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ESTIMATION OF MINERAL LEAD CONTENT IN FERTILIZED AND NON-FERTILIZED SOILS

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ABSTRACT

Heavy metals have become a worldwide problem in soil contamination, resulting in losses in agricultural yield and hazardous health effects as they enter the food chain. A survey was conducted to investigate the levels of (Pb) in fertilized soils in areas characterized by intensive agricultural activities and non-fertilized soils in Libya. Four farms from two locations in the rural areas of Al-Ajelat (Sanit Khmlej and Al-galmia) were selected for this study. Eight samples were at a depth of 0-20 cm for each of the two areas. The mineral content of lead in these soils was estimated by uv-vis spectroscopy at a wavelength of 750 nm. (A, B, C, D, E, F, G, H) were codes used for each sample. The concentration of Lead in the samples were as follows:
(30.5, 20.0, 1.5, 1.5, 15.0, 15.5, 15.0, 15.5) mg/kg (ppm) respectively. From the results, all samples A, B, C, D, E, F, G, and H agreed with the permissible limit, according to the world health organization of 100mg/kg of lead concentration in the soils.

Key words— lead pollution, environmental contamination, (uv- vis) spectrophotometer.

الملخص:

أصبحت المعادن الثقيلة مشكلة عالمية في تلوث التربة، مما أدى إلى خسائر في المحصول الزراعي وآثار صحية خطيرة عند دخولها السلسلة الغذائية. تم إجراء مسح لمعرفة مستويات الرصاص في التربة المسمدة في المناطق التي تتميز بالنشاط الزراعي المكثف والتربة غير المسمدة في ليبيا. تم اختيار أربع مزارع من موقعين في ريف العجيلات (سانية خملج والغالمية) لهذه الدراسة. ثمانية عينات كانت على عمق 0-20 سم لكل من المنطقتين، من ناحية تم فيها استخدام الأسمدة الكيماوية أثناء استصلاحها، ومن ناحية أخرى لم يتم استخدام الأسمدة أثناء استصلاحها الزراعي. تم تقدير المحتوى المعدني للرصاص في هذه التربة بواسطة التحليل الطيفي للأشعة المرئية وفوق البنفسجية بطول موجي يبلغ 750 نانومتر. تم استخدام رموز(A، B، C، D، E، F، G، H)لكل عينة. وكان تركيز الرصاص في العينات على النحو التالي:
(30.5، 20.0، 1.5، 1.5، 15، 15.5، 15، 15.5)ملجم / كجم (جزء في المليون) على التوالي. من النتائج، كل العينات (A,B,C, D, E, F, G,H)اتفقت مع الحد المسموح به وفقًا لمنظمة الصحة العالمية البالغ 100 مجم / كجم من تركيز الرصاص في التربة.
الكلمات المفتاحية –التلوث بالرصاص، التلوث البيئي، جهاز قياس الطيف الضوئي للأشعة فوق البنفسجية.

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1INTRODUCTION:

Heavy metals occur naturally in the soil environment from the pedogenetic processes of weathering ofparent materials at levels that are regarded as trace (<1000mg kg^{-1}) and rarely toxic (Kabata-Pendias, 2001). Due to the disturbance and acceleration of nature's slowly occurring geochemical cycle of metals by man, most soils of rural and urban environments may accumulate one or more of the heavy metals values high enough tocause risks to human health, plants, animals, ecosystems, or other media (Mlitan et al, 2013). Heavy metals have become a worldwide problem in soil contamination, resulting in losses in agricultural yield and hazardous health effects as they enter the food chain, as a consequence of modern land-use techniques, or activities thatmobilize heavy metals (France & Coquery 1995), many soils are contaminated by different agents, especially heavy metals, pesticides and mineral fertilizer use has resulted in toxic metal pollution of land, plant, and water resources (Yilmaz, et al, 2009).

2.LITERATURE REVIEW:

Regarding their roles in biological systems, heavy metals are classified as essential and nonessential. Essential heavy metals are important for living organisms and may be required in the body in quite low concentrations. Nonessential heavy metals have no known biological role in living organisms. Examples of essential heavy metals are Mn, Fe, Cu, and Zn, while the heavy metals Cd, Pb, and Hg are toxic and are regarded as biologically nonessential (Ali et al, 2019). Heavy metal pollution has emerged due to anthropogenic activity which is the prime cause of pollution, primarily due to mining the metal, smelting, foundries, and other industries that are metal-based, leaching of metals from different sources such as landfills, waste dumps, excretion, livestock and chicken manure, runoffs, automobiles and roadworks. Heavy metal use in the agricultural field has been the secondary source of heavy metal Pollution (Briff et al, 2020). A large amount of chemicals is annually applied at the agricultural soils as fertilizers and pesticides, such applications may result in the increase of heavy metals, it can also accumulate in the soil due to application of liquid and soil manure (or their derivate, compost, or sludge) or inorganic fertilizers. (Atafar, et al,2010). There are three main ways in which the human body can be exposed to trace metals in the soil: (I) oral absorption; (II) absorption by dermal contact (skin exposure); and (III) inhalation of floating soil particles (respiratory exposure). Studying the carcinogenic and non-carcinogenic risks to human health through these three exposure pathways can not only reveal high-risk exposure pathways and trace metal species, but they can also help farmers to avoid risks in their agricultural businesses. According to the list of carcinogens published by the World Health Organization's International Agency for Research on Cancer on 27 October 2017, As, Cd, Cr(VI), and Ni compounds are a class of carcinogens. Inorganic Pb is a Class 2A carcinogen, and Ni, Pb, and Cr(III) are Class 2B carcinogens (Gong, et al 2019). The term heavy metal alludes to any metallic chemical element that has a comparatively high density and is poisonous at low concentrations (Isak, 2019). Heavy metals like cadmium (Cd), lead (Pb) and arsenic (As) metalloid have been found in fertilizers and are considered the most important of health concern. These elements are regarded toxic and classified as carcinogenic. World health organization (WHO)reported that poisoning by Pb in Nigeria killed more than 500 children, and left thousands in severe health conditions in 2010 (WHO, 2015). Pb is cubic crystal, silver blue-white, soft. Lead has atomic number 82, atomic mass 207.2, density 11.4 g/cm3, melting point 601K° and boiling point 2013 K°. Lead is a naturally occurring and found as a mineral combined with other elements such as Sulphur (PbS, $PbSO_4$) and oxygen ($PbCO_3$(Arora et al, 2017). Lead (Pb) can cause side effects, such as abnormal hemoglobin synthesis and anemia, hypertension, kidney damage, abortion, nervous system disorders, brain damage, child's decreased ability of learning and behavioral disorders in children, such as aggression and hyperactivity (Amouei et al, 2020). Recent studies, have demonstrated that and other toxic heavy metals like Cd and Pb were responsible for causing a chronic kidney disease, known as toxic nephropathy, in contaminated areas in Siri Lanka (Jayasumara, et al, 2015). (Mausi et al,2014(, indicated that the permissible level of Pb (0.3 mg/kg) in oranges and mangos fruits was exceeded as they recorded mean values of 0.65 and 0.61 mg/kg, respectively, these high levels were attributed to the use of pesticides, fertilizers and wastewater (Mausi et al, 2014). Moreover,) Ghrefat et al (, pointed out that fertilizers application induced high levels of Cd (4.6 ppm) and Pb (58.4 ppm) in soils located beside the Zerqa River, Jardon (AlKhader, 2015). Lead is considered one of the environmentally hazardous elements because, it poses a particularly high risk of disturbing the chemical balance in the ecosystem. The content of lead in the soil is directly related to its mineral composition. The natural content of lead in the soils formed of sands does not normally exceed 16 mg per kg of soil, and in more packed soils it is usually within the range of 13 to 60 mg per kg of soil (Wuana et al,2011). Toxic metals, including Pb, are some pollutants that are most dangerous to human health. This is especially true in countries witnessing rapid industrialization. Lead (Pb) is the second most toxic metal on Earth and is toxic to humans and other living things. In 2015, Pb was listed as the number one heavy metal on Earth. It is generally toxic to most plants at a soil concentration higher than 30 mg/kg (Usman et al, 2020). Many researches on analysis of lead were done most of them mainly to wards determination of lead in roadsidesoil. However, there is no more consideration about health effect of lead in society. The result of the analysis of lead in the soil of a given area is very crucial for comparison with WHO's permissible limit and take corrective measures for the wellbeing of inhabitants (Sisay, 2019). This study may be serve as an important tool for policy makers to make decisions concerning the environment and to secure the wellbeing of the community or promoting health care services by minimize the level of lead in the soil. Therefore, the objective of this study is: (I) determination of concentration of one trace metal (Pb) in fertilized soils in two rural regions of farms in Alajilat –Libya; (II) estimation of potential risks of fertilizer application to the accumulation of trace metals in the soil; and (III) simulation of potential human health risks following exposure to fertilizer containing trace metals.

3.MATERIALS AND METHODS

3.1COLLECTIONS OF SOIL SAMPLES:

A total of 8 surface soil samples (0–20 cm) were collected from four farms in two locations characterized by intensive agricultural activities in Libya locations in the rural areas were selected for soil sampling during the spring period of 2016. The farm was divided into two sectors and 1kg of soil sample was collected from each section with auger sampler at depth of 0–20 cm. A total of eight samples were collected from the eight sectors for analysis. Soil samples were collected in clean polyethylene bags, labeled properly and transferred to the laboratory for analysis. Uncultivated and undisturbed soil samples were also collected from area nearby to the study area. Uncultivated and undisturbed soil sample was considered as a reference soil.

3.2SOIL SAMPLE PREPARATION:

All glassware and plastic containers were immersed in 5% (v/v) nitric acid solution for 24 h and then rinsed with ultrapure water and reserved for use. All collected soil samples were air-dried to constant weight at room temperature.

3.3ANALYTICAL CHARACTERISTICS:

Calibration curves were prepared for element with aspiration of the standard solutions (1-1.5 mL). Analysis of each sample was carried out three times with integration time of 3 seconds to obtain a relatively standard deviation of 5% or less within the calibration range. In this study, 6 working standard solutions1 were obtained for Pb (0.00, 0.01, 0.02, 0.03, 0.04 and 0.05 mg/L), and 6 standard solutions2 for Pb (0.00, 0.1, 0.2, 0.3, 0.4 and 0.5 mg/L), which were prepared from the standard stock solution (1000 mg/L) purchased from Merck (Germany). Serial dilution solutions were carried out and acidified using nitric acid 2%.

3.4EXPERIMENTAL PROCEDURE:

The dried soil samples (~1g) sample was placed in 300ml beaker and boiled with aqua-regia (HCl: HNO3, 3:1 ratio) (15 mL) at 110 C° (hotplate) for 4-5 h. The digest was cool down, filtered through filter paper (Whatman no. 42). the digested solution was filtered and placed in a 100 mL Pyrex glass beaker and diluted with distilled water up to 50 mL. triplicate samples were analyzed for the sample determination, the metal concentrations were determined by (Uv-Vis/ Spectrophotometer-PerkinElmer LAMBDA 1050, USA) at 750 nm wave length (Rahman, et al 2012).

3.5SAMPLE CODING:

After taking the samples from their different areas what the researcher needed was making codes to deal with the different samples, the codes were assembled by taking the rural areas. The below table gives more detail about the codes.

Table 1: Sample Codes and Their Distribution.

No	Code	Sample
1	A	Fertilized (Al-galmia)1
2	B	Fertilized (Al-galmia)2
3	C	Non-fertilized (Sanit Khmlej)1
4	D	Non- Fertilized (Al-galmia)2
5	E	Fertilized (Sanit Khmlej)1
6	F	Non- fertilized (Al-galmia)1
7	G	Fertilized (Sanit Khmlej)2
8	H	Non-fertilized (Sanit Khmlej)2

3.6STATISTICAL ANALYSIS:

Comparison of the Lead content before fertilization and after harvesting was done with t test analysis in SPSS software version22.

4.RESULTS:

CONCENTRATIONS OF LEAD IN SOIL SAMPLES:

The Experimental work were done in Higher Institute of Water and Soil Affairs (Ajilat-Libya). The total concentrations of Lead (Pb) in the cultivated soils of the study area are given in Table 4 and 5. Average concentration of Lead in the studied cultivated soil was (30.5, 20, 1.5, 1.5, 15, 15.5, 15,15.5) mgkg-1 (ppm) respectively. From the results, all samples A, B, C, D, E, F, G and H, they show that the content of lead does not indicate contamination with this element in any of the collection sites. That agreed with the permissible limit according to the world health organization of 100mgkg-1 of lead concentration in the soil.

5.DISCUSSION:

Trace metals have always been the focus in fertilized soil standards. Establishing and implementing limit standards for trace metals in fertilized soils could prevent agricultural pollution. Compliance with these standards ensures that fertilizers are safe for use; however, there is no guarantee that they will meet the specific need of end use. As shown (Table4) the soil were taken from Al-Ajelat (Sanit Khmlej and Al-galmia) that recorded as the lead content with concentration of (30.5, 20, 1.5, 1.5, 15, 15.5, 15, 15.5mg/kg) with the level which was taken from different sites. The highest point of Lead concentration was found in Al-galmia (A) which was 30.5mgkg^{-1}as expected because this area is fertilized agricultural soil, and the lowest point of Lead concentration was in (Sanit Khmlej and Al-galmia area) (C, D) respectively, as expected and was been 1.5 mgkg^{-1}, (there is no source of pollution). No elevated level of lead in soil (lower than 100 mgkg^{-1}) was detected in all four sites investigated. Lead concentration in all sites was found to be within the estimated natural concentration range of 1.5 to 30.5 mgkg^{-1}. Generally, the fertilized areas have highly a pollution source that doesn't in the non-fertilized area.

Wafaa Sahib Abbood Alawsy College of Agriculture-University of Qadisia and Eman Abdul Mahdi Oleiwi College of Agriculture-University of Baghdad, 2014 "MSc" (Study the Pollution of some Calcareous Soils with Cadmium and Lead and Its Relationship with the Accumulative Effect of Used Engines Oils on Mineralogical Soil Separates) were done work on lead pollution in Soil of some areas in Iraq and their ranging was high between 12.8 – 13.6 ppm.

Mohamed Elmubarek, 2012 "PhD" (Environmental Levels of Lead in Soil and Drinking water in some areas in Khartoum and Gezira State, university of Gezira), was did the same analysis on the soil in Khartoum area and get ranging about 11.24 ppm, by using the same method.

5.2CALCULATION FORMULA:

metal (mg/kg) = Conc of metals (mg/L) × Final volume (ml) / Initial sample weight (g).

Example: 0.61x 50 / 1 = 30.5 mg/kg

Table2: Standard Solutions1 for Lead Chloride.

Concentration	Absorption	Back Ground	Corrected Absorption
0.01	0.00123	0.001	0.00023
0.02	0.00170	0.001	0.00076
0.03	0.00245	0.001	0.00140
0.04	0.00265	0.001	0.00165
0.05	0.00280	0.001	0.00180

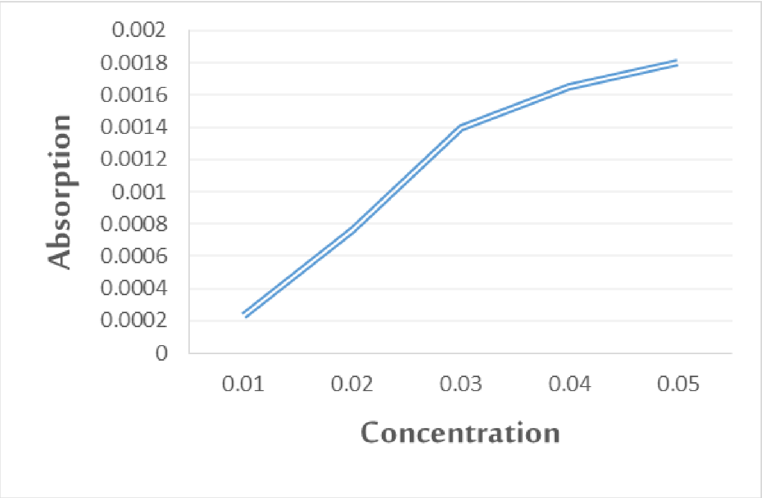

Fig.1Calibration curve for lead standard solution1.

Table3: Standard Solutions2 for Lead Chloride.

Concentration	Absorption	Back Ground	Abs - BG	Corrected Absorption
0.1	0.004	0.002	0.0040-0.002	0.0020
0.2	0.007	0.002	0.0070-0.002	0.0050
0.3	0.0097	0.002	0.0097-0.002	0.0077
0.4	0.0127	0.002	0.0127-0.002	0.0107
0.5	0.0156	0.002	0.0156-0.002	0.0136
0.6	0.0185	0.002	0.0185-0.002	0.0165
0.7	0.0216	0.002	0.0216-0.002	0.0196

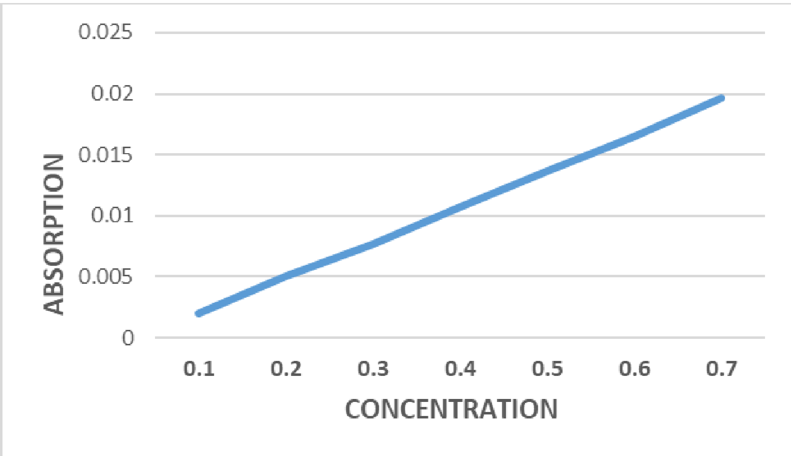

Fig2: Calibration curve for lead standard solution2

Table4: Lead content of fertilized soil samples.

NO	Sample Batch	Lead Concentration (mg/L)	Corrected Lead Concentration (mg/L)	Lead Concentration in Samples mg/Kg	Expected value
1	**A**	**0.612**	**0.61**	**30.5**	**20.12±7.31**
2	**B**	**0.402**	**0.40**	**20**	
3	**E**	**0.302**	**0.30**	**15**	
4	**G**	**0.302**	**0.30**	**15**	
				Mean= 20.12	

Table5: Lead content of non-fertilized soil samples.

NO	Sample Batch	Lead Concentration (mg/L)	Corrected Lead Concentration (mg/L)	Lead Concentration in Sample mg/Kg	Expected value
1	**C**	**0.031**	**0.03**	**1.5**	**8.50 ± 8.01**
2	**D**	**0.031**	**0.03**	**1.5**	
3	**F**	**0.312**	**0.31**	**15.5**	
4	**H**	**0.312**	**0.31**	**15.5**	
				Mean = 8.50	

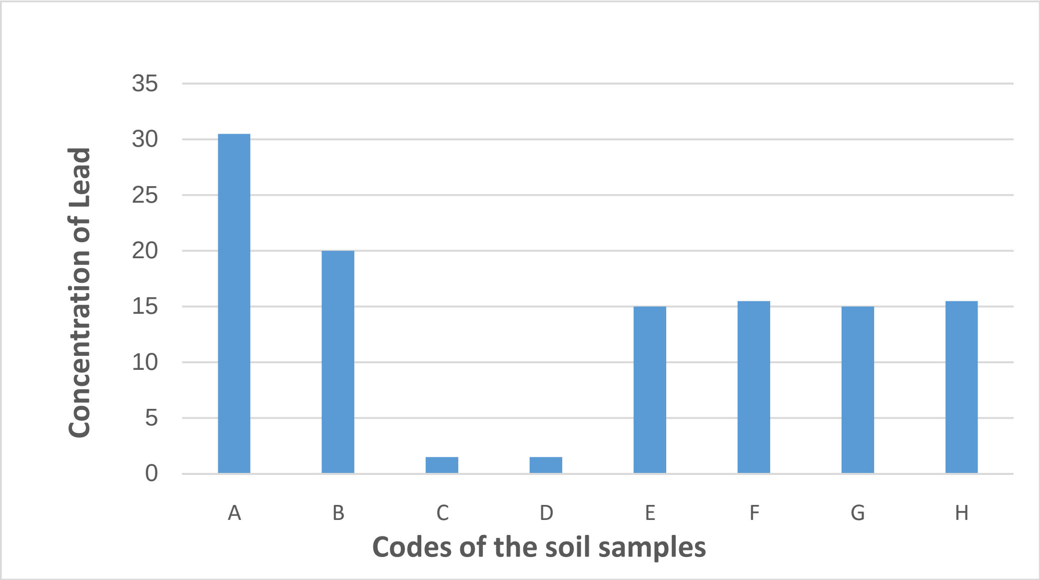

Fig3: Concentration of Lead content in the soil samples

6.CONCLUSIONS:

Reducing trace metal inputs in agricultural soils is an important strategy to protect farmland and ensure food safety. Estimation of the impact of the application of fertilizer on soil and human health is urgently needed to develop sound management practices and policies, which require information on the trace metals present in fertilizer. In this study, research was conducted in Alajilat in Libya to determine the metal contents in fertilized soil. A total of 8 fertilized and non-fertilized soil samples were collected, the study result indicated there is no sampling sites recorded a lead concentration beyond the world health organization (WHO) permissible limit of 100 mg/kg. However, the concentration of such a heavy metal in these sampling sites were below the world health organization permissible limit the soil sample taken from sampling site of farms exposed to fertilizers emission shows a considerable difference in concentration of lead in relative to the soil of non-fertilized area. Generally, in this study the concentration of lead in the two farms of Al-Ajelat (Sanit Khmlej and Al-galmia) area the mean Lead level is less than 100mg/kg I conclude that the Lead concentration in the soil is low enough that is not a danger to the public based on the results of this study. The low concentration of Lead in the soil may be attributed to its continuous removal by vegetables grown in the designated areas.

RECOMMENDATION:

We recommend, certain precautionary measures must be conducted in order to prevent possible ingestion of soil containing lead. Hence a routine analysis of these kind of the study must be carried out to ensure the safety of the consuming populace. Further studies on this area by increasing the sample size to make it more representative. And more research must be completed for another heavy metals.

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