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Heavy Metals Accumulation in Leaves of Five Plant Species as a Bioindicator of Industrial Pollution From a cement Factory in Benghazi City, Libya.

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Abstract

The present study aimed to evaluate the levels of heavy metals in leaves of five plants Eucalyptus gomphocephala, Olea europaea, Pinus halepensis, Nicotiana glauca and Ricinus communis surrounding AlHawari cement factory(polluted site) in Benghazi, Libya with comparison in plants away from the factory used as control(unpolluted site). Samples of these plant leaves were collected, treated, and then assayed for Zinc(Zn), Copper(Cu), Cadmium(Cd) and lead(Pb) using atomic Absorption spectrometry(AAS). The values obtained were compared against the permissible limits established by the Food Agriculture Organization (FAO) and World Health Organization(WHO), the results revealed the significant higher accumulation of all heavy metals in polluted plants in comparison with unpolluted plants, except for Pb in E.gomphocephala leaves, which implies that the source of these metals as pollutants cannot be attributed to the cement factory only but may be also to vehicular traffic. On the other hand, all metals concentration in both sites were below the WHO/FAO, Only concentration of Cd exceeded the WHO limits collected from the polluted site. In general, the mean concentration of heavy metals followed this pattern Zn> Cu> Pb

>Cd. Positive correlation were recorded for most of these metals, indicating that they might be derived from similar sources . Ricinus communis showed the ability to absorbed accumulate of heavy metals in leaves when compared to other plants. This is attributed to its high biomass production, strong absorption and accumulation for heavy metals. As a result, it is an effective bioindicator for industrial area and can be used in phytoremediation applications for further research.

Keywords: Heavy metals, Bioindicators, Accumulation, Cement factory, Air pollution, Ricinus communis.

* Introduction

Heavy metals are the most toxic pollutants that enter the environment through industrial and human activities (Ogunkunle et al., 2013; Abimbola et al., 2007). Cement manufacturing as the most polluting industries in the world. 2022, global cement production reached 4.1 billion metric tons, a considerable increase from 1.39 billion tons in 1995 (Etim et al., 2021; Ige et al., 2024). With the world's population on the rise and industrialization progressing, cement production is projected to escalate by 12-23% by 2050 (IEA). Libya has recently focused on improving its overall industry, particularly the cement industry (Hokoma, 2008). Since 1969, Libya has seen significant industrial and urban development.

Dust particles released from the cement industry contains pollutants such as dioxin, heavy metals, and particulate matter, carbon monoxide, sulfur dioxide, nitrogen oxides, and hydrocarbons(Yahaya et al., 2013; Adeyanju et al., 2019), this dust can spread over large areas through wind and rain and accumulated in soil and plants and subsequently humans in through the food chain effect(Stanley et al., 2014; Ogunkunle et al., 2013; El-Abssawy et al., 2011), which depends on the size of the dust particles. It is now accepted that plants can be used effectively as filters to reduce air pollution produced from the industrial factory and also as bioindicators of air quality (Salaa et al., 2017).

Cement plants are the main sources of heavy metals such as cadmium (Cd), chromium (Cr), lead (Pb), nickel (Ni), manganese (Mn), copper, and zinc(Zn) (Yahaya et al., 2013; Ogunkunle et al., 2014; Awuah et al., 2022) .Heavy metals can be detected and quantified in various samples using analytical techniques such as inductively coupled plasma atomic emission spectrometry(ICP-AES) and atomic absorption spectrometry (AAS) (Llorent-Mart et al., 2011).

From previous studies in other countries have reported the adversely affect of the cement factories on the surrounding area of the humans, soil and plants (Kpeglo et al., 2011). So, this study come to detect the concentration of selected heavy metals in the five plants surrounding the cement factory and to compare them with allowable limits of Food Agriculture Organization (FAO)and World Health Organization (WHO) in order to predict associated health risks on consumption of this plants.

* Materials and Methods

* Study Area Description

In the current study, two different locations were selected. The first site is located south of Benghazi city (coordinates32° 02' 06" N and 20° 03' 42" E) from now called an unpolluted area, which was used as control area because it is far the main traffic road and any source of pollution. The second site is located near the traffic road and also El Hawari cement factory near it (coordinates32° 00' 06" N and 20° 08' 36" E) from now called polluted area. Al Hawari factory, which was started in 1964 and is located of about 18 km in the southwest part of Benghazi city, Libya. The elevation of the site is 136 m above mean sea and production capacity of 1 million tons per year. The location of the sampling sites as shown in (Figure. 1).

The study area is part of city of Benghazi, which climate is classed as BSh (Semi - arid) and CSa (Mediterranean) according to koppen classification system (Karas et al., 1997). The rainy season over Benghazi starts from September to May, with 99% of total annual precipitation, which estimated by approximately 270 mm/year. The relative humidity varying between 55% to 61% and mean annual temperature of 25%.

Figure1. The map of two studied sites (Control and Polluted sites).

* Sampling Collection

Leaves of five selected species of higher plants: Eucalyptus gomphocephala, Olea europaea, Pinus halepensis, Nicotiana glauca and Ricinus communis were collected from control and polluted sites in January 2023. Four samples from healthy and mature leaves were cut from different sides of a small lower branch and placed in labeled plastic bags and then transported to the laboratory in the Department of Botany, University of Benghazi for further processing.

*** Sampling Digestion**

Collected leaves were washed with tap water to remove soil particles and twice with distilled water. The plant leaves of Eucalyptus gomphocephala, Olea europaea, Pinus halepensis, Nicotiana glauca L . and Ricinus communis were cut into small pieces and then oven dried at 60˚C for 48 hour (AOAC 1984) . Extraction of heavy metals from plant leaves were done by wet digestion according to (Antonious et al., 2003).The concentration of heavy metals; Zinc(Zn), Copper(Cu),Cadmium(Cd) and Lead(Pb)in the solution were determined by using Atomic Absorption Spectrometer(AAS) (SHIMADZU AA- 6800). This was calibrated using the standard solution.

*** Statistical Analysis**

The data analysis were carried out by using SPSS (Version 28). Independent t-test was used for comparison of heavy metals concentration in plant leaves between the unpolluted site and contaminated site for each plant species. $P \leq 0.05$ was considered to be statistically significant. Pearson correlation was used for founding the relationships between heavy metals in plants. values were presented as means ± standard deviation.

* Results and Discussion

* Heavy Metals Content

Air pollution by heavy metals are one of the most significant factors causing environmental pollution in this century (Yang et al., 2018; Karahan et al., 2020; Adejoh, 2016). As a result of Human activities such as cement manufacturing, mining, coal processing, traffic and agriculture are the most important sources of heavy metals in the environment (Adejoh, 2016; Stihi et al., 2006).

Table 1 shows the concentration (mean ± SD)of Zn and Cu in leaves of Eucalyptus gomphocephala, Olea europaea, Pinus halepensis, Nicotiana glauca and Ricinus communis in both control and polluted sites. The results showed that the leaves concentration of these metals in the contaminated site were significantly higher than that of the control site in all plant species.

Table 1: Zinc and Copper concentration in leaves of plants grown in control and polluted areas.

Plants	*Zn mg/kg*		*Cu mg/kg*	
	Control	Polluted	Control	polluted
Eucalyptus gomphocephala	14.63+0.12	22.45+0.64	3.90+0.16	12.77+0.17
Olea europaea	5.90+0.14	10.57+0.09	4.00+0.11	8.58+0.22
Pinus halepensis	11.58+0.05	17.78+0.15	6.37+0.05	7.57+0.09
Nicotiana glauca	3.43+0.05	9.13+0.23	4.60+0.11	6.67+0.15
Ricinus communis	10.48+0.05	24.85+0.25	9.92+0.26	16.70+0.14
Total	9.20+4.13	17.35+6.52	5.96+2.26	10.46+3.86
FAO/WHO limit mg/kg	99.4		40	

Value were expressed as mean ± SD (n=4)

Metals such as Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se and Zn, which have atomic weights are above 5 g cm^{-3} are called as heavy metals (Salzer, 1999; Duffus, 2002; Yalcin, et al., 2020). Heavy metals such as Cu, Fe, Mn, Mo, Zn and Ni are needed for living things up to a certain dose; these elements are called microelements. Zinc (Zn) is one of an essential micronutrients for plants, but when their concentration become toxic can lead to avariety of harmful effects in bio-physico-chemical systems in plants (Bankaji, et al., 2019; Sidhu et al., 2020). Copper (Cu) is also an essential elements for plant growth and development , Cu acts as a cofactor for several metal proteins and is a key player in several physiological and biochemical processes(Zhang et al., 2019). However, Cu at toxic levels affects photosynthesis because it decreases Rubisco enzymatic activity and stomatal conductance (Li et al., 2021; Yusuf et al., 2021). Overall, the concentration of Zn and Cu in all plant species that were grown in the control site were below the permissible limits set by the FAO/WHO (FAO/WHO 2011) Table 1

The results of our analysis showed that there are significant differences (P≤0.05) for Zn and Cu concentration in all plant species between sampling sites in control and polluted area. The same results are obtained by (Salih and Aziz 2019) who observed a higher concentration of Zn and Cu in Olea sp, Eucalptus sp and Nerium spin the polluted site when compared with unpolluted area. This study reports that the concentration of Zn and Cu in all plant species that were grown in control and polluted sites are below the FAO/WHO limits of 40 and 99.4 mg/kg respectively (FAO/WHO 2011). Contrarily, heavy metals such as As, Cd, Cr, Hg and Pb are not essential for living things and even small amounts of them can show toxic effects(Altay et al., 2013; Ozyigit et al., 2016; Karahan et al., 2020). Among these metals, Cadmium (Cd) is one of the most toxic and dangerous heavy metals for living things. The importance of Cd as an industrial and environmental pollutant has become more evident in recent years (Mishra et al., 2019). Some plant species, known as accumulators, have the ability to accumulate higher levels of cadmium in their tissues without showing visible signs of toxicity. These plants can then transfer cadmium through the food chain when consumed by animals(Goncharuk, 2023).

Table 2 shows the concentration (mean ± SD)of Cd and Pb in leaves of Eucalyptus gomphocephala, Olea europaea , Pinus halepensis , Nicotiana glauca and Ricinus communis in control and polluted sites. The results showed that the leaves concentration of these metals in the contaminated site were significantly higher than that of the control site in all plant species except Olea europaea was Cd below detection limits in both sites.

Table 2: Cadmium and Lead concentration in leaves of plants grown in control and polluted areas.

Plants	*Cd mg/kg*		*Pd mg/kg*	
	Control	polluted	Control	polluted
Eucalyptus gomphocephala	0.10±0.00	2.35±0.05	0.10±0.00	0.17±0.05
Olea europaea	BDL*	BDL*	BDL*	0.17±0.05
Pinus halepensis	0.10±0.00	0.30±0.00	*BDL	0.12+0.05
Nicotiana glauca	BDL*	BDL*	0.12±0.05	0.20±0.05
Ricinus communis	0.10±0.00	3.25±0.10	0.20±0.05	0.30±0.05
Total	0.06±0.05	1.56±1.14	0.08±0.08	0.21±0.09
FAO/WHO limit mg/kg	0.2		0.3	

Value were expressed as mean ± SD (n=4) ;*BDL= Below Detection Limit.

Significant differences ($P \leq 0.05$) in our analysis for Cd concentration in Eucalyptus gomphocephala, Pinus halepensis L. and Ricinus communis L. leaves between sampling sites in control and polluted area. Cd concentration in these plant species that were grown in polluted area exceeded the WHO limits of 0.2mg/kg (FAO/WHO 2011) comparting to control area, due to its more easily absorbed and accumulated by plants than the others, whereas Cd concentration in obtained from Olea europaea L. and Nicotiana glauca L. that were grown in control and polluted sites were below the detection limits. Lead (Pb)is one of a limited class of metals that can be described as purely toxic , and capable of causing environmental pollution in small amount and health problem in many parts of the world (Seema, and Tripathi 2012; Beardsley et al., 2021).The results of our studies showed that there were significant differences ($P \leq 0.05$) for Pb concentration in Olea europaea, Pinus halepensis, Nicotiana glauca L and Ricinus communis leaves between sampling sites in control and polluted area. The same results were obtained by(Warrah et al., 2020) , who observed high concentration of Cd and Pb in different plants species near a cement company in Sokoto, Nigeria. However, these results contrast with those of (Nomor et al., 2021) , who detected permissible levels of Cd and Pb in samples of casava and pawpaw leaves obtained around the Dangote Cement Company in Gboko, Benue State, Nigeria. No significant differences (P>0.05) for Pb concentration in Eucalyptus gomphocephala leaves were grown in control and polluted sites was 0.10 and 0.17mg/kg respectively.

Olea europaea and Pinus halepensis grown in control site showed Pb concentration below the detection limits. The Pb concentrations grown in polluted sites within permissible limits , at 0.17 and 0.12 mg/kg, respectively. The concentration of Pb in Ricinus communis leaves were grown in polluted site was approximately equal to FAO/WHO limits of 0.3mg/kg . These results show that R.communis has a higher potential for removing heavy metals from contaminated areas than other plants due to its ability to grow in extremely polluted soil, as well as its capability for metal ion accumulation and rapid growth rate (Rajkumar and Freitas 2008; Shi and Cai 2009). Furthermore, it has a considerable amount of biomass both above and below ground (Bauddh and Singh 2012a; Bauddh and Singh 2012b) . These trails make R.communis a candidate species for phytoremediation (Zhuang et al., 2007; Yi et al., 2014) . Generally, the elevated levels of Zinc(Zn), Copper(Cu), Cadmium(Cd) and Lead(Pb) in leaves of five plants species collected around cement factory were attributed to emissions from the cement factory as well as to influence of vehicular traffic. According to our finding the order of heavy metals in five plane leaves were found in as Zn> Cu> Pb >Cd.

*** Pearson Correlation between Heavy Metals Concentrations**

Correlation is a statistical measurement of the relationship between two different parameters. The high correlation coefficient (near+1or -1) mean a good relation between two variables, and its concentration around zero indicated that there is no relationship between the variables. The correlation between heavy metals analyzed in the present study are shown in(Table 2).

Table 2: Pearson correlation(r) between heavy metals concentration in plants from the study area.

Heavy metals	Cu mg/kg	Pb mg/kg	Zn mg/kg	Cd mg/kg
Cu mg/kg	1			
Pb mg/kg	0.742**	1		
Zn mg/kg	0.801**	0.404	1	
Cd mg/kg	0.884**	0.763**	0.620**	1

Correlation is significant at the 0.01 level (2-tailed).

The results showed a strong positive correlation at ($p<0.01$) level were found between (Cu-Pb)(r=0.742),(Cu-Zn)(r=0.801)(Cu-Cd)(r=0.884),(Cd-Pb)(r=0.763) and (Cd-Zn)(r=0-620), A high positive correlation among studied metals which may indicate that these metals are from the same sources(Jose et al., 2017; Lv et al., 2015) . On the other hand, non- significant correlation ($p>0.01$) were observed between (Zn-Pb)(r=0.404) and a similar relationship was obtained by (Najmi et al., 2023) between(Zn-Pb)(r=0.131). However, these results contract with (Olowoyo et al., 2015) ,who observed a strong positive correlation between(Zn-Pb)(r=0.99).

* Conclusions

This study showed that plants such as Eucalyptus gomphocephala, Olea europaea, Pinus halepensis, Nicotiana glauca L and Ricinus communis grown around cement factory (polluted area) in Benghazi were higher concentration of Copper(Cu), Zinc(Zn), Cadmium(Cd) and Lead(Pb) than control site(unpolluted area). In general, the concentration of these metals in all samples analyzed was below the FAO/WHO standard, except for Cd in polluted site. Correlation between heavy metals in different plants and different sites were calculated and a positive correlation is observed. Ricinus communis leaves showed significant accumulation of heavy metals within the atmosphere close to the polluted area were more other plants in this study, therefore our data indicate the R.communis can be a highly useful biological indicator.

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