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Evaluation of Lead, Copper and Iron Concentrations in *Cyprus papyrus* and Rivers in Iraq

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Abstract: In February 2023, samples were gathered from the research location. Five samples were taken from each leaf of the aquatic plant *Cyprus papyrus*, which is a member of the Cyperaceae family, as well as from the Tigris and Euphrates rivers. The primary heavy metals detected were lead (Pb), iron (Fe), and copper (Cu). Samples were collected from various areas in Iraq, including the Diyala River site, AL Rustamiya site, Karbala site, Babylon site, and AL-Rashdiya site as a control. The samples collected from each site consisted of water and *Cyprus papyrus*. The ICP-AES analysis successfully determined the concentration of elements in the samples. The results indicated that the Pb average concentration in plants varied across different sites, with the highest levels recorded in Diyala River, followed by AL Rustamiya, Babylon, Karbala, and Rashdiya sites (Control) at 3.67, 2.11, 0.55, 1.26, and 0.046 ppm, respectively. These values were compared with the UNEP standard of 0.01 ppm. Similarly, water samples also exhibited elevated levels of Pb average concentration in the same order of sites, with values of 2.97, 0.48, 0.41, 0.35, and 0.0891 ppm, compared with the UNEP standard of 0.005 ppm. Furthermore, the analysis of Fe average concentrations in plants revealed the highest levels in Diyala River, Babylon site, AL Rustamiya site, Karbala site, and Rashdiya (Control) at 0.5, 0.4, 0.3, and 0.1 ppm respectively. In water samples, Fe average concentrations were also found to be elevated in the same order of sites, with values of 1.3, 0.07, 0.06, 0.03, and 0.01 ppm. The presence of Cu was not detected in any of the samples collected from either plants or rivers. The aim of this study was to evaluate the levels of heavy metals in the Iraqi environment and examine their impact on living organisms.

Key words: Heavy metal, *Cyprus papyrus*, lead, iron, copper.

Introduction

Heavy metals (HV) are defined as elements with a density exceeding 5 gr/cm^3. These HV can be further categorised into two groups: essential and non-essential elements. Selenium (Se), cobalt (Co), chromium (Cr), zinc (Zn), manganese (Mn), and Cu are vital components necessary for fundamental cellular processes, specifically enzymatic reactions, in all living organisms at minimal concentrations. Higher levels of HV can have toxic effects on the body and disrupt its normal functioning (Ali & Khan, 2018). The accumulation and transfer of these metals in the environment can increase the chances of them entering the food chain, leading to the development of various diseases in humans (Shah & Daverey, 2020). Aquatic systems contain varying amounts of HV, which include both essential and non-essential metals. Inadequate

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metal concentrations can lead to adverse physiological, histological, and morphological effects (Al-Taee et al., 2020). Contaminant levels in fish are a significant issue as they pose risks to human and public health (Al-Sarraj, 2013; Jasim, 2017). The polluted waterways of Iraq, such as the Euphrates and Tigris rivers, stand as the largest rivers in Iraq and serve as crucial resources for the advancement of aquaculture. Over the years, these rivers have been utilised for various purposes including human consumption, agricultural irrigation, and industrial operations. The presence of pollutants in their natural state can result in harm to the aquatic ecosystem and may also present a health hazard to humans. Various harmful external substances, such as organic pesticides, polynuclear aromatic hydrocarbons (PAHs), phytoplankton, algae, excessive chemotherapeutic agents, and sodium chloride, are introduced into the aquatic environment (Al-Mayahi et al., 2021). HV poses a significant challenge to aquatic organisms (Authman et al., 2015). Due to their resistance to biological degradation, HV tends to accumulate in the aquatic ecosystem, either in the form of sediment or by becoming concentrated within aquatic plants and animals. Additionally, these metals may also interact with other components present in the water column, resulting in the creation of even more toxic compounds (Oguzie, 2003). Fishes can be exposed to HV either indirectly through their skin and gills or directly through the ingestion of contaminated water or food sources (Rajesh kumar & Li, 2018). Consequently, the presence of HV can have detrimental effects on various organs, including the intestine, liver, and other bodily tissues, even when present in low concentrations. The presence of HV, i.e., Pb, can cause significant damage to these organs (Jaber et al., 2021; Yousif et al., 2021).

Material and Methods

Overview of the Study Region

The pollution levels in the Tigris and Euphrates rivers in Iraq were investigated in relation to various sources such as residential areas, industrial petrochemical materials, sewage, crude oil waste, and electrical energy (Figure 1). In order to assess the impact of these pollutants on the surrounding environment, five specific locations were chosen based on the dominant plant species and water characteristics. These sites included the Diyala river site (Water, *Cyprus papyrus*), AL Rustamiya site (Water, *Cyprus papyrus*), Karbala site (Water, *Cyprus papyrus*), Babylon site (Water, *Cyprus papyrus*), and AL-Rashdia site as a control (Water, *Cyprus papyrus*).

Samples

The specimens were gathered from the research location in the month of February 2023. Ten replicates of leaf samples of each site from the aquatic plant *Cyprus papyrus*, which belongs to the Cyperaceae family, were collected. The leaves were thoroughly rinsed with deionised water and dried outdoors at room temperature for 3-5 days. Subsequently, they were ground with a mill and sifted through a 1 mm diameter sieve in preparation for analysis. In total, there were 50 plant samples collected from the sites.

Figure 1: Location of pollution in Tigris and Euphrates rivers *Cyprus papyrus* in Iraq.

Ten replicates of water samples of each site were gathered from the surface water. In total, there were 50 water samples from the sites; with each sample being collected using 20-liter containers, from a depth of approximately 30 cm below the surface. Water samples were obtained by means of a Van Dorn water sampler, subsequently undergoing immediate filtration through 0.45µ Millipore filters. The filtrates were stored in glass or plastic containers and subsequently frozen until the time of analysis, in accordance with established protocols (Ahmad & Bajahlan, 2009; Pearson & Havill, 1988).

Experimental Procedure

Preparation of Samples for Analysis Using Top Wave

Ataro et al. (2008) stated that in the digestion preparation of all leaf plant samples, water samples were filtered through filter paper to determine the levels of Pb, Cu, and Fe. The conversion of the leaf of the *Cyprus papyrus* plant into a liquid form necessitates the implementation of a precise regulatory method, involving the processes of melting and validation. This is crucial in order to facilitate the subsequent analysis of the liquid sample using the Top wave.

In the case of leaf *Cyprus papyrus* samples, a quantity of 0.3 g of the samples should be weighed and subsequently transferred into vessels. Then, 7.5 ml of nitric acid, HNO_3, 65% should be added to the vessels. After ensuring the mixture is thoroughly mixed either by shaking it carefully or stirring it with a clean glass bar, it is advised to wait for a minimum of 20 minutes before closing the vessels (Figure 2).

Inductively Coupled Plasma Emission Spectrometry (ICP-AES) to Identify the Concentration of HV in Plants and Water

The specimens were diluted in a 1:1 ratio with 0.2% (v/v) HNO_3 and subjected to centrifugation at 2000 rpm for a duration of 20 minutes. Prior to utilisation, all sample vials, sample cups, and glassware underwent a cleaning process involving immersion in a solution of 10% (v/v) HNO_3 and rinsing with deionised water. The suitable criteria for every component were established based on the concentration levels of the elements found in the samples. An inductively coupled plasma atomic emission spectrometer (ICP-AES) operates by introducing a finely dispersed aerosol generated from a liquid sample into the core of argon plasma. This plasma is formed by subjecting a stream of gas to a high-energy field, resulting in gas ionization and the generation of significant heat. The temperatures within the ICP plasma can soar up to 10000K. Upon introduction of the sample into the plasma, the mist undergoes dissociation of its chemical compounds due to the high temperature. This energy absorption leads to excitation and ionization, resulting in the breakdown of the compounds into distinct spectral lines. Subsequently, a computer interprets these spectral lines and converts them into concentrations for a specific set of elements according to the guidelines set by the American Public Health Association (APHA, 2005), as shown in Figure 3.

Figure 2: Top wave for digest leaves of plants.

Figure 3: Inductively coupled plasma emission spectrometry (ICP-AES) to identify the concentration of HV in plants and water.

Result and Discussion

Pb in a Leaf of Plants

The findings indicated variations in the levels of Pb concentration in plants across different regions, which can be attributed to their varying capacity to absorb this particular element. Specifically, the levels were observed to be highest in the Diyala river area, followed by the AL Rustamiya site, Babylon site, Karbala site, and finally the Rashdia site (Control) as Figure 4. These variations in Pb concentration could potentially signify the presence of pollution in the study areas, thus serving as an indicator for contamination. The levels indicated align with certain scientists in regional investigations (Ajmi, 2012; ALeh et al., 2015) discovered Pb in *Ceratophyllum demersum* ranging from 0.3 to 1.9 ppm and in *Phragmites australis* ranging from 0.6 to 1.8 ppm. Howari & Banat (2001) documented the highest Pb concentration in a plant (*C. demersum*) at 0.23-2.01 ppm. Aquatic plants have been observed to possess the ability to accumulate Pb from their surrounding environment (Ajmi, 2010). Their widespread distribution according to Brancovic et al. (2010). The elevated levels of Pb found in leafy plants can be attributed to the absorption of inorganic complexes due to their increased surface area relative to their volume as indicated by Kasowska et al. (2017). The typical concentration of Pb in the leaf tissues of fully-grown plants cultivated in uncontaminated soil typically falls within the range of (0.01-0.1ppm). If the Pb concentration exceeds (3 ppm), it can be harmful to the plant (UNEP, 2012).

Pb in Water

The analysis of water samples revealed elevated levels of Pb concentration, particularly in the Diyala River, AL Rustamiya site, Babylon site, and Karbala site, while the Rashdia site served as the control group as shown in Figure 4. The discharge of pollutants into water is considered one of the most significant environmental hazards. The current study reveals a positive correlation between the presence of trace metals in the environment and the accumulation of elements resulting from untreated industrial waste, sewage water, and agricultural pesticides. This cumulative source of pollution has persisted for many years, as highlighted by the World Health Organization. It is considered an environmental crime that impacts all forms of life,

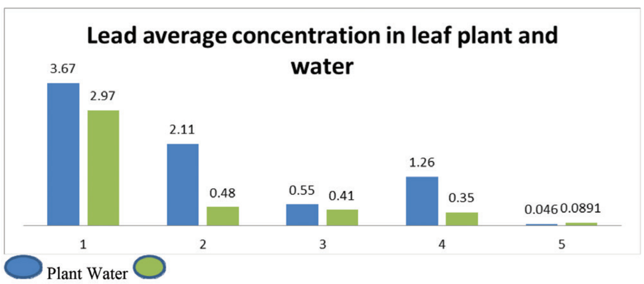

Figure 4: Average concentration of Pb of leaf plant and water samples in all sites.

leading to alterations in the genetic makeup of aquatic organisms, soil, and water elements. The findings demonstrate the detrimental impact resulting from the elevated levels of Pb in plants and the surrounding water in each region. A site was designated as a disposal area for industrial waste, and sewage water, and an oil company was established to extract crude oil, as shown in Figure 4.

Fe in Plants

The findings of this research indicate that the greatest levels of Fe in plants were detected in the following order: Diyala River > Babylon site > AL Rustamiya site > Karbala site >Rashdia (Control) as Figure 5. The Fe element values in plant samples from Shatt Al-Arab, as reported by Talal et al. (2020), range from 16.12 to 42.12 ppm. On the other hand, the average concentration of Fe in Mangrove plants from the Al-Budhai region, Red Sea Coast, Kingdom of Saudi Arabia is 560.45 ± 95.36, according to Al-Mur (2021). In a study conducted by Rani et al. (2021), it was discovered that the concentration of Fe (Fe) in *Nardostachys jatamansi* obtained from the Indian Wholesale Market-Khari Baoli was recorded as (8.716 ± 0.386 ppm). Similarly, Fagbote & Olanipekun (2010) reported that the concentration of Fe in *Chromolaena odorata* during the dry season was found to be 44.80±3.31 ppm, while during the rainy season it was measured as 35.77±3.68 ppm. Additionally, Al-Khlaifat & Al-Khashman (2007) determined that the leaves of *Phoenix dactylifera L.* contained a value of 265 ppm of Fe at industrial sites. Fe is an essential component of enzymes and pigments, and it plays a crucial role in the metabolic processes of both plants and animals. Fe toxicity is a relatively infrequent occurrence; nevertheless, it can pose a toxic threat if consumed in excess of the allowable thresholds. The elevated concentrations of Fe can be ascribed to the extensive industrial operations in the vicinity and the assimilation of Fe from the soil by the roots of plants (Celik et al., 2005).The typical concentration of Fe in the leaf tissues of fully developed plants cultivated in unpolluted soil falls within the range of 100 to 500 ppm. Fe levels exceeding 500 ppm are considered harmful to the plant's health (Neenu & Ramesh, 2020).

Fe in Water

The Fe concentration in water samples was found to be elevated, with high levels detected in various locations including Diyala River, Babylon site, AL Rustamiya site, Karbala site, and Rashdia (Control) as Figure 5. The research conducted analysed the concentrations of HV present in both soil and water samples collected from the Heshkaro stream located in Duhok city, Northern Iraq. The findings revealed that the levels of Fe ranged from 0.0032 to 2.2 ppm (Zeki & Dilshad, 2019). Similarly, investigations carried out in the Tigris River during the dry season indicated concentrations ranging from 0.062 to 2.03 ppm, whereas, during the wet season, the levels were recorded between 0.12 and 0.29 ppm (Aljanabi et al., 2022). Furthermore, a study by Salah et al. in Amiriyah Fallujah, Anbar reported a concentration of 0.340 ppm (Salah et al., 2015). In the northern part of Shatt Al-Arab, the Fe content in water samples ranged from 9.52 to 14.97 ppm (Talal et al., 2020). The Fe content in the waters of River Ghagga varied from 0.11 to 2.2 ppm (Pareek et al., 2018). The research conducted by Igwemmar found evidence of HV presence in various fish species. Among the metals detected, Fe was the most prevalent across all fish species, with tilapia fish exhibiting the highest concentration at 6.12 ppm (Igwemmar et al., 2013). The typical concentrations of Fe in household, tap, and aquatic environments are 0.3, 1.0, and 0.1 ppm as reported by De (2005).

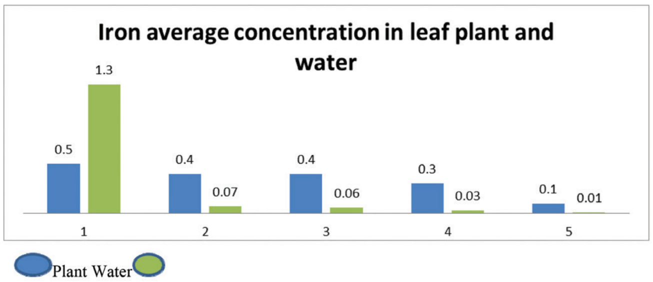

Figure 5: Average concentration Fe of leaf plant and water samples in all sites.

Mercury

Copper levels in both the *Cyprus papyrus* plant and water in at all sites, as detected by the ICP-AES instrument appeared negative when compared to the calibration and the results cannot be used (below the detection limit). Therefore, it is ignored and marked as zero. In our investigation, we observed that none of the concentrations examined posed any detrimental effects on the environment, in accordance with global standards. This holds true for both aquatic organisms residing in rivers and plants that serve as a vital source of sustenance for living beings. Consequently, it is not viable to rely on these concentrations as indicators of pollution in ecological contexts.

Conclusion

Our research findings indicate that the plant *Cyprus papyrus* serves as a phytoaccumulation agent for HV, offering environmental benefits. However, it is important to note that this can also pose a threat because the plant is consumed by animals. Furthermore, rivers are contaminated with HV due to various sources including factories, sewage, and other pollutants.

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