic complex called molybdopterin, which has bound an oxidized molybdenum atom through adjacent sulfur (or occasionally selenium) atoms.

Although oxygen once promoted nitrogen fixation via making molybdenum available in water, it also directly poisons nitrogenase enzymes. Thus, in Earth's ancient history, after oxygen arrived in large quantities in Earth's air and water, organisms that continued to fix nitrogen in aerobic conditions were required to isolate and protect their nitrogen-fixing enzymes in heterocysts, or similar structures which protect them from too much oxygen. This structural isolation of nitrogen fixation reactions from oxygen in aerobic organisms continues to the present (Enemark et al., 2004).

Though molybdenum forms compounds with various organic molecules, including carbohydrates and amino acids, it is transported throughout the human body as MoO_4^{2-} (Mitchell and Phillip, 2003). At least 50 molybdenum-containing enzymes were known by 2002, mostly in bacteria, and their number is increasing with every year (Mendel and Bittner, 2006; Enemark et al., 2004); those enzymes include aldehyde oxidase, sulfite oxidase and xanthine oxidase (Fischer et al., 1998). In some animals, and in humans, the oxidation of xanthine to uric acid, a process of purine catabolism, is catalyzed by xanthine oxidase, a molybdenum-containing enzyme.

The activity of xanthine oxidase is directly proportional to the amount of molybdenum in the body. However, an extremely high concentration of molybdenum reverses the trend and can act as an inhibitor in both purine catabolism and other processes. Molybdenum concentrations also affect protein synthesis, metabolism and growth (Mitchell and Phillip, 2003).

In animals and plants a tricyclic compound called molybdopterin (which, despite the name, contains no molybdenum) is reacted with molybdate to form a complete molybdenum-containing cofactor called molybdenum cofactor. Save for the phylogenetically-ancient molybdenum nitrogenases discussed above which fix nitrogen in some bacteria and cyanobacteria, all molybdenum-using enzymes so far identified in nature use the molybdenum cofactor (Fischer et al., 1998). Molybdenum enzymes in plants and animals catalyze the oxidation and sometimes reduction of certain small molecules, as part of the regulation of nitrogen, sulfur and carbon cycles (Kisker 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).

Iron is abundant in biology. Iron-proteins are found in all living organisms, ranging from the

evolutionarily primitive archaea to humans. The color of blood is due to the hemoglobin, an iron-containing protein (McKetta and John, 1989). As illustrated by hemoglobin, iron often is bound to cofactors, e.g. in hemes. The iron-sulfur clusters are pervasive and include nitrogenase, the enzymes responsible for biological nitrogen fixation. Influential theories of evolution have invoked a role for iron sulfides in the iron-sulfur world theory (Wildermuth et al., 2000).

Iron is a necessary trace element found in nearly all living organisms. Iron-containing enzymes and proteins, often containing heme prosthetic groups, participate in many biological oxidations and in transport. Examples of proteins found in higher organisms include hemoglobin, cytochrome (see high-valent iron), and catalase (Lippard and Berg, 1994). The main subjective of this study was to evaluation of Fe and Mo 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 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. Data was analyzed by SPSS software.

3. Results

Data related to the 5 area are showed in the table 1.

Table 1: trace element content of soil samples in summer

Cu (PPM)	Fe (PPM)	Mo (PPM)
2.73±0.79	7.42±0.92	2.21±0.97

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

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

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

4. Discussion and conclusion

The widespread occurrence of micronutrient problems was shown for first time by the results of a survey conducted by Schutte (1954), who concluded from his study that soils in Africa, in general, have a low micronutrient status. Kang and Osiname (1972) in a review on micronutrient investigation stated that B, Mo and Zn problems were more prevalent and more economic important and suggested that better understanding of the contents and distribution of trace elements in the soils is necessary. Micronutrient problems are expected to increase in the future because of the increase in cropping intensity, the use of high-yielding varieties and the more extensive use of nitrogen, phosphorus and potassium fertilizers. A great effort should therefore be made to conduct systematic micronutrient investigation in the areas, particularly in the drier areas. Because, micronutrient problems, which today are considered only local, may become more serious in future, spreading extensively over new areas and creating complicated production restrictions if they are not properly studied and controlled on time. Liu et al. (1991) stated that in agriculture, fertilization with trace elements on deficient soils had proved to be a simple, convenient and economic measure to increase the yield. In Ethiopia the past, few, investigations (Sillanpaa, 1982; Fekadu, 1987; Godfrey et al., 1987; Saleh et al., 1990) were either incidental or exploratory in nature, which made it difficult to obtain a real assessment of magnitude of micronutrient problems. Due to these factors, there is very little information available in Iran about micronutrient levels in soils.

From the frequency distribution and referring to the critical level (4.8 mg kg⁻¹) according to Lindsay and Norvell (1978) and Halvin and Soltanpour (1981), most of the extractable Fe samples were in sufficient range.

From the frequency distribution and referring to the critical level (0.5-0.6 mg kg⁻¹) reported by Makarim and Cox (1983), the amounts of extractable Cu from soil samples were in deficient ranges.

From the frequency distribution and referring to the critical level (0.1-0.5 mg kg⁻¹) according to Grigg (1953), the amounts of extractable Mo in all of the samples were in the sufficient range.

The greenhouse experiment therefore suggested that the critical level might be at 4.56 mg Fe kg⁻¹ or lower in Andisols. Omission of Fe in soil resulted in significant depressive effects in plant height at all observed stages and in Fe uptake by maize and showed a non-significant trend of decrease in dry matter yield of maize. But the laboratory assessment indicated that extractable Fe in this soil was above the critical level. The greenhouse experiment showed

that the critical level was above 5.20 mg Fe kg⁻¹. These results did not therefore support the critical level of Lindsay and Norvell (1978) and Halvin and Soltanpour (1981). These might be due to differences in properties of the soils or plant species used. In that experiment revealed that omission of Cu application to soil resulted in significant decreases in plant height at 30 and 45 days after landing and in uptake of Cu by maize while showed non-significant trends of decrease in height at 50% silking and in dry matter yields. Basing on the critical levels reported by Makarim and Cox (1983). The greenhouse experiment also showed mostly responses to application of Cu fertilizer.

They also showed that the omission of Mo in soil resulted in significant negative response in plant height at 50% silking stage and showed non-significant negative responses in the other parameters (Baissa et al., 2005). 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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