Concentration of Some Micronutrient Heavy Metals in Selected Commonly-used Fertilizers in Saudi Arabia

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Abstract—A wide range of fertilizers are used in Saudi Arabia. Most fertilizers producing companies only mention the main components on the pack of their product. In this study, 24 industrial fertilizer samples, collected from the Saudi market, were elementally analyzed for assessment of Mn, Fe, Co, Ni, Cu, and Zn concentrations. The samples were analyzed using NAA technique. The results obtained have shown acceptable balance in the antagonistic elements Mn, Fe, Cu and Zn, for most of the 24 fertilizer samples. The concentrations of the studied heavy metals in the samples were generally in the accepted ranges. The Ni concentration in sample 12L was relatively high. The results indicate the necessity for periodic monitoring of soils heavy metals compositions, particularly in case of long-term fertilization.

Keywords—fertilizer, heavy metals, toxicity, antagonistic elements.

I. INTRODUCTION

Fertilizers have a significant importance in our life because of their strong relation to our daily food. Fertilizers, organic or inorganic, are used to enrich soil so as to provide certain elements to promote or enhance plant growth and appearance. Many plants require about 16 elements, for normal growth and for completion of their life cycle. These elements are called the essential plant nutrients. Some of these elements are considered as macronutrients, e.g. nitrogen (N), phosphorus (P), and potassium (K), and some are considered as micronutrients, e.g. manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), and zinc (Zn). Some soils do not contain sufficient amounts of these nutrients to meet plant's requirements for rapid growth and good production. In such cases, supplemental micronutrient applications in the form of commercial fertilizers must be made. Micronutrients are defined as those elements required in small quantities for higher plant growth and reproduction [1]-[3].

Most fertilizers (NPK fertilizers) are usually composed of the primary elements for plants, which are one or more of the major three elements, N, P and K. These elements are crucial elements that have to be added to most fertilizers in considerable quantities in the form of a suitable compound. These compounds are usually labeled on the package of fertilizers with 3 numbers, e.g., 10-10-15, meaning 10% N, 10% P (as P₂O₅) and 15% K (as K₂O) [4].

Some fertilizers also contain various concentrations of heavy and trace elements that are potentially harmful for human health and environment.

Heavy metals are those metals and semimetals with potential human or environmental toxicity. Elements, lead (Pb), mercury (Hg), and cadmium (Cd) are prime examples of heavy metals or “toxic metals”.

Heavy metals occur naturally in all soils in minute quantities, but can accumulate in agricultural soils from various sources, such as fertilizers, organic supplements, atmospheric deposition and urban and industrial activities. Accumulation of heavy metals in soil has potential to restrict the soil function, cause toxicity to plants, and contaminate the food chain.

In some countries, industrial waste materials are used in commercial fertilizers as a mean of waste products recycling. The industrial wastes often poison the soil and can introduce heavy metals or toxic chemicals into the food chain [5]. Lack of knowledge of the proper use of fertilizers can lead to significant damage to the plants and human health, because of potential diverse effects of excess concentrations of some elements. Therefore, it is of great importance to know the concentration of each component of a fertilizer.

Although some heavy metals are essential micronutrients, their uptake in excess to the plant requirements result in toxic effects [6], [7]. Manganese (Mn), for example, is a trace element, which is important in the human diet, but accumulation of excessive manganese in leaves of plants causes a reduction of photosynthetic rate, and accumulation of a high level of H₂O₂ [6], [8], [9]. Iron (Fe) is an essential element in many metabolic processes, and is indispensable for all organisms. It is a component of heme-containing protein such as hemoglobin. On the other hand, it has been reported that iron excess, and hence toxicity, has led to inhibition of photosynthesis, which in turn induces drastic decrease in plant growth [6], [10]-[12]. Cobalt (Co) complex is found in the form of vitamin B12. Although very little information is available regarding the toxicity effect of excess Co, it has been reported [13] that high levels of Co affected the translocation of P, Mn, Zn and Cu from roots to tops in cauliflower. Nickel (Ni) is recognized as another essential micronutrient for living organisms. Excess of Ni²⁺ in soil causes various physiological
alterations and diverse toxicity symptoms. Plants grown in high-Ni	2- containing soil showed impairment of nutrient balance and resulted in disorder of cell membrane functions [14]-[17]. It is known that high Ni concentrations on sandy soils can clearly damage plants. Copper (Cu) is also considered as a micronutrient for plants, and as a trace element, which is important in the human diet [8]. Cu is concentrated in roots of plants and plays a part in nitrogen metabolism [6], [9], [18]. Zink (Zn) is also important for several enzymatic reactions in the human body. It may serve as cofactor and activators of enzyme reactions [19]. Plants often have a zinc uptake that their systems cannot handle, due to the accumulation of zinc in soils. On zinc-rich soils only a limited number of plants has a chance of survival. That is why there is not much plant diversity near zinc-disposing factories [20].

Since 1964, researchers believe that some of the phosphate fertilizers, manufactured from phosphate rocks, are sources of some heavy elements in soils and thus in plants [21]-[23].

Most of producing companies of the studied fertilizers only mention the main components, on package of their product (e.g. NPK as three bold numbers). They mention other elements as "other additives" or "other impurities". Some elements are antagonists, so that one blocks the toxic effect of the other. This makes identifying relations between soil and some diseases difficult [24]. Micronutrients Mn, Fe, Cu and Zn are important for human and plant health, but because they are antagonists, they need to be in balance in fertilizers to avoid a serious deficit of one or more [2], [24], [25].

In the Kingdom of Saudi Arabia, verity of local and imported fertilizers are used. Various, but not many, studies have been conducted on different types of fertilizers in the Kingdom to determine the heavy elements composition of these fertilizers.

Modaihsh et al. [26], for example, have elementally analyzed 74 different types of fertilizers, used in Saudi Arabia, for heavy metals Pb, Cd, Ni, Co, and Cr. They have concluded that the average heavy metal contents of the studied fertilizers were within the limits of those used worldwide, and their use is not expected to be harmful with regards to heavy metals pollution.

In more recent studies, El-Taher et al. [27] have analyzed 30 different phosphate and organic fertilizers used in Saudi Arabia. They have determined the natural radioactivity in addition to the same heavy metals analyzed by Modaihsh et al. [26], and reported the same conclusion. Farooq et al. [28] have analyzed only one di-ammonium phosphate (DAP) fertilizer sample and determined many elements in that sample and reported high levels of Cd, Ni and Pb, which might be harmful to health if large quantity of the fertilizer is used.

In the present study, 24 samples of local and imported industrial fertilizers, collected from the Saudi market, were elementally analyzed. The aim of the study was to assess concentrations of Mn, Fe, Cu, and Zn in the multi-nutrient fertilizers, as these elements are antagonistic to each others, and also to assess concentrations of Co and Ni in the studied fertilizers, as high concentrations of these two heavy metals are considered harmful compared to the others under study.

II. EXPERIMENTAL

Some details of the fertilizers, as indicated by their manufacturers, are given in Table 1. The samples were analyzed using Neutron Activation Analysis (NAA) technique. The fertilizers samples were irradiated using the NETL 1.1 MW Triga Mark II reactor at the University of Texas, Austin, USA. The irradiation was performed using thermal neutron flux of \(1.4 \times 10^{12} \text{n cm}^{-2} \text{s}^{-1}\).

The samples were analyzed as-received. Neither chemical treatment nor addition of reagent was required to prepare the samples for analysis, thus, contamination from excess sample handling and reagent addition is eliminated.

Two portions of each sample was placed in a pre-cleaned polyethylene vial and sealed. The irradiation time, decay time (time between irradiation and counting), and counting time, are functions of the element to be measured, and can be optimized to maximize the induced activity and minimize interference from other elements. Therefore, portions of the samples were then irradiated for enough times for different half life isotopes.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>NPK (%)</th>
<th>Other additives (TE)</th>
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<tbody>
<tr>
<td>Sample</td>
<td>N</td>
<td>P</td>
</tr>
<tr>
<td>1A</td>
<td>11</td>
<td>52</td>
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<tr>
<td>2B</td>
<td>11</td>
<td>29</td>
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<tr>
<td>3C</td>
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<td>4D</td>
<td>14</td>
<td>38</td>
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<td>5E</td>
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<tr>
<td>6F</td>
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<td>7G</td>
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<td>8H</td>
<td>12</td>
<td>48</td>
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<tr>
<td>9I</td>
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<tr>
<td>24Z</td>
<td>10</td>
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</table>
The irradiated samples were allowed to decay, before performing the activity counting, for periods of time varied from few minutes, for the short-lived isotopes, to about 40 days, for the long-lived ones. The irradiated samples were then counted using a high-purity germanium (HPGe) detector.

III. RESULTS AND DISCUSSION

Concentrations of Mn, Fe, Co, Ni, Cu, and Zn in the studied fertilizers are shown in Fig.1 and Fig. 2. As expected, insignificant concentrations of heavy metals were found in samples 3C, 9I and 22X. Sample 3C is a local urea fertilizer (nitrogenous fertilizer), whereas 9I is an Epsom salts (magnesium sulphate) fertilizer, and 22X is a potassium salt fertilizer.

The other samples, which are either NPK or multi-nutrients fertilizers, were found to contain different concentrations of the studied heavy metals. Sample 18T is an exception. It is an imported mono-ammonium phosphate (MAP) NP fertilizer. No concentrations of any heavy metal were found in this sample, which may indicate the purity of the fertilizer. In the rest of samples, the Fe concentrations were the highest, ranging from 75 mg/kg (sample 21W) to 4698 mg/kg (sample 13M) for the NPK fertilizers, and from 28231 mg/kg (sample 7G) to 64318 mg/kg (sample 15P), for the multi-nutrients fertilizers.

![Fig. 1 Concentrations of Mn, Fe, Cu and Zn in the fertilizer samples.](image1)

![Fig. 2 Concentrations of Co and Ni in the fertilizer samples.](image2)

Sample 15P, which contain the highest Fe concentration, is an imported fertilizer intended to treat iron deficiency. The actual total iron content of a soil may exceed 50,000 mg/kg, however the portion available to plants may be less than 5 mg/kg [2].

Elements with a similar structure in the arrangement of their electrons, such as Fe, Cu and Zn, tend to be biological antagonists [24]. On the other hand, Mn has an antagonistic interaction with Fe. As Mn concentrations in plant tissues increase, Fe concentrations generally decrease, and vise versa. The ratio of Fe to Mn in most growing medium is maintained between 1.5 and 2.5 to maintain plant health [2]. Hence, Mn, Fe, Cu and Zn need to be in balance to avoid a serious deficit of one or more, for the multi-nutrition fertilizers. In the samples of fertilizers which are intended to plant multiple nutrition feeding, the results have shown (Fig. 1) that the adverse impact of the antagonistic elements on each others may have been taken into account by the manufacturers.

Sample 11K is an imported NPK fertilizer which is supposed to contain Cu among other additives (Table 1), but the results have shown that no Cu is present in this sample.

Some countries have set tolerance limits for some heavy metal additions to soil [20], [29], [30]. Presently, there are no regulations in Saudi Arabia governing maximum permissible concentrations of heavy metals in fertilizers [26].

The highest concentration for Co (43.1 mg/kg ) was found in sample 10J. Although cobalt is not considered as hazardous pollutants, some countries and organizations,
have set a safe limit for cobalt in agricultural soils, which ranges between 20 and 50 mg/kg [30].

The sample 12L, which is an imported multi-nutrient fertilizer, has shown a very high concentration of Ni (335 mg/kg) compared with the suggested limit of 75 mg/kg, by the European Union [31]. It is known that high Ni concentrations on sandy soils can clearly damage plants [8].

IV. CONCLUSION

As a conclusion, the heavy elements concentrations fertilizers samples obtained in the present study, are generally accepted, except for sample 12L. Mn, Fe, Cu and Zn concentrations, in most of the multi-nutrients fertilizers, were in balance which is acceptable for limiting adverse antagonistic effect of these elements on each others.

The high concentration of Ni found in sample 12L can be harmful if large quantity of this fertilizer is used. Long term use of considerable quantities of the studied fertilizers is expected to cause high accumulation of heavy metals in soils. This increases the need for periodic monitoring of heavy metals composition of the soils, as sources of contamination.

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REFERENCES