Scientific Papers. Series E. Land Reclamation, Earth Observation & Surveying, Environmental Engineering. Vol. XI, 2022
Print ISSN 2285-6064, CD-ROM ISSN 2285-6072, Online ISSN 2393-5138, ISSN-L 2285-6064

THE USE OF *PECTINATELLA MAGNIFICA* AS BIOINDICATOR FOR HEAVY METALS POLLUTION IN DANUBE DELTA

Ira-Adeline SIMIONOV, Mădălina CĂLMUC, Alina ANTACHE, Valentina CĂLMUC, Ștefan-Mihai PETREA, Aurelia NICA, Victor CRISTEA, Mihaela NECULIȚĂ[3]

"Dunarea de Jos" University of Galati, 47 Domneasca Street, Galati, Romania

Corresponding author email: ira.simionov@gmail.com

Abstract

Water pollution with heavy metals is a persistent and hazardous issue, due to these pollutants incapacity to decompose and their tendency to accumulate in biota. These effects extend on the aquatic ecosystems from Danube Delta, which are subjected to anthropogenic pressures, due to intensive agriculture practices, intense tourism activities and the lack of sewage systems. In the context of global warming effects, alien species are developing in the waters of Danube Delta, such as Pectinatella magnifica. The present study explores the hypostasis according to which the aforementioned bryozoan can be used as a suitable bioindicator for heavy metals pollution in Soschi Lake, Danube Delta. Samples of water, sediments and biota were collected from the study area and the following metals were analysed: cadmium, lead, nickel, chromium, iron, zinc, copper, manganese and cobalt. The bioaccumulation factor was calculated, in order to highlight the accumulation potential of the bryozoan. The obtained values of metals concentration were compared to the national regulation related to the quality of surface waters. The following accumulation trend was identified in the bryozoan: Fe>Zn>Mn>Cu>Ni>Cr>Co>Cd>Pb.

***Key words**: bioindicator, Danube Delta, bryozoan, heavy metals.*

INTRODUCTION

Water resources are essential for sustaining human and animal life (Zamora-Ledezma et al., 2021). However, the quality of water resources is compromised by the global pollution crisis generated by urbanization and industrialization (Dai et al., 2022). Heavy metals are ubiquitous and persistent pollutants in an aquatic ecosystem due to their inability to decompose (Obinna & Ebere, 2019). Even though heavy metals are those metallic elements from the periodic table with an atomic density higher than water, a hazardous potential poses mainly lead (Pb), cadmium (Cd), nickel (Ni), and chromium (Cr), (Kinuthia et al., 2020).

In aquatic ecosystems, heavy metals represent a group of pollutants of priority concern, due to the associated health risks that they can pose on human consumers through transfer via the food chain (Dey et al., 2021). Also, the presence of heavy metals in water systems is considered an efficient tool for assessing the health of the ecosystem and levels higher after a certain limit can cause deleterious effects on the resident biota (Hasan et al., 2022). Thus, the need to monitor and assess water quality is well justified (Poshtegal & Mirbagheri, 2019). However, continuous monitoring of aquatic ecosystems involves the coverage of high spatial and temporal dimensions, which generate high economic costs (Rao et al., 2013).

In order to optimize the economic sustainability of the water quality monitoring activities, the scientific community proposes the use of bioindicators to assess the impact of a certain contaminant on the aquatic environment in which is present (Kadim & Risjani, 2022; Parmar et al., 2016; Zaghloul et al., 2020). Biological indicators are represented by any living organism (microorganisms, plants and animals) that is used as an instrument to detect pollutants in a target ecosystem (Zaghloul et al., 2020). The use of bioindicators for heavy metals water pollution has a series of advantages including the identification of early stages of pollution at relatively low concentrations (Kadim & Risjani, 2022; Parmar et al., 2016).

The ecological importance of Danube Delta is well known, being the largest river delta wetland in Europe and due to its abundant species biodiversity (Gómez-Baggethun et al., 2019; Güttler et al., 2013). Also, given the fact that global warming positively influences the spread of non-native species beyond their native habitat, it is expected that new species will arise as bioindicators for the invaded ecosystem (Finch et al., 2021).

Therefore, the present study aims to establish if an invasive bryozoan can be used as an efficient bioindicator for heavy metals pollution in Soschi Lake, Danube Delta.

MATERIALS AND METHODS

Samples of water, sediments and bryozoans were collected from Soschi Lake, Danube Delta (Figure 1) in September 2020.

The biological material used in the present paper is represented by the bryozoan *Pectinatella magnifica* (Leidy, 1851), which was retrieved from Soschi Lake, Danube Delta. This is the first time that the presence of this organism is reported in the Sfântu Gheorghe branch part of the Danube Delta. *P. magnifica* is a freshwater invertebrate specie, native to Mississippi River, eastern part of North America (Kollar et al., 2016; Todorov et al., 2020).

The magnificent bryozoan develops around submerged vegetation by forming large gelatinous colonies with ciliated tentacles. Each layer of zooids is attached to the firm and transparent jelly (Wang et al., 2016). The presence of this organism in water systems generates an increase in water transparency due to its feeding behaviour (Todorov et al., 2020). The magnificent bryozoan feeds through water filtration and it consumes high quantities of autotrophic and heterotrophic organisms such as diatoms, green algae, cyanobacteria, dinoflagellates, rotifers, protozoa, small nematodes, microscopic crustaceans (Năstase et al., 2017).

The biological material was stored in polyethylene bags and kept on ice until transportation to the laboratory (MoRAS Research Centre, "Dunărea de Jos" University of Galați) (Figure 2).

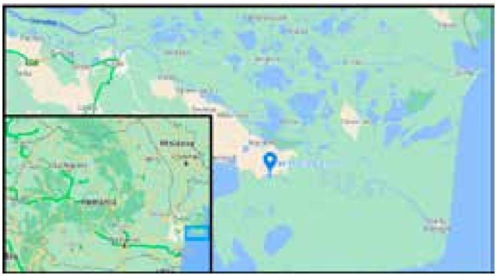

Figure 1. Study area – Soschi Lake, Danube Delta

Figure 2. *Pectinatella magnifica* (Leidy, 1851); (Bryozoa: Plumatellida:Pectinatellidae)

Sediment samples were place in Petri dishes and dried for 24 hours at 105ºC (Figure 3).

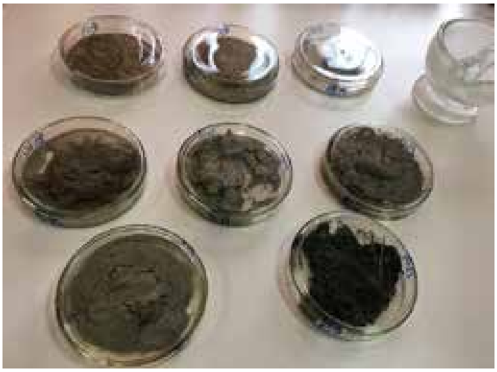

Figure 3. Dried sediment samples

Prior to analysis all samples were digested using nitric acid (Suprapure HNO_3 65-69%) and hydrogen peroxide (H_2O_2 38-40% for EMSURE Analysis) in a 5 step digestion program and by using TopWave equipment by Analytik Jena, Germany (Table 1).

Table 1. Techical parameters of the digestion program

Step	Temperature	Pressure	Ramp	Power
1	180	50	6	90
2	50	0	1	0
3	50	0	1	0
4	50	0	1	0
5	50	0	1	0

The digested sediment samples were filtered before analysis (Figure 4).

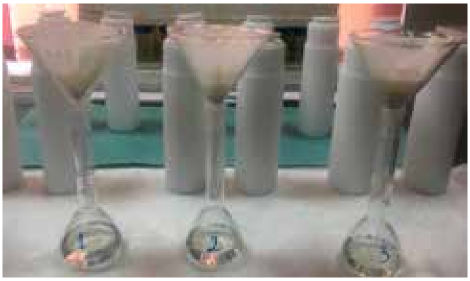

Figure 4. Sediment samples filtration

For the quantification of metals in the samples, the high resolution continuum source atomic absorption spectrometry was used (flame and graphite furnace techniques). The following elements were determined from the samples: potassium (K), sodium (Na), magnesium (Mg), iron (Fe), zinc (Zn), nickel (Ni), copper (Cu), chromium (Cr), manganese (Mn), cobalt (Co), lead (Pb) and cadmium (Cd).

In order to highlight the accumulation potential of *Pectinatella magnifica* the bioaccumulation factor (BAF) was calculated:

$$BAF = \frac{concentration\ of\ element\ in\ organism\ (\mu g\ g)}{concentration\ of\ element\ in\ sediments\ (\mu g\ g)}$$

RESULTS AND DISCUSSIONS

Macro-elements such as K, Na and Mg play an important role in heavy metals toxicity in aquatic environments. It is well known that the aforementioned ions compete with heavy metals for binding spots and that high concentrations of water hardness decreases the toxicity of heavy metals. The concentration of K, Na and Mg was significant much higher in the water (dissolved state) compared to the sediments (Figure 5). For instance, the concentration of Na registered values 20 times higher in the water compared to the sediments. The same phenomenon was observed in case of K and Mg. In case of iron concentration, the values registered in the sediments (9857 µg/g) were much higher than those in the water (26.98 µg/L). This could be explained by the fact that in highly oxygenated waters the iron dissolved in the water precipitates as $FeOH_3$.

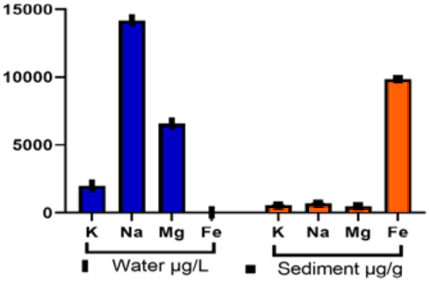

Figure 5. The concentration of K, Na, Mg and Fe in water and sediment samples

In case of the rest analysed heavy metals, it is highlighted that they concentrate in the sediments. For instance, the hydro-solubility of Cu is relatively low and this element tends to accumulate in the sediments (Weber et al., 2013). This phenomenon was observed in the present study also. As well, high amounts of Cu accumulate in water ecosystems due to the use of fungicides in agricultural activities, and the use of copper sulphate in the irrigation channels (Micó et al., 2006).

The toxicity of Zn decreases in waters with high alkalinity and salinity. Thus, in the present study it can be assumed that Zn precipitates in the sediments (25.97 µg/g) due to the high concentration of Na in the water column. Another metal which has the tendency to accumulate at the level of sediments was Mn and it registered values 7 times higher (110.27 µg/g) than those in the water (16.7 µg/L).

The toxicity of Ni is positively influenced by low values of water hardness and pH. In an aquatic ecosystem, Ni is found in trace amounts at the level of the water column and more than 90% of its concentration is associated to the particulate matter in the sediments. This phenomenon is highlight in our study also and the values in the sediments were approximately 20 times higher (37.330 µg/g) compared to those registered in the water matrix (1.781 µg/L).

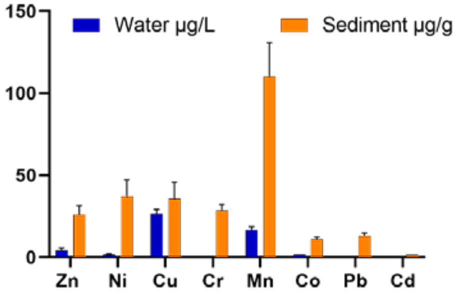

Figure 6. The concentration of different metals in water and sediment samples

The values registered for Cd and Pb concentrations were the lowest in the water samples (0.09, 0.06 µg/L respectively), compared to the sediments.

In the water column the analysed metals presented the following concentrations trend: K>Mg>K>Fe>Cu>Mn>Zn>Co>Ni>Cd>Pb.

In case of sediments samples, the accumulation trend registered the following decreasing values Fe>Na>K>Mg>Mn>Ni>Cu>Cr>Zn>Pb>Co>Cd.

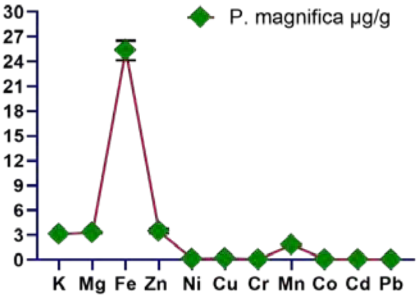

Figure 7. The concentration of elements in *P. magnifica*

The accumulation trend of the analyzed elements in the statoblasts of *Pectinatella magnifica* was as it follows: Fe>Zn>Mg>Na>Mn>Cu>Ni>Cr>Co>Cd>Pb.

Some metals are essential for the normal functioning of the living organism and they are involved especially in the enzymatic system. However, concentrations above a certain limit may become toxic. The highest concentration from all the analyzed metals, in the freshwater bryozoan was in case of Fe (25.337 µg/g) and the lowest was in case of Pb (0.015 µg/g). Iron is a component of some antioxidant enzymes such as catalase and peroxidase (Ben Salem et al., 2014). The toxicity of Fe in water ecosystems is enhanced by low values of pH and dissolved oxygen concentration.

The second most abundant metal in the *P. magnifica* was Zn (3.492 µg/g). According to (Trifan et al., 2015) Zn is a co-factor for over 200 enzymes and proteins involved in the redox process within the organism. The accumulation of Zn by aquatic organisms is dependent on the concentrations of nitrates within the surrounding environment (Anu et al., 2018).

In case of Cd and Pb, even low concentrations can pose a risk on the wellbeing of contact biota. In the living organism, Pb and Cd are not involved in any biological process, and thus, their presence in tissues can generate the inhibition of mineral absorption (through competing with the minerals for binding spots), disrupt the enzyme activity and deactivate the sulfhydryl antioxidant bonds. In natural waters, Cd and Pb are present in trace amounts and they are generated by natural phenomenon such as weathering of rocks. Both Cd and Pb are present in the aquatic environment as soluble and insoluble forms.

The bioaccumulation factor (BAF) was calculated only for the metals with the highest toxicity potential and are presented in Table 2.

Table 2. Results for the bioaccumulation factor

Element	BAF
Ni	0.003
Cu	0.006
Cr	0.001
Mn	0.01
Co	0.002
Fe	2.68
Zn	0.14

The BAF factor was computed as the ratio between the concentrations of elements in the *P. magnifica* to the concentrations in the sediment matrix. In this study it was chosen to use the sediment matrix instead of the water matrix due to the fact that the freshwater bryozoan develops on submerged vegetation, very close to the sedimentary substrate. The BAF is a reliable instrument for assessing the risks that heavy metals pose in the environment in which they are found in. Values for BAF above 1 indicate that accumulation is probable however only values greater than 100 are considered significant (Feng et al., 2020).

Thus, as it can be observed in Table 2, accumulation is probable only in the case of Fe. Meanwhile, in case of the rest analyzed metals (Ni, Cu, Cr, Mn, Co, Zn) the BAF registered values below 1 (Table 2), which indicates that accumulation is not manifested.

According to Jain et al. (2010) a suitable bioindicator presents specific characteristics such as:

- indication ability (has a measurable response to the presence of a certain contaminant);
- abundant and common in the study area
- well-studied (taxonomy well studied)
- be available all the year (in all seasons) in the study area.

Given the fact that the gelatinous mass of the freshwater bryozoan dissolves when water temperature drops, it should be considered that the accumulation of contaminants would be ceased during cold season. Thus, the data provided can not be reliable. This phenomenon is highlighted in the present study by the low values of BAF registered for the metals with highest toxicity potential.

CONCLUSIONS

Even though the freshwater bryozoan *Pectinatella magnifica* showed a potential for Fe accumulation, it can be concluded that it cannot be considered a suitable bioindicator in Danube Delta due to low BAF values for Ni, Cu, Cr, Mn, Co and Zn. Further studies are needed in order to apply more complex accumulation factors that can provide more information on heavy metals accumulation pattern of the studied organism.

ACKNOWLEDGEMENTS

This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS/CCCDI – UEFISCDI, project PN -III-P2-2.1-PTE-2019-0697, within PNCDI III.

This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number PN-III-P1-1.1-TE-2019-2062, within PNCDI III.

REFERENCES

Anu, P.R., Bijoy Nandan, S., Jayachandran, P.R., Don Xavier, N.D., Midhun, A.M., & Mohan, D. (2018). Toxicity effects of zinc on two marine diatoms, under varying macronutrient environment. *Marine Environmental Research*, *142*, 275–285. https://doi.org/10.1016/j.marenvres.2018.10.013

Ben Salem, Z., Capelli, N., Laffray, X., Elise, G., Ayadi, H., & Aleya, L. (2014). Seasonal variation of heavy metals in water, sediment and roach tissues in a landfill draining system pond (Etueffont, France). *Ecological Engineering*, *69*, 25–37. https://doi.org/10.1016/j.ecoleng.2014.03.072

Dai, C., Tang, J., Li, Z., Duan, Y., Qu, Y., Yang, Y., Lyu, H., Zhang, D., & Wang, Y. (2022). Index System of Water Resources Development and Utilization Level Based on Water-Saving Society. *Water*, *14*(5), 802. https://doi.org/10.3390/w14050802

Dey, M., Akter, A., Islam, S., Chandra Dey, S., Choudhury, T.R., Fatema, K.J., & Begum, B.A. (2021). Assessment of contamination level, pollution risk and source apportionment of heavy metals in the Halda River water, Bangladesh. *Heliyon*, *7*(12), e08625. https://doi.org/10.1016/j.heliyon.2021.e08625

Feng, W., Wang, Z., Xu, H., Zhang, D., Zhang, H., & Zhu, W. (2020). Species-specific bioaccumulation of trace metals among fish species from Xincun Lagoon, South China Sea. *Scientific Reports*, *10*(1), 21800. https://doi.org/10.1038/s41598-020-77917-y

Finch, D.M., Butler, J. L., Runyon, J.B., Fettig, C.J., Kilkenny, F.F., Jose, S., Frankel, S.J., Cushman, S.A., Cobb, R.C., Dukes, J.S., Hicke, J.A., & Amelon, S.K. (2021). Effects of Climate Change on Invasive Species. In T.M. Poland, T. Patel-Weynand, D.M. Finch, C.F. Miniat, D.C. Hayes, & V.M. Lopez (Eds.), *Invasive Species in Forests and Rangelands of the United States: A Comprehensive Science Synthesis for the United States Forest Sector* (pp. 57–83). Springer International Publishing. https://doi.org/10.1007/978-3-030-45367-1_4

Gómez-Baggethun, E., Tudor, M., Doroftei, M., Covaliov, S., Năstase, A., Onără, D.-F., Mierlă, M., Marinov, M., Doroșencu, A.-C., Lupu, G., Teodorof, L., Tudor, I.-M., Köhler, B., Museth, J., Aronsen, E., Ivar Johnsen, S., Ibram, O., Marin, E., Crăciun, A., & Cioacă, E. (2019). Changes in ecosystem services from wetland loss and restoration: An ecosystem assessment of the Danube Delta (1960–2010). *Ecosystem Services*, *39*, 100965. https://doi.org/10.1016/j.ecoser.2019.100965

Güttler, F.N., Niculescu, S., & Gohin, F. (2013). Turbidity retrieval and monitoring of Danube Delta waters using multi-sensor optical remote sensing data: An integrated view from the delta plain lakes to the western–northwestern Black Sea coastal zone. *Remote Sensing of Environment*, *132*, 86–101. https://doi.org/10.1016/j.rse.2013.01.009

Hasan, M., Rahman, M., Ahmed, A. al, Islam, Md. A., & Rahman, M. (2022). Heavy metal pollution and ecological risk assessment in the surface water from a marine protected area, Swatch of No Ground, north-western part of the Bay of Bengal. *Regional Studies in Marine Science*, *52*, 102278. https://doi.org/10.1016/j.rsma.2022.102278

Jain, A., Singh, B.N., Singh, S.P., Singh, H.B., & Singh, S. (2010). Exploring Biodiversity as Bioindicators for Water Pollution. *Nd May*, 7.

Kadim, M.K., & Risjani, Y. (2022). Biomarker for monitoring heavy metal pollution in aquatic environment: An overview toward molecular perspectives. *Emerging Contaminants*, *8*, 195–205. https://doi.org/10.1016/j.emcon.2022.02.003

Kinuthia, G.K., Ngure, V., Beti, D., Lugalia, R., Wangila, A., & Kamau, L. (2020). Levels of heavy metals in wastewater and soil samples from open drainage channels in Nairobi, Kenya: Community health implication. *Scientific Reports*, *10*(1), 8434. https://doi.org/10.1038/s41598-020-65359-5

Kollar, P., Šmejkal, K., Salmonová, H., Vlková, E., Lepšová-Skácelová, O., Balounová, Z., Rajchard, J., Cvačka, J., Jaša, L., Babica, P., & Pazourek, J. (2016). Assessment of Chemical Impact of Invasive Bryozoan Pectinatella magnifica on the Environment: Cytotoxicity and Antimicrobial Activity of P. magnifica Extracts. *Molecules (Basel, Switzerland)*, *21*(11), E1476. https://doi.org/10.3390/molecules21111476

Micó, C., Recatalá, L., Peris, M., & Sánchez, J. (2006). Assessing heavy metal sources in agricultural soils of an European Mediterranean area by multivariate analysis. *Chemosphere*, *65*(5), 863–872. https://doi.org/10.1016/j.chemosphere.2006.03.016

Obinna, I.B., & Ebere, Enyoh Christian. (2019). A review: Water pollution by heavy metal and organic pollutants: Brief review of sources, effects and progress on remediation with aquatic plants. *Analytical Methods in Environmental Chemistry Journal*, *2*(03), 5–38. https://doi.org/10.24200/amecj.v2.i03.66

Parmar, T.K., Rawtani, D., & Agrawal, Y.K. (2016). Bioindicators: The natural indicator of environmental pollution. *Frontiers in Life Science*, *9*(2), 110–118. https://doi.org/10.1080/21553769.2016.1162753

Poshtegal, M.K., & Mirbagheri, S.A. (2019). The Heavy Metals Pollution Index and Water Quality Monitoring of the Zarrineh River, Iran. *Environmental and Engineering Geoscience*, *25*(2), 179–188. https://doi.org/10.2113/EEG-1996

Rao, A.S., Marshall, S., Gubbi, J., Palaniswami, M., Sinnott, R., & Pettigrovet, V. (2013). Design of low-cost autonomous water quality monitoring system. *2013 International Conference on Advances in Computing, Communications and Informatics (ICACCI)*, 14–19. https://doi.org/10.1109/ICACCI.2013.6637139

Todorov, M., Kenderov, M., Botev, I., Hubenov, Z., & Trichkova, T. (2020). First Records of Pectinatella magnifica (Leidy, 1851) (Bryozoa: Plumatellida: Pectinatellidae) in the Bulgarian Shoreline Zone of the Danube River. *Acta Zoologica Bulgarica*, *72*, 611–617.

Trifan, A., Breabăn, I., Sava, D., Bucur, L., Toma, C.-C., & Miron, A. (2015). Heavy metal content in macroalgae from Roumanian Black Sea. *Revue Roumaine de Chimie*, *60*, 915–920.

Wang, B., Wang, H., & Cui, Y. (2016). Pectinatella magnifica (Leidy, 1851) (Bryozoa, Phylactolaemata), a biofouling bryozoan recently introduced to China. *Chinese Journal of Oceanology and Limnology*, *35*. https://doi.org/10.1007/s00343-017-6052-2

Weber, P., Behr, E. R., Knorr, C.D.L., Vendruscolo, D.S., Flores, E.M.M., Dressler, V.L., & Baldisserotto, B. (2013). Metals in the water, sediment, and tissues of two fish species from different trophic levels in a subtropical Brazilian river. *Microchemical Journal*, *106*, 61–66. https://doi.org/10.1016/j.microc.2012.05.004

Zaghloul, A., Saber, M., Gadow, S., & Awad, F. (2020). Biological indicators for pollution detection in terrestrial and aquatic ecosystems. *Bulletin of the National Research Centre*, *44*(1), 127. https://doi.org/10.1186/s42269-020-00385-x

Zamora-Ledezma, C., Negrete-Bolagay, D., Figueroa, F., Zamora-Ledezma, E., Ni, M., Alexis, F., & Guerrero, V.H. (2021). Heavy metal water pollution: A fresh look about hazards, novel and conventional remediation methods. *Environmental Technology & Innovation*, *22*, 101504. https://doi.org/10.1016/j.eti.2021.101504