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Detection the Contents of Minerals of (Sodium, Potassium and Calcium) and Some Metals of (Iron, Nickel and Copper) in some vegetable and soil samples collected from Al-Marj Region, Libya

[1] Wesam FA Mohamed, [2] Hamad M Adess Hasan, [3] Enam F Mohammed

[1] Faculty of Education, Omar Al-Mukhtar University, Al Bayda', Libya

[2] Department of Chemistry, Faculty of Science Omar AL-Mukhtar University, Al Bayda', Libya

[3] Department of Chemistry, Faculty of Education, Al-Marj, Benghazi University, Al Bayda', Libya

Corresponding Author: **Wesam FA Mohamed**

Abstract

The contents of minerals of Sodium, Potassium and Calcium) and some metals of (Iron, Nickel and Copper) in some vegetable samples collected from Al-Marj Region, Libya, were measured, the contents of minerals were determined by Flam photometer. On the other hand, the contents of heavy metals were estimated by rapid, sensitive and accurate method by Spectrophotometer, the results recorded that: the contents of minerals were fluctuated in the ranges of the results showed that the concentrations of Na of soil samples were ranged between (11-24),while the concentrations of Ca were ranged between (4-11) ppm and the concentrations of K were ranged between (18-27) ppm. For the vegetable samples, the results showed that the concentrations of sodium, calcium and potassium were ranged as following: (13-54), (4-17) and (27-69) ppm, respectively, the contents of heavy metals in soils which selected in this study were fluctuated in the following ranges: (0.012-0.033), (0.560-1.207) and (0.057-0.219) ppm. For the metals of (Copper, Iron and Nickel), respectively. While in the vegetable samples were ranged as following: (0.002-0.037), (0.007-0.060) and (0.009-0.027) ppm for (copper, iron, and Nickel), respectively, the concentrations of copper (Cu) iron (Fe), Nickel (Ni) and Nitrogen (N) of the studied samples (µg/g).

Keywords: Minerals, Flam photometer, Libya

Introduction

Scholars have different opinions about the definition of heavy metals and the criteria for their classification depending on the scientific field, while biologists believe that the density of an element is not a primary criterion in classification of heavy metals, while chemists and environmental scientists consider the density of the element one of the most important criteria for determining heavy metals, and on the basis of which the chemical elements are classified into light with a density less than 4g/cm^3 and heavy with a density more than 5 g/cm^3. Some believe that the density of the chemical element must to exceed 7g/cm^3 to be classified as a heavy element, and some depend on the atomic weight and atomic number of the chemical element or on the toxicity of the element and its ability to accumulate in living bodies as criteria for classifying heavy metals (Duffus, 2002) [5]. According to Victoria (2015) [23] heavy metals are defined as chemical elements with a specific density of more than 5 g/cm3 that are present in the soil in an ionized state or in the form of complexes that exist in the environment naturally and in low concentrations, some of which are included in the nutritional needs of the plant, but in low quantities and the most important are (Zn, Fe, Co, Ni, Cu) (Mudgal *et al*., 2010) [13]. Some of heavy metals which determined in this study and their importance were described as following:

Iron:

It is an essential trace metal. A very small amount of Fe is required for cellular functions of body; Iron is a major constituent of hemoglobin in red blood cells which transport oxygen to the body cells. Men and Women of all the age groups require Fe at various amount, Post-menopausal women and men require 8mg/day, Women with Pre-menopausal stage Require 18mg/day, Pregnant Women Require 127mg/day and a child about six require 11 mg/day. The deficiency of Fe cause Anima shortness of breath at night and spoon shaped nails, its high dose decrease the absorption of Zn and cause liver cancer and heart disease (Das *et al*., 2008) [3].

Copper:

It is a vital trace heavy metal. Copper is required for the production of energy in cells. It approximately makes 9 gram of body weight; it is found in enzymes involve in oxygen reactions. Copper is involved in metabolism of estrogenic which is required for Women's fertility to maintain pregnancy, deficiency of copper effect thyroid function, central nervous system (CNS) disorder & hair abnormalities. Toxicity of Cu causes deficiency of Hemoglobin, erythrocytes level, cancer and death (Das *et al.*, 2008) [3].

Nickel:

It is a trace heavy metal and present in many enzymes in microorganisms, Plants and humans. It plays important role in physiological processes, it acts as a co-factor in Iron absorption from intestine. It also involves in immune system, excess of Ni cause decrease in body weight, increased heart and decreased liver weight. Heavy metals in the soil pose a great and harmful danger to the environment and life, when heavy metals are present in the ecosystem above certain levels that vary according to the type of metal, the nature of the soil and the type of organism affected by these minerals (Duffus, 2002) [5]. It is transmitted to humans through food chains, causing Chronic diseases such as respiratory and heart diseases, some nervous system diseases, and cancers (Triassi *et al.*, 2015) [20].

However, long term storage of some toxic metals takes place in hard tissues such as teeth and bones. Additionally, samples of keratinous tissue components such as hair and nails are commonly used for routine clinical screening and diagnosis of longer-term exposure of metals (Janssen, 1997) [9]. Progress in the fields of genomics and proteomics is also reported, and more recent attention is focused on proteomics technologies involved in finding new and relevant biomarkers for metal assessment. For example, preclinical changes in people exposed to heavy metals were recently monitored by proteomics biomarkers. In addition to urine and blood analysis proteomic profiling of serum samples, one representing the metal-exposed group and the other a control group, revealed three potential protein markers of preclinical changes in humans chronically exposed to a mixture of heavy metals (Kossowska *et al.*, 2010) [10]. Despite the dangers of heavy metals to human health, they have medical and scientific benefits, for example, x-ray absorbance properties and thus are valuable in x-ray imaging, as with barium meal. Also, heavy metals can be used in Transition Electron Microscope (TEM) to create specific contrast and expose fine detail.

Minerals:

In the context of nutrition, a mineral is a chemical element required as an essential nutrient by organisms to perform functions necessary for life. However, the four major structural elements in the human body by weight (oxygen, hydrogen, carbon, and nitrogen), are usually not included in lists of major nutrient minerals (nitrogen is considered a "mineral" for plants, as it often is included in fertilizers). These four elements compose about 96% of the weight of the human body, and major minerals (macro minerals) and minor minerals (also called trace elements) compose the remainder (Zoroddu *et al.*, 2019) [24]. Nutrient minerals, being elements, cannot be synthesized biochemically by living organisms. Plants get minerals from soil. Most of the minerals in a human diet come from eating plants and animals or from drinking water. As a group, minerals are one of the four groups of essential nutrients, the others of which are vitamins, essential fatty acids, and essential amino acids. The five major minerals in the human body are calcium, phosphorus, potassium, sodium and magnesium (Berdanier *et al.*, 2016). Minerals are divided into two classes, namely macro minerals (the body needs in large quantities) and micro minerals (the body needs in small quantities). Minerals included in the macro minerals are sodium, potassium, magnesium, and calcium. Minerals included in the micro minerals are iron and zinc.

Sodium:

It is the most important cation in extracellular fluid by contributing to the regulation of acid base balance, regulation of membrane potential and osmotic pressure of body fluids, activation of nerve and muscle impulses, regulation the absorption process of monosaccharide, amino acids and bile salts (Hathaway and Oldfield, 2004) [8].

Potassium:

It is the most important cation in intracellular fluid by contributing to the regulation of acid base balance, regulation of membrane potential and osmotic pressure of body fluids, delivery of nerve and muscle impulses, regulation of glycol genesis processes. It serves as an active component of several enzyme systems with thiamin pyrophosphate as cofactors, an important component of several enzyme activators, bone and tooth structure, and enzyme compositions (Soetan *et al.*, 2010) [17].

Calcium:

It serves as a major component of bone and tooth structure, nerve regulation and muscle function, blood coagulation, and enzyme activation. Vegetables like broccoli and cauliflower are often consumed by the public, whether eaten raw, boiled, or cooked (stir fry or soup). Processes experienced by vegetables such as boiled may allow a decrease in the minerals content and phytochemicals in the vegetables to be consumed (Ethke and Ansky, 2008) [7]. The main aims of this study is determine the contents of minerals and some metals collected from some Libyan region (Al-Marj Sector).

Description of the Studied Area

The area of study is located in the northern east of Libya at (ALMarj region, Libya) which has a semi-humid environment with an average annual rainfall of around 382 mm/year. The farms are spread out over a large region. The zone has been heavily impacted by pollutants from agricultural chemicals and some human activities. The soil classified under the Rendolls class, which is rich in calcium carbonate and is immature, with no deep profile on the prospects for well known for farmers' inclination toward irrigated agriculture, which has prompted the increased use of fertilizers to boost soil fertility, as well as the increased use of chemical pesticides for pest control, which has expanded owing to the growth of irrigated agriculture. Ten Samples locations were selected in this study including: (line 16 farms, Old ALMarj, New Al-Marj, Almhaadi, Farzogha-Agsenta-Zawet algosor-Awiliyah-Al-Ahmadah and AL slayaya).

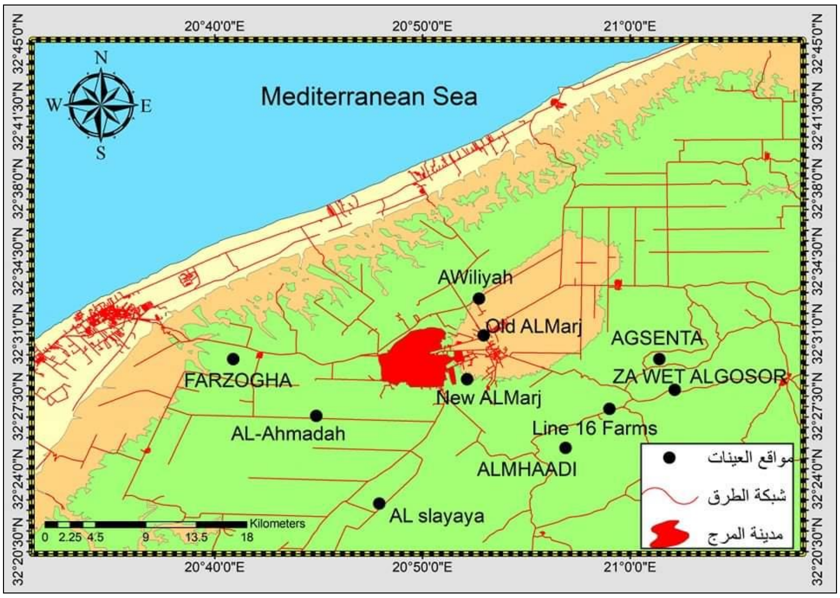

Fig 1: The study locations

Sampling and Preparation of Samples

Vegetable Samples:

The vegetable samples were collected randomly from several locations at some farms, During (2022) which covering about 100 km^2. Five species of vegetable types (Cucumber, Zucchini, Bean, Cabbage and Peas) selected in this study. These vegetable samples were product in five locations as shown in Table (1). Approximately (2 kg) of each vegetable samples were taken; the studied samples are shown in the Table (1). Also, ten locations were selected for soil samples, where the samples collected from the locations of vegetable farms in addition to (samples) collected the area around Al-Marj region which not product vegetables at the sampling time. (1 Kg) of surface soil samples were collected each farm. Both soil and vegetable samples were protected in plastic bags and transported to the laboratory. Fresh samples were washed with tap water, then by deionized water, air dried and then carefully weighed. The samples were dried after chopped into small pieces. Then dried again in oven at 75 °C for 36 hours, grinded to homogeneous small pieces by using food processor (blender), then grinded to powder and sieved through a 2 mm nylon sieve to obtain a representative sample. And appropriate volume of sample was transferred into specimen cans.

Table 1: Vegetable sample locations

S. No	Vegetables	Site
1	Cucumber	New ALMarj
2	Zucchini	Awiliyah
3	Bean	Old ALMarj
4	Cabbage	Al-Ahmadah
5	Peas	Farzogha

Collection and Preparation of the Soil Samples:

Soil samples (about 1 Kg) were collected and transferred into a clean polyethylene bags from the same sites of the vegetable samples (for each vegetable type separately), where Ten samples were taken from 0-20 cm depth using a steeliness steel auger and pooled together to form composite sample. The collected soil samples were transported to central laboratory of chemistry at faculty of science (Omar Al-Mukhtar University). The soil samples were air dried in a dry and dust free place at room temperature of (25 °C) for 5 days, followed by an oven dry at 100 ^{0}C for 24 h. The samples were grinded with a pestle to pass through a 2 mm sieve and homogenized. The dried, sieved and homogenized soil samples were finally stored in polyethylene bags and kept in desiccators until digestion and analysis (APHA, 1995) [2].

Digestion of Vegetable and Soil Samples for Heavy Metals Determination:

For the determination of selected heavy metals, about 0.5 g of homogenized sample was weighed and transferred into a (100-ml) beaker then 5 ml of concentrated HNO_3 was added. Vegetable and soil samples were digested according to the procedure used by (APHA, 1995) [2]. On a hot plate in the digestion chamber (fume hood), 0.5 g of finely ground powder was wet digested in a 100-ml conical flask by adding a 3 ml mixture of distilled water and 5 ml of nitric acid (Conc HNO_3). Heating and digestion continued until the liquid became colorless or bubbles appeared. The liquid was further heated to a volume of 2-3 ml, then lifted aside to lose the heat. Leave the solution to cool, then dilute with distilled deionized water in a 100 ml volumetric flask. Finally, the diluted sample is filtered by the filter paper and stored in a polyethylene bottle for measuring heavy metals.

Chemical Analysis

Heavy Metals (HMs) Analysis:

The heavy metals were determined in the central laboratory of chemistry at the faculty of science by using modified method by UV/VIS spectrophotometer at wavelengths of (550, 745, and 480 nm), which represents the concentrations of Ni, Cu, and Fe, respectively. The method based on used specific reagents for each metal, where concentrate ammonia solution was used to determined Cu, DMG was used to estimate Ni and SCN^- solution was used for estimated Fe, all the concentrations of the studied samples were calculated from standard curves of each metal solutions at the central laboratory of chemistry of faculty of science (Omar Al-Mukhtar University).

Minerals (Na, Ca and K):

The concentrations of the major elements of Minerals (Na, Ca and K) were measured by using **Flamphotmeter** (**Type Jenway**), all the concentrations were calculated from the standard curves of each element.

Results and Discussion

The Major Element Contents:

Some of the chemical particles entering to the environment are not considered risk for environment system. Other materials have direct and indirect effects on life forms and it causes seriousness damage. They may also change form and become available to the biological food chain, furthermore affecting life, including human life, by causing chronic and acute disorders. The major metals are not usually disposal from the environmental system by natural processes, in conversely to most organic pollutants (Drever, 1997) [4].

Most of the land around the world is affected by salt which causes a significant loss of agriculture. Salt stress referees to an excess amount of soluble salts in the root of plant that stimulates osmotic stress and ground water. This is the result of the melting of the parent rock. Sodium is more mobile in soil than potassium and so it is used often as an indicator of human impacts to shallow ground water. Sodium is also a common chemical in minerals. Like potassium, sodium is gradually released from rocks. Therefore, increase of concentrations with time (Abdul Wakeel, 2012) [1]. Calcium is an essential element of the meny that you get from the soil through the root.

Calcium decomposes in the soil and water Calcium in the soil is linked to the metal structure of the rocks inside the mineral soil, which prevents it from dissolving in water. Calcium from soil to surface water is an essential element of aquatic plants and animals (Markewitz *et al*., 1998) [11].

Table 2: The Concentrations of Na, Ca and K of the studied samples

Type of Sample	Samples	Na	Ca	K
Soil	S1	22	10	20
	S2	24	5	27
	S3	24	4	18
	S4	11	4	22
	S5	20	6	21
	S6	18	6	19
	S7	23	4	24
	S8	16	11	23
	S9	14	5	22
Vegetable	S10	14	7	21
	V11	24	17	69
	V12	15	4	30
	V13	26	13	41
	V14	13	6	27
	V15	54	17	55

Potassium is one of the most important substances used as fertilizer and strongly resists clay particles in the soil so the filtration of potassium during soil and groundwater is very important. Potassium is common in meny rocks where some dissolve, so potassium concentrations increase in the groundwater with time (Minnesota Pollution Control Agency, 1999) [12]. In this studied samples of the selected region the contents of sodium (Na), calcium (Ca) and potassium (K) were determined in soil and Vegetable samples, the results were shown in Table 2.

The results showed that the concentrations of Na of soil samples were ranged between (11-24), while the concentrations of Ca were ranged between (4-11) ppm and the concentrations of Kwere ranged between (18-27) ppm. For the vegetable samples, the results showed that the concentrations of sodium, calcium and potassium were ranged as following: (13-54), (4-17) and (27-69) ppm, respectively, as shown in Table 2.

The difference of the mineral contents is mainly attributed to the geological composition for the studied area which may be content ores as calcite or dolomite. The contents of the studied minerals are lie in permissible limits. Also, the result recorded that the highest concentrations of sodium (Na), (K) and calcium (Ca) were recorded in vegetable samples comparing to soil samples, but the concentrations of potassium (K) of vegetable samples are higher than the other samples (soil) **(**Pasławski and Migaszewsi, 2006) [14].

The Heavy Metals Contents:

Most heavy metals are toxic and their accumulation over time in bodies can cause severe diseases. Prolonged exposure to heavy metals can lead to physical, neurological and muscular degenerative processes that may lead to Alzheimer's disease and muscular dystrophy (Baldwin and Marshall, 1999). The sources of heavy metals in soils are caused by both natural and anthropogenic factors. The natural conditions affecting the contents of heavy metals in soils are: the parent rock, soil formation processes, soil sorption capacity, grain size distribution of a given soil, plant cover (Tran and Popova, 2013) [19]. Moreover, soil pollutants can originate from the weathering of parent rock (Kabata-Pendias, 2004), from emissions by industries from landfills (Szymañska-Pulikowska, 2012) [18]. Other sources of contamination include some mineral fertilizers and plant protection chemicals (Qiao *et al.*, 2011) [15]. The highest quantities of heavy metals enter soils from the metallurgic and mining industries (Vásquez-Murrieta *et al*., 2006) [22], and from transportation routes in addition to emission of fumes (Duong and Lee, 2011) [6].

The contents of heavy metals in soils which selected in this study were shown in Table 3 and Figures of (3.10-3.12). The concentrations were fluctuated in the following ranges: (0.012-0.033), (0.560-1.207) and (0.057-0.219) ppm. For the metals of (copper, iron and Nickel), respectively. The concentrations of the studied metals in vegetable samples were ranged as following: (0.002-0.037), (0.007-0.060) and (0.009-0.027) ppm for (copper, iron, and Nickel), respectively, as shown in Table 3. The concentrations of copper (Cu) iron (Fe), Nickel (Ni) and Nitrogen (N) of the studied samples (µg/g).

Table 3: The Concentrations of Cu, Fe and Ni of the studied samples

Type of Sample	Samples	Cu	Fe	Ni
Soil	S1	0.026	0.560	0.150
	S2	0.026	1.207	0.114
	S3	0.030	0.850	0.128
	S4	0.021	0.894	0.127
	S5	0.033	0.993	0.183
	S6	0.012	0.725	0.061
	S7	0.017	1.108	0.124
	S8	0.015	1.115	0.078
	S9	0.024	0.993	0.057
vegetables	S10	0.029	0.686	0.219
	V11	0.004	0.007	0.009
	V12	0.037	0.052	0.010
	V13	0.004	0.058	0.014
	V14	0.002	0.060	0.016
	V15	0.006	0.059	0.027

The results showed that the concentrations of heavy metals comparing with the global composition reveals that all the studied samples. The heavy metal concentrations of Cu, Fe, and Ni, which consider to be a good indicators for no heavy metals be pollution caused by human activities, are characterized by lower concentrations than the WHO (World Health Organization), where (Skordas and Kelepertsis, 2005) reported that the soil pollution by ultrabasic rocks, resulting in low concentrations of the previously mentioned elements (Cu, Fe, and Ni) due to the weathering and dispersion of the parent materials, which these metals are predominant. The average concentrations of heavy soil samples depending on many factors where, the soils can be ascribed to the ferromagnesian minerals of the rocks. In respect to the published mean metal values. The results of soil samples recorded high value of Fe compared with the values of the other samples. This is mainly attributed to the mineralization that occurs on the weathered surface of the serpentinites and peridotites, which are considered the parent rocks of the mineralization **(**Vardaki and Kelepertsis, 1999) [21]. Table 4 shows the permissible levels for human tissues and Daily intake for the studied metals and minerals.

Table 4: The permissible levels in human body

Element	Muscle (ppm)	Bon (ppm)	Blood (mg/dm^3)	Daily Intake (mg)
Cu	10	1-26	1.01	0.5-6
Fe	180	3-380	447	6-40
Ni	1-2	<0.7	0.01-0.05	0.3-0.5
Na	2600-7800	10000	1970	2-15
K	16000	2100	1620	1400-7400
Ca	140-700	170000	60.5	600-1400

Conclusion

According to the results recorded in this study the levels of minerals (Na, Ca. and k) and heavy metal (Fe, Cu and Ni) concentrations for vegetables and Soil samples in Almarj region-Libya, the contents of the studied major elements in the all samples recorded the small values Na and Ca in vegetable samples, and high average concentrations of potassium was recorded in the vegetable samples. On the other side the small concentrations of heavy metal were recorded in the selected samples.

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