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A Comparison between two Polychaete species; *Marphysa gravelyi* and *Dendronereis aestuarina* in terms of Heavy Metal Accumulation from three differently Polluted Mangrove Ecosystems of Northern Kerala, India

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ABSTRACT

Three separate mangrove ecosystems in Kerala's Kannur district were examined for trace metal build-up in sediment and two polychaete species, *Marphysa gravelyi* and *Dendronereis aestuarina*. By classifying the areas according to the intensity of anthropogenic activity, metal deposition in polychaete tissue was investigated. ICP-MS was used to assess the heavy metal load and the accumulation of metals in sediment in the range of, Zn 24.37-59 mg/kg, Ni 23.67- 59.25 mg/kg, Cu 11.27- 38.6 mg/kg, Pb 4.5- 16.4 mg/kg, Cd 0.1-1.8 mg/kg, Fe 1.25- 3.67 %, and Al 0.65-2.43 %. The soil sample's Zn concentration was at its highest and heavy metals accumulated in the pattern Zn>Ni>Cu>Pb>Cd. By just switching the concentrations of Ni and Cu, polychaetes' trace metal concentrations follow the same pattern as those found in soil, however, *M. gravelyi* was discovered to have larger amounts of accumulation when compared to *D. aestuarina*, mostly for metals like Zn and Pb. Based on data compiled from all stations, the average concentration of accumulation for Zn was 62.34 mg/kg & 43.45 mg/kg, and for Pb, it was 6.59 mg/kg & 1.86 mg/kg in *M. gravelyi* and *D. aestuarina*, respectively. Most metal buildup is found in mangrove soil, which has higher levels of organic carbon and clay particles. The findings imply that *D. aestuarina* is an organism that is sensitive to pollution and that *M. gravelyi* is a species that is extremely tolerant of pollution, suggesting that the species can be used to anticipate the state of its surrounding environment.

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INTRODUCTION

One of the most varied ecosystems, mangroves serve as habitats and nurseries for a wide range of animals and plants (Tangah et al., 2022). Mangroves provide a multitude of ecosystem services, such as flood protection, soil erosion control, water filtration, and wildlife habitat. However, one of the most significant functions of mangroves is their ability to regulate global climate change by sequestering a significant amount of carbon in the biosphere and mitigating the effects of increased CO2 emissions into the atmosphere (Navarro & Rodríguez-Santalla, 2023). In addition to their ecological significances, mangroves are very important from a human perspective for several additional reasons, including fisheries, aquaculture, forest products, firewood, local sustenance (Walters et al., 2008). In Kerala, the northern part has the highest mangrove cover and Kannur holds the maximum in district-wise analysis (Praveen et al., 2016). Due to the extensive human use of mangroves and the ecosystem, both nationally and internationally, total

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cover and variety have declined in recent years. Anthropogenic contamination has been the main cause of this loss, and important contributions include mining, urbanisation, fish farming, overfishing, and excessive wood removal for byproducts (Alongi, 2014; Bhowmik et al., 2022). The system is made vulnerable for the creatures in that environment by these human and natural actions. Land-based anthropogenic activities, including runoff from agriculture, the discharge of trash and wastewater, other commercial and mined wastes, and pollution from petroleum products, are the main causes of contamination of the mangrove environment (Dehghani & Karbassi, 2015). Owing to significant human involvement and the unique characteristics of the mangrove ecosystem, it not only absorbs more heavy metals from tidal water but also acts as a sink for those metals, which contributes to a high incidence of contamination (Tam & Wong, 2000; Parvaresh et al., 2011). Pollution is one of the main causes of the increase of heavy metals in the mangrove environment and the sediment contributes to the biogeochemical cycle of metals (Agoramoorthy et al., 2008). Numerous data from several nations indicate that the mangrove system is under increased stress because of the rise in heavy metal poisoning, and the situation is made worse by fast industrialization and urbanisation (Yan et al., 2017; Farooq et al., 2020; Guo et al., 2023). The assemblage of various organism varieties in mangroves is largely influenced by metal contamination in the ecosystem; greater accumulation leads to decreased abundance of susceptible populations and increased richness of resistant species (Roe et al., 2020). Due to the impacts of the dangerous heavy metal load, which ultimately poses a threat to life linked with the vital system, mangrove estuarine ecosystems around the world are experiencing the same problem and are on the verge of collapse (Chakraborty et al., 2009). The form and quantity of heavy metals released can have a long-lasting effect on an ecosystem, even though they might not have an immediate effect. Broad accumulation might also result from slow release (Bat et al., 2019). Benthic organism in mangrove has a great role in decomposition of organic matter, microbial mineralization, and sediment oxidation and finally make the system balanced (Heilskov et al., 2003; Lewis et al., 2014). In benthos, polychaetes are one of the largest groups with more than 80 families and play a crucial role in an ecosystem for evaluating ecological state of that particular environment (Bandekar et al., 2017; Pamungkas et al., 2019). Polychaetes have several specialised body characters to withstand the special environment including external gills, hard jaws, and elongated sensory appendages etc., (Glasby et al., 2021). The diversity and abundance of some polychaetes can vary based on the soil conditions in the area, which can aid in the assessment of environmental quality (Ghaffar et al., 2018). The majority of polychaetes in the mangrove ecosystems are detritivores or deposit feeders, so they will accumulate these contaminants through the food chain in their bodies. A small subset of these organisms, however, will migrate to the nearby, less polluted area if they are unable to survive in the polluted environment (Waring & Maher, 2005). The abundance and variety of polychaete species in a particular ecosystem can also be influenced by soil properties, such as particle size and nutrient availability, as well as anthropogenic contamination (Hutchings, 1998; El-Gendy et al., 2012; Farooq et al., 2020). Several research examined the sensitivity and tolerance of polychaete species to various metals and contaminants (Mtanga & Machiwa, 2007; Mdaini et al., 2020), but not in the specific species. In order to evaluate the level of heavy metal accumulation in two different polychaete species and its relationship to the local soil characteristics, an investigation was carried out.

MATERIALS AND METHODS

Study area

Three environmentally distinct mangrove ecosystems were selected by categorizing mangrove habitats according to the degree of anthropogenic activity in the system. The stations are spread over three distinct estuary systems in the northern region of Kerala (Fig.1.). Station

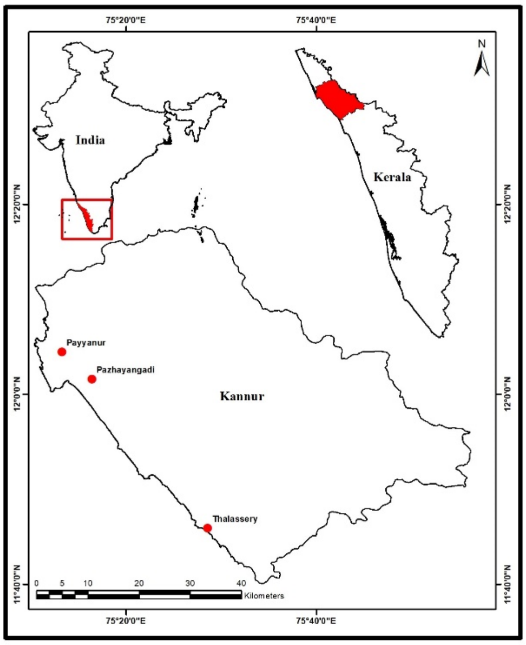

Fig. 1. The map shows sampling stations from three different estuary systems

1, Thalassery (S1) mangrove ecosystem is located on the Kuyyali River banks with moderate human activity and situated away from town. The station 2, Pazhayangadi (S2) mangrove system is situated along the banks of the Kuppam River, where there has been a disproportionate amount of human intervention, large amount of domestic trash disposal and situated very near the main settlement. Station 3, Payyanur (S3) mangrove system located on the bank of Perumba and has comparably less anthropogenic activity, garbage deposition and is situated very far from any urbanised area.

Sample collection

For the work two polychaete species which is most abundant and easily recognizable were selected (*Marphysa gravelyi* & *Dendronereis aestuarina*). Triplicate soil samples were collected from these three-ecosystem using random sampling method. After retaining a portion of the soil for analysis, the remaining soil was properly sieved (600 microns). In order to reduce mistakes, the segregated live polychaetes chosen for trace metal analysis were kept in treated brackish water to remove the gut dirt content. The collected soil samples dried and powdered and were kept in proper manner for analysing the key heavy metals (copper, nickel, zinc, lead, and cadmium), certain essential soil characteristics (pH and organic carbon), as well as iron and aluminium.

Pollution indices, such as the enrichment factor (EF) and geo-accumulation index (Muller, 1969), are used to determine the degree of heavy metal contamination of sediment. To monitor the effects of these metals' contamination on the mangrove ecosystem, variations over seasons and stations were evaluated. Additionally, using the Sediment Quality Guidelines Values (SQGV) method (Long et al., 1995; Simpson and Batley, 2016), the results of heavy metals were compared.

EF (Turekian & Wedepohl, 1961) was determined (for all metals with Fe as the conservative element) by using the equation:

$$EF = (M/Fe)_S / (M/Fe)_b$$

Where M_s and Fe_s are the concentrations of the heavy metal and iron in the sediment sample, while M_b and Fe_b are the concentrations of the specific metals in the appropriate baseline value.

geo-accumulation index calculated using the formula:

$I_{geo} = \log_2 (C_n/1.5\ B_n)$

Where, C_n is the measured concentration of metal in the sediment, B_n is the geochemical background value of the particular element in average shale and 1.5 is the background value correction owing to lithogenic influences.

Analysis of heavy metal accumulation

Polychaete samples that were separated and stored in brackish water were chosen for heavy metal analysis. A representative sample from the same group that has been identified up to the species level. The oven dried samples of two species and sediments were each measured, homogenised, and turned into 1g. The samples were then added to the concentrated nitric acid in a different beaker, and then digested on a hot plate. A constant volume of dissolved solution was collected for the detection of heavy metals. The trace metal concentration of the soil and polychaete tissues was determined using inductively coupled plasma mass spectrometer (ICP-MS, Thermo Scientific, iCAP RQ, USA), DST-SAIF, at STIC, CUSAT, Kochi. Both the pH (Jackson, 1958) and the amount of organic carbon (Walkley & Black, 1934) in the soil were measured. Granulometric analysis was employed for estimating the percentage contribution of the sediment particle size.

RESULT AND DISCUSSION

In the present study, sediment and two polychaete species groups were collected from three distinct sampling stations in the Malabar region of Kerala, and the concentrations of heavy metals (Zn, Cu, Ni, Fe, Pb, and Cd) and main physico-chemical parameters were determined. Metals differ significantly across the stations and the two species as well.

Sediment characteristics Physico-Chemical analysis

All sediment characteristics and measurements that were examined showed a similar pattern everywhere. Details about soil organic carbon, pH, temperatures, and the ratios of sand, silt, and clay are provided in Table 1. While the pH of the sediment at S1 and S2 is roughly neutral, that at S3 is slightly acidic. All stations had organic carbon levels that ranged from 1.9 to 3.93%, and S2 contained the highest percentage. When S1 and S2 are compared, S1 has sandy soil that contains 49.2 percent coarse sand. In comparison to the other two stations, S2 has the largest concentration of clay particles (56.4%) and the lowest percentage (23.9%) of coarse sand (Table. 1). However, coarse sand (62.5%) silt (16.6%), and clay (20.9%) were the most prevalent materials at S3.

Heavy metal accumulation in Sediment

The accumulation of metals in sediment in the range of, Zn 24.37-59 mg/kg, Ni 23.67- 59.25 mg/kg, Cu 11.27- 38.6 mg/kg, Pb 4.5- 16.4 mg/kg, Cd- 0.1-1.8 mg/kg, Fe 1.25- 3.67 % and Al 0.65-2.43 %. With the exception of Al and Fe (metals that are common in the earth's crust), the pattern of the accumulation of heavy metals in sediment was Zn>Ni>Cu>Pb>Cd. Except for the concentration of Ni from S2, all metals tested were below the range recommended by the Sediment Quality Guidelines Values (SQGVs), implying they cannot possibly harm

Table 1. Shows the percentages of clay, silt, and sand along with other important soil characteristics at three stations.

Station	pH	Temperature (°C)	Sand (%)	Silt (%)	Clay (%)	OC (%)
1	6.7	24	49.2	23.8	27	2.91
2	7	23	23.9	19.7	56.4	3.93
3	5.9	21	62.5	16.6	20.9	1.9

Table 2. Shows the correlation between key soil characteristics and heavy metal accumulation in soil

	1	2	3	4	5	6	7	8	9	10	11
pH	1										
TOC	0.966	1									
Sand	-0.907	-0.985	1								
Silt	0.644	0.427	-0.262	1							
Clay	0.815	0.936	-0.983	0.081	1						
Ni	0.843	0.953	-0.991	0.131	0.999	1					
Cu	0.988	0.916	-0.831	0.754	0.716	0.750	1				
Zn	0.988	0.916	-0.831	0.754	0.716	0.750	0.999	1			
Cd	0.782	0.916	-0.971	0.028	0.999	0.995	0.678	0.678	1		
Fe	0.997	0.983	-0.935	0.587	0.855	0.879	0.974	0.974	0.825	1	
Pb	0.996	0.986	-0.942	0.572	0.864	0.888	0.970	0.970	0.836	0.999	1

the creatures that live in the mangrove region (Long et al., 1995; Simpson and Batley, 2016). Long et al. (1995) proposed two guidelines: Effective Range Low and Effective Range Median. Except for Ni, Cu, and Pb, the metals in the current study's estimated value fall below the ERL value, indicating that their effects on benthic creatures are rarely detected. Since Cu, Pb, and Ni (S1 & S3) are located between ERL and ERM, the organisms in the area may "occasionally" be impacted. Ni concentration values from S2 over the impact range medium (ERM) "frequently" have the potential to damage benthic organisms in the mangrove ecosystem. Following EF was determined, a moderate enrichment value for Ni from S2 and a minor enrichment for Cu and Pb from S1 and S2 were found; Birch (2003) states that EF<1 denotes no enrichment, EF<3 denotes minor enrichment, and EF= 3-5 denotes considerable enrichment. According to the assessment of I_{geo} the heavy metal data from all stations fall into index class 1, with levels ranging from moderately contaminated to uncontaminated ($0<I_{geo}<1$). Other soil factors also influence how these metals are deposited in the ecosystem, as shown by the discovery that all metals followed the same pattern of fluctuation between stations.

According to the analysis, S2 (which is close to an adjacent town) has a greater quantity of pollutants than other stations. This is because more residential garbage is dumped there, which has led to higher levels of these metals in that area. unparalleled growth in industry and trash pollution in the adjacent town area is the reason for the non-essential heavy metal contamination in the south Gujarat estuaries (Dudani et al., 2017). Metals from this system are not dispersed due to the low water movement at S2. Guo et al. (2023) claimed that the metal pollution in an environment result from increased deposition caused by water with poorer hydrodynamics. Even the smallest amount of lead in the sediments of S2 can have negative consequences and endanger the life inside the system when it is produced as a result of numerous anthropogenic and industrial activities near the ecosystem. Pb, a non-essential heavy metal, is ingested by benthic organisms in minute amounts, where it slowly accumulates, and even shorebirds that devoured these animals were significantly impacted by their eating behaviour (Pandiyan et al., 2021). Heavy metals accumulate more readily in soil of S2 that has a larger proportion of organic matter and less sand (clay soil). Soil organic carbon and clay soil exhibit a positive relationship to soil heavy metals (Table. 2). The size of the sediment plays a critical role in the binding of the heavy metal in the mangrove and estuarine ecosystem. It is generally known that sediments with higher levels of mud and organic content have higher levels of metal enrichment (Mdaini et al., 2020). On the other hand, as sediment particle size decreased, the quantities of heavy metals increased. The greater surface area in small particles makes them more likely to bind to metals than coarse sediments, as observed by Zhang et al. in 2014, and the fine-grain particles significantly increased the metal concentration. Al concentrations in S2 material are higher than those in other sediments, indicating that the soil there contains more clay than other stations. According to Idardare et al. (2008), the Moroccan lagoon's Khnifiss sediment has a greater level of Al concentration than Qualidia sediment because of its more clay component.

Due to its location away from frequent anthropogenic operations and being practically devoid of human input, S3 contains relatively less metal than other stations. As the distance from the primary disposal spot increased, the proportion of metal content decreased. The sediment at these stations has a lower concentration of metals and a lower pH value, whereas soils with higher pH have a propensity for metal adsorption, precipitation, and redeposition to the sediment surface from water (Atkinson et al., 2007; Zhang et al., 2014). This region has adequate hydrodynamics and less soil pH, that prevents accumulation of higher quantity of heavy metal. Because of the overall sandy texture of the S3 soil, the levels of Fe and Al are lower. S3 has a higher rate of metal build-up due to its relatively higher sand concentration and slightly lower organic carbon content.

Heavy metals and polychaetes

In the provided Figure 2, the build-up of heavy metal in sediment and polychaetes was highlighted. The two polychaetes *M. gravelyi* & *D. aestuarina* and the quantity of metal in the sediments differed depending on the location. *M. gravelyi* displays significantly higher amounts of metal build-up than the other. The heavy metal concentration in *M. gravelyi* were in the order Zn>Cu>Ni>Pb>Cd. The metal accumulation sequence in polychaetes was identical to that of metal concentration in sediment, with one notable difference being that Ni superseded Cu. The accumulation in *M. gravelyi* is ranged between Zn 30.5- 94.18 mg/kg, Cu 10.74- 31.47 mg/kg, Ni 10.3- 20.56 mg/kg, Pb 1.5- 11.67 mg/kg, Cd- 0-0.7 mg/kg, Fe 0.02- 0.14 % and Al 0.04-0.29. A similar sequence of metal deposition is followed by *D. aestuarina* like *M. gravelyi* but lower in quantity. The accumulation is ranged between Zn 25.6-61.29 mg/kg, Cu 6.27-27.96 mg/kg, Ni 6.18-13.16 mg/kg, Pb 0.63-3.1 mg/kg, Cd- Below Detectable Limit, Fe 0.01-0.07% and Al 0.02- 0.09% etc. The pattern of distribution of metals from central Black Sea region of Turkey follows the same trend (Bat et al., 2019). The heavy meal accumulation from China following almost same order (Zn>Cu>Pb>Cd>Ni) only except Ni (Fan et al., 2014). *M. gravelyi* had more metal in its body than *D. aestuarina*, which is consistent with the concentration of soil nearby. The proportion of zinc accumulation in polychaetes was higher compared to that in sediment, and several investigations (Bat et al., 2019; Mtanga & Machiwa, 2007) have shown the same pattern. Only Zn content was found to be higher in two polychaetes than sediment among the six heavy metals examined. Zn concentrations were highest in polychaete *M. gravelyi* from S2 (94.18 mg/kg) followed by Cu. Studies indicate that Zn and Cu have a better potential for accumulation than Ni, Alam et al. (2010) found a higher level of biomagnification of Zn and Cu while transferring from lower to higher organisms through predation.

Pb and cadmium content in the soil was quite low compared to other metal concentrations, but it was slightly greater in S2. In this station, clay soil has a positive relationship with these metals' biomagnification in *M. gravelyi*. When compared to other metals, Ni concentration in polychaetes collected from all sites was substantially lower in trend and did not exhibit a positive relationship with Ni in the soil. Except for the content of Ni, Fan et al. (2014) revealed that metal accumulation in polychaetes from Jinzhou Bay, China significantly relates to its sediments. Other bio essential elements such as Fe and Al, accumulated to their ideal levels in polychaetes. Which are necessary at a minimum level for these worms' basic bodily metabolic functions.

The variation of body metals among polychaete species is because of their preferred habitat and eating habits. *M. gravelyi* is a member of the Eunicidae family and according to Yonge (1954) it primarily consumes on small mollusks, ostracods, chaetognaths, and some debris. When *Marphysa formosa*, a species of this family, is placed on stones covered with algae during

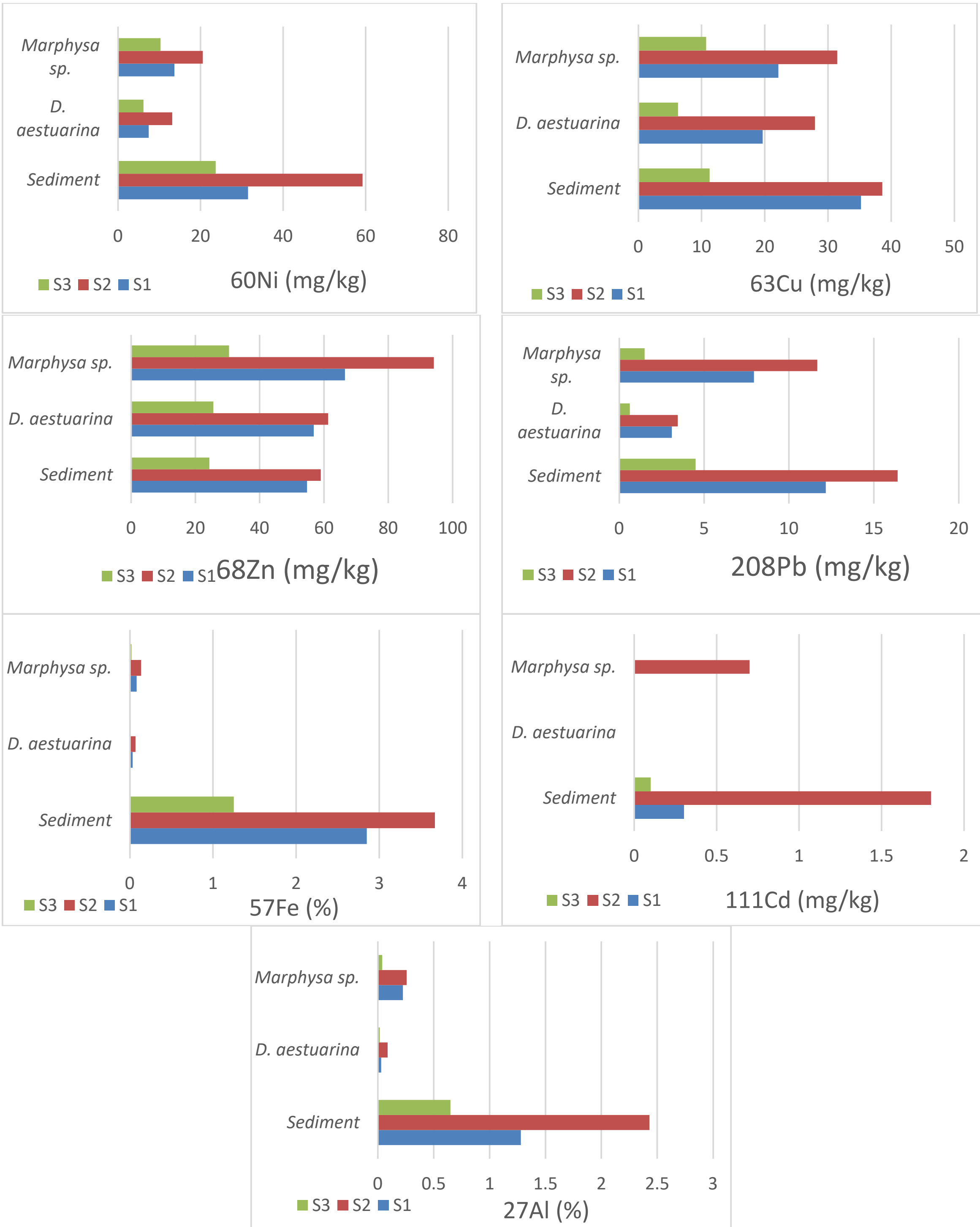

Fig. 2. Showing heavy metal concentration of sediment and two polychaete species from three different stations.

an experiment by Pardo & Amaral (2006), it will use its mouth to forage, scraping the entire surface bare before being left to its delicate tube. The body of polychaete will unintentionally acquire metals through its feeding of smaller creatures. Additional research is needed to fully understand the two species' feeding mechanisms. The greater concentration of metals in detritivores' bodies may be mostly due to their food. Earlier, Watts et al. (2013) demonstrated the deposition of organo-arsenic compounds in detritivore species like *D. arborifera.*

The *D. aestuarina* exhibits very little preference for areas where residential trash is deposited in greater quantities. These species may not have been present near the dump since there was less oxygen available and more hydrogen sulphide present. The creature favours habitats with high water circulation and low pollution levels. Typically, the presence of heavy metals and the reaction cause an area's variety to decrease by removing delicate species from a contaminated habitat (Pilo et al., 2015). The polychaete *M. gravelyi* is relatively dispersed across all sites, with no predilection for any particular habitat in terms of metal-contaminated areas. The ability of *M. gravelyi* species to tolerate extremely low oxygen levels helps them endure the hostile environment. The bioremediation species *M. gravelyi* can thrive in organically rich environments, play a key role in bioturbation in contaminated areas, and improve oxygen availability in sediment (Mandario et al., 2019). Since *D. estuarina* is a pollution-sensitive organism and *M. gravelyi* is a highly pollution-tolerant species, more research on these animals will be helpful in predicting the state of their environment with regard to metal pollution because they serve as indicator species.

CONCLUSION

The accumulation of heavy metals in sediment was Zn>Ni>Cu>Pb>Cd. Of all the metals tested, zinc levels in sediment and polychaetes were the highest; nonetheless, they all fell within the recommended range of the Sediment Quality Guidelines, with the exception of nickel from sediment of S2, which is capable of harming benthic creatures in the mangrove ecosystem since it is above the impact range medium. According to the analysis, S2 (which is close to an adjacent town) has a greater quantity of metals than other stations. Metals from S2 has higher metal accumulation may due to the higher organic carbon, higher clay content and poor water movement etc. The metal accumulation sequence in polychaetes was identical to that of metal concentration in sediment, with one notable difference being that Ni superseded Cu. Studies indicate that Zn and Cu have a better potential for bioaccumulation. Pb and Cd were less in soil but showing positive correlation of biomagnification in polychaete while compares with Ni which show a negative relation. In this sense metal content in the soil, it provides a clear indicator of the particular species' preferred habitat. Metal concentrations in polychaetes did not significantly exceed those in sediment. Therefore, it might not have any immediate effects, but considering its role in trophic level and a particular habitat, a rise in heavy metal levels will have some effects on the organisms that make up the ecosystem.

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CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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