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# ASSESSMENT OF HEAVY METALS IN SEDIMENTS AND PHRAGMITES AUSTRALIS IN TIRANA RIVER, ALBANIA

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## ABSTRACT

In recent years, rivers and coastal waters were seriously polluted by the pollutants of industrial and urban establishments discharged in them, and heavy metal was the main pollution. The objective of current study was to assess the occurrence of heavy metals in sediments and investigated in Phragmites australis samples from the bed of the Tirana River in Albania. The genus Phragmites has proven ability to mitigate the environmental pollution of its surroundings. Five sampling points were selected to collected sediment samples and common reeds (5 roots and 5 leaves ). The heavy metals contents in sediments were in the following ranges (mg/l) Zn 36.6-53.9 (±6.53), Cu 125.4- 188.9 (±25.93), Ni 137.8- 165.8 (±10.9), Cr 120.8-175.9 (±26.35), Mn 584.9 -1098.6 (±191.96), Fe 28864.2 - 38465.5 (±4316.41). Sediments sample were collected in depth 0-20 cm and were prepared accordin to standart procedures. Heavy metals in sediment and in plants were analized with atomic absorption spectrophotometer technique. The degree of sediment pollution was evaluated by using Bioconcentration Factor (BCF) and Translocation ability (TA*)*. The research proved a strong positive correlation between the concentrations of metals in the sediment and all common reed. Concentrations in belowground organs were usually higher than aboveground organs, and the general decreasing trend of element content was roots > leaves.

**Keywords:** Heavy metals, plant organ, sediment, Tirana River.

## INTRODUCTION

Sediment analyses are more useful to detect pollution problems and sources, especially for contaminants that are rapidly absorbed by particulate matter and consequently would not remain in water samples for long. Knowing the mechanism of accumulation, distribution and metabolism of metals in aquatic macrophytes is of great ecological, scientific and practical importance (Kastori *et al*., 1997). In aquatic ecosystems, rooted macrophytes such as reeds *P. australis* are under greater influence from metals coming from sediments than those coming from the water, and therefore bioaccumulation is greater if the sediment contains higher concentration of metals (Zwolsman *et al*., 1993).

As a good bioacumulator of chemical elements, (Duman *et al*., 2007; Bragato *et al*., 2009), the common reed has found a wide application in the treatment of municipal and industrial wastewater loaded with metals (Bragato *et al*., 2009; Lesage *et al*., 2007). Numerous studies have pointed to a positive correlation between the metals in the sediment and various reed organs (Peverly *et al*., 1995; Wang *et al*., 1997; Bonano and Lo Giudice, 2010; Bonano, 2011).

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In this study it has been found the level of heavy metals in sediment and in common reed in Tirana river bed exactly at Laknas bridge. Therefore, the objectives of this paper are: to give a pilot screening of metals content in aquatic plants from various and to determine the degree of contamination of the Tirana River.

## MATERIALS AND METHODS

### Study area

This study analyzed metals in *P. australis* (Cav.) Trin. et Steud. 1841 and the sediment from the Tirana river in Albania. The samples of the sediment and the plants are taken at Laknas bridge with latitude 41$^{o}$ 22’33’’N and longitude 19$^{o}$ 44’51’’E. Tirana River is one of the branches of the Ishmi river, which flows into the Adriatic Sea near the Rodoni Bay. It has a length of 35 km and is the shortest river of this region compared with Erzeni and Terkuza. This river stems in the Hurmëza village being supplied with water selita and several streams that floë into his bed. Passes through the Shali area, Zall Dajtit, Brar, Tufinë, Ferraj and traverses the field of Tirana, pervades Domje village and join with Terkuza river to forming Ishmi river, which continues the path to shed in the Adriatic Sea. Anthropogenic influences cause permanent pollution from communal, industrial or agricultural activities.

### Sample collection

All plant material was sampled at five point at Laknas bridge in Tirana river. Laknas bridge was at 30 km from of the flow refer to the upstream distance from the confluence with the Ishmi River. Each sampling point, were collected within a 5 m distance between them. All the plant species had the same habitat, weather conditions dhe with an average height. Sampling of the plant material was conducted in areas bordering the river bank, and subject to periodic flooding. After collection, the plant samples were put in sealed plastic bags to avoid extraneous contamination.

The month of September was chosen because it coincides with the peak of the vegetative period of the common reed during which trace element concentrations generally show the highest values in the plant organs (Bonano, 2011). Sediment samples were collected along the Tirana river using a metalic corer. After sampling sediments were packed in polyethylene bags and transported to the laboratory.

***Figure 1.*** *Study area. Five sites of plant samples (5 rhizome and 5 stems with leaves) and five sediment sample.*

**Sample analysis**

At the Laknas Bridge is analised the heavy metals in sediment and common reed at five location. Plant samples were preliminarily dissected into roots and leaves which were homogenized in an electric blender and stored in plastic bags until analysis. The samples were taken in 0-20 cm depth. In the laboratory the sediment samples were dried, were pounded in a porcelain mortar and pestle to break up to the aggregates. All the concentration of heavy metals were express in mg/l. Heavy metals were analyzed according Atomic Absorber Spectrophotometry method (AAS), at Technologies Transfer Center in Fushĕkrujë.

**Data analysis**

*Bioconcentration Factor (BCF)*

The *BCF* provides an index of the ability of the plant to accumulate the metal with respect to the metal concentration in the substrate.The *BCF* was calculated using Equation 1.
*BCF* = [Metal] plant / [Metal] sediment. (Eq.1)
A larger ratio of BCF implies better phytoaccumulation capability. (Gakwavu et al., 2012 ).

*Translocation ability (TA)*

The translocation ability was calculated by dividing the concentration of an element accumulated in the root. *TA* was calculated using Equation 2.
*TA* = [Metal] root / [Metal] part of the plant. (Eq.2)
*TA* > 1 indicates that plants efficiently translocated metals between different organs (Baker *et al*., 1994).

**RESULTS & DISCUSSION**

Contents of metals (in mg.l of dry mass) in the sediment of the Tirana River bed are given in *Table 1*.

***Table 1.*** *Heavy Metal concentrations (Zn, Cu, Ni, Cr, Fe, Mn,) in sediments (in mg/l).*

| **Sample location** | **Zn** | **Cu** | **Ni** | **Cr** | **Mn** | **Fe** |
|---|---|---|---|---|---|---|
| **L1** | 45.7 | 188.9 | 137.8 | 172.3 | 768 | 38465.5 |
| **L2** | 50.7 | 145.8 | 145.9 | 128.9 | 584.9 | 37756.3 |
| **L3** | 53.9 | 132.9 | 158.7 | 120.8 | 890.5 | 30456.8 |
| **L4** | 46.3 | 166.8 | 150.6 | 175.9 | 934.2 | 28864.2 |
| **L5** | 36.6 | 125.4 | 165.8 | 169.3 | 1098.6 | 32472.9 |
| **Min** | 36.6 | 125.4 | 137.8 | 120.8 | 584.9 | 28864.2 |
| **Max** | 53.9 | 188.9 | 165.8 | 175.9 | 1098.6 | 38465.5 |
| **Mean** | 45.25 | 157.15 | 151.8 | 148.35 | 841.75 | 33664.9 |
| **SD** | 6.53 | 25.93 | 10.90 | 26.35 | 191.96 | 4316.41 |

***Table 2.*** *Heavy metal concentrations in root and leave at plant at different localities in mg/l.*

| **Samp Locat.** | **Zn** | | **Cu** | | **Ni** | | **Cr** | | **Mn** | | **Fe** | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Root** | **Leave** | **Root** | **Leave** | **Root** | **Leave** | **Root** | **Leave** | **Root** | **Leave** | **Root** | **Leave** |
| **L1** | 13.8 | 12.2 | 4.0 | 3.1 | 0.9 | 0.6 | 0.09 | 0.03 | 0.5 | 0.2 | 3.9 | 2.0 |
| **L2** | 13.2 | 12.6 | 4.0 | 5.0 | 0.9 | 0.8 | 1.07 | 0.08 | 0.4 | 0.3 | 3.0 | 2.1 |
| **L3** | 12.9 | 12.5 | 5.2 | 4.0 | 0.8 | 0.5 | 0.06 | 0.08 | 0.4 | 0.2 | 2.4 | 2.8 |
| **L4** | 12.6 | 13.0 | 3.4 | 4.5 | 0.8 | 0.6 | 0.05 | 0.07 | 0.3 | 0.3 | 2.1 | 3.2 |
| **L5** | 12.8 | 12.0 | 2.9 | 3.1 | 0.4 | 0.4 | 0.07 | 0.04 | 0.2 | 0.2 | 2.1 | 2.0 |
| **Min** | 12.6 | 12.0 | 2.9 | 3.1 | 0.4 | 0.4 | 0.05 | 0.03 | 0.2 | 0.2 | 2.1 | 2.0 |
| **Max** | 13.8 | 13.0 | 5.2 | 5.0 | 0.9 | 0.8 | 1.07 | 0.08 | 0.5 | 0.3 | 3.9 | 3.2 |
| **Mean** | 13.2 | 12.5 | 4.05 | 4.05 | 0.65 | 0.6 | 0.56 | 0.055 | 0.35 | 0.25 | 3 | 2.6 |
| **SD** | 0.466 | 0.384 | 0.860 | 0.844 | 0.207 | 0.148 | 0.448 | 0.023 | 0.114 | 0.054 | 0.764 | 0.549 |

Based on the results obtained, conclusions can be made about the concentrations of the tested metals in the ecosystem of the river Tirana. Contents of metals (in mg/l of dry mass) in the sediment of the Tirana River bed are given in *Table 1*. The declining trend of metal concentrations in the sediment is the following: Fe>Mn> Cu> Ni> Cr> Zn. Fe followed by Mn had the highest accumulation values for all sites. The contents of metals (in mg/l of dry mass) in roots and leaves of the common reed (*Table 2*) at different localities revealed a trend of decline as follows:

• In roots: Zn > Cu > Fe > Ni > Cr > Mn

• In leaves: Zn > Cu > Fe > Ni > Cr > Mn

Considering the average values for the contents of metals, bioaccumulation was the greatest in the roots of the common reed, and least in the leaves.

Based in the analizes value the metals as Zn, Ni, Cr, Mn dhe Fe showed the hight concentration in root than in leaves.

***Bioconcentration Factor (BCF)***

Plants playing an important role in metal removal via filtration, adsorption, cation exchange, and through plant–induced chemical changes in the rhizosphere.
The greatest *BCF* values were recorded for Zn and the lowest for the other metals (*Table 3*).
***Table 3.*** *Biological Concentration Factor.*

| **Metals** | **L1** | | **L2** | | **L3** | | **L4** | | **L5** | |
|---|---|---|---|---|---|---|---|---|---|---|
| | **Root/ sedim** | **Leave/ sedim** | **Root/ sedim** | **Leave/ sedim** | **Root/ sedim** | **Leave /sedim** | **Root/ sedim** | **Leave/ sedim** | **Root/ sedim** | **Leave/ sedim** |
| **Zn** | 0.301 | 0.266 | 0.26 | 0.248 | 0.23 | 0.231 | 0.272 | 0.28 | 0.349 | 0.327 |
| **Cu** | 0.021 | 0.016 | 0.027 | 0.034 | 0.039 | 0.03 | 0.02 | 0.026 | 0.023 | 0.024 |
| **Ni** | 0.006 | 0.004 | 0.006 | 0.005 | 0.005 | 0.003 | 0.0053 | 0.0039 | 0.0024 | 0.0024 |
| **Cr** | 0.0005 | 0.0001 | 0.0083 | 0.00062 | 0.0004 | 0.00066 | 0.0002 | 0.00039 | 0.00041 | 0.00023 |
| **Mn** | 0.0006 | 0.0002 | 0.0006 | 0.0005 | 0.0004 | 0.0002 | 0.0003 | 0.0003 | 0.0001 | 0.0001 |
| **Fe** | 0.0001 | 0 | 0 | 0 | 0 | 0 | 0 | 0.0001 | 0 | 0 |

***Translocation ability (TA)***

The risk of metal transfer from soil to plant is evaluated on the basis of TA. In this study, interpretation of this parameter is done according to Baker (1981) Table 4.

***Table 4.****Interpretation of value of translation ability (TA)*

| ***Value of TA*** | ***Categorization of plant*** |
|---|---|
| *>1* | Accumulator- the plant has acucumulated metal |
| *~1* | Indicator- the plan is not influenced by the metal |
| *<1* | Excluder- the plant excludes the metal from the uptake |

***Table 5.*** *Translocation ability (TA) between the rhizome and emerged organs of reeds ( leaf) for particular metals at all five localities.*

| **Metals** | **Root /sediment** | **Root /leave** |
|---|---|---|
| Zn | 0.29 | 1.05 |
| Cu | 0.025 | 1 |
| Ni | 0.004 | 1.08 |
| Cr | 0.003 | 10.18 |
| Mn | 0.005 | 1.4 |
| Fe | 0.0004 | 1.15 |
| **Average values** | 0.053 | 2.64 |

The values of metal translocation ability are given in Table IV. Translocation between different parts of *P. australis* depended on the type of metal and the sampling period. All the investigated metals showed the highest translocation from the root to the above-ground organs. The most mobile metals were Cr, Mn and Fe, while the metals from root to sediment showed the lowest mobilities.

The research proved a strong positive correlation between the concentrations of metals in the sediment and all reed organs (roots and leaves). Accumulated metals in the common reed are not distributed evenly, but there are target organs for bioaccumulation. The underground

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organ (root) shows a higher storage capacity than the above ground parts (leaves). All common reed organs show a little *BCF* for the tested metals.

**Concentration of metals in Sediment and Plant**

Cr is not essential for plants and it is toxic even at low concentrations (A. M. Zayed..,2003). Chromium is a relatively scarce metal. Its occurrence and amounts in aquatic ecosystems are usually very low. Most elevated levels of chromium in aquatic ecosystems are a consequence of industrial activity (Anon b, 1996). In these investigations, Cr had the lowest bioaccumulation capacity of the examined concentrations in sediment and plants. The mean concentrations of chromium in sediments were in the range of 137.8–165.8 mg/1. The average values of the *BCF* for Cr during the entire investigation period were the lowest. The results of this study show that most of the adopted Cr was found in the roots than in leaves (Table I).

Copper is one of the world's most widely used metals (Anon b, 1996), and is regarded as a potential hazard (Anon e, 2003). Copper concentration in the sediment of the river Tirana (125.4 - 188.9 mg/l) (*Table 1*) is higher, while the value of the copper in the common reed is below the threshold of hytotoxicity (2.9–5.1 mg/l), according to Chaney (1989). Siedlecka *et al*. (2001) found a tendency to accumulate copper in the roots with very little mobility to the aboveground organs. However, the concentrations of copper in this study show the same values in the roots and the leaves (*Table 2*). It is one of the essential elements needed for the various enzymatic activities of plants.

Iron is the fourth most abundant element in the earth's crust and may be present in natural waters. It is an essential micronutrient for all organisms. The mean concentrations of iron in sediments were in the range of 28864.2–3846.5 mg/l. There were significant variations in the iron concentration found in the plants, which ranged from 2 to 3.9 mg/l. Iron has a low *BCF* because in the sediment it originates from the decomposition of rocks. The iron content in the sediment is linearly correlated to its presence in the plant organs and roots show very high values, while mobility through the tissues of *P. australis* is low (Bonanno, 2011), which was confirmed in this study.

Manganese is an essential micronutrient for plants and animals. The mean concentrations of manganese in sediments were in the range of 584.9–1098.6 mg/l. The content of manganese in the common reed (*Table 2*) was below the threshold of toxicity for plants which is 50–500 μg/g according to Allen (1989). The movement of manganese is especially fast towards the meristem tissue and reproductive organs, thus younger plant organs, whoseh metabolic processes are more intensive, are usually richer in manganese than older plants (*TA* between the roots and leaves is 1.4) (*Table 5*).

Nickel is a natural element of the earth's crust. It occurs naturally in the environment at low levels in sediment and plant. The obtained values for nickel in the sediment of the river Tirana (137.8 – 165.8 mg/l) (*Table 1*) were higher than the concentration determined in the reed roots can be considered dangerous for the plant (*Table 5*). Recently, nickel was recognised as one of the necessary elements for higher plants, because it was determined that it represents a component of enzymes important for normal life processes. Low concentrations of nickel are essential for plants, but at higher concentrations its toxic effects have been proved (Parida *et al*., 2003; Demirezen *et al*., 2007).

Zinc is an essential micronutrient for all organisms as it forms part of the active site in various metalloenzymes.The concentrations of zinc in the sediment of the river Tirana's bed (36.6-53.9 mg/l) (*Table 1*) were higher while the concentration of zinc in the common reed (*Table 2*) is 12-13.8 mg/l. According to these studies, Ni is a poorly accumulated element of sediment and has the lowest bioconcentration ratio BCF=1.05 for *P. australis.*

## CONCLUSIONS

The concentration of metals in various organs of *P. australis* varies depending on the location and time of sampling. Concentrations of Fe, Mn Cr, are below maximum legal concentration, except Ni and Zn. The common reed is a good indicator of the condition of the environment because a strong positive correlation was found between the concentrations of metals in the sediment and all reed organs (roots and leaves). Accumulated metals in the common reed are not distributed evenly, the underground organ (roots) shows a higher storage capacity than the above ground parts (leaves). Generally, metal mobility through the plant, from roots to leaves, is generally higher than from sediment to the plant.

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