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Baseline

Assessment of metal concentrations (Cu, Zn, and Pb) in seawater, sediment and biota samples in the coastal area of Eastern Black Sea, Turkey

Hasan Baltas[a,*], Murat Sirin[a], Goktug Dalgic[b], Esra Yilmaz Bayrak[a], Aysel Akdeniz[a]

[a] Recep Tayyip Erdoğan University, Faculty of Art and Science, Department of Physics, 53100 Rize, Turkey
[b] Recep Tayyip Erdoğan University, Faculty of Fisheries, 53100 Rize, Turkey

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ABSTRACT

This study investigated the contents of Cu, Zn and Pb in seawater, sediment, different shell sizes of mussel (*Mytilus galloprovincialis*) and sea snail (*Rapana venosa*) samples collected from four different provinces of the Eastern Black Sea Region. With the exception of Zn, all the metal concentration values measured in the sea snail were observed to be higher than those of mussels in all stations. While the correlation between mussels and sea snail according to metal concentrations was found to be positive ($p < 0.05$), this relation was not observed between the other parameters, such as the shell sizes, salinity and pH ($p > 0.05$). Although the mean concentration values of Cu, Zn, and Pb for mussel and sea snail are significantly above the tolerable levels, the estimated daily intake values for mussel were below the daily intake recommended.

The Black Sea, with a surface area of approximately 4.2×10^5 km^2, a volume of 5.3×10^5 km^3 and a maximum depth of 2200 m, constitutes one of the world's largest inland basins (Bat and Öztekın, 2016). Several different cities and countries border the sea. It is an important area for fishing and aquaculture (Unsal, 2001). Besides the seaport, industrialization, shipyards and various factories lying along the coast, it is known that there are some mining industries along the rivers that flow into the Black Sea (Tuncer et al., 1998). The heavy metal levels in the Black Sea marine environment have increased due to oil pollution and airborne contaminants (Topcuoğlu et al., 2002). The concentration of metals has also increased through rivers contaminated with industrial waste (Topcuoglu et al., 2003; Balkis et al., 2007). Furthermore, as a result of uncontrolled use of chemical fertilizers, the underground water sources can be polluted; heavy metals can mix into the food sources and put human health in danger. It receives an enormous quantity of pollutants containing sedimentary material being fed from all sides by several large rivers and many streams, each of which possesses a large drainage area (Unsal, 2001). Moreover, the main metal pollution problem in the eastern Black Sea coast of Turkey is related to agricultural run-offs and sewage effluents with deficient or no treatment (Topcuoglu et al., 2003). Also, the Eastern Black Sea region has rich Cu, Zn and Pb mine reserves. For this reason, the wastes of the mines transported to the marine environment through the rivers constitute the main source of pollution in the aquatic environment in the Eastern Black Sea region (Cevik et al., 2008).

The contamination of the Black Sea waters, sediments and organisms with a wide range of pollutants has become a matter of great concern over the last few decades (Secrieru and Secrieru, 2002; Bat et al., 2009; Ergül et al., 2008; Boran and Altınok, 2010). Many marine organisms have the potential to bioconcentrate high levels of metals from their environment (Bazzi, 2014; Ahdy et al., 2007). Metal biomagnification by marine organisms has been the subject of considerable interest in recent years because of serious concern that high levels of metals may have detrimental effects on the marine organisms and may create problems in relation to their suitability as food for humans (Ahdy et al., 2007). The pollution levels of the aquatic environment by heavy metals can be estimated by analysing water, sediments and marine organisms (Bazzi, 2014). While contaminated site assessment typically involves the analysis of water and sediment to measure total contaminant concentrations, often this analysis is not a good predictor of contaminant toxicity to biota (Topcuoglu et al., 2003).

Compared to sediments, marine organisms exhibit greater spatial sensitivity and therefore are the most reliable tool for identifying sources of biologically available heavy metal contamination (Bazzi, 2014). Consequently, aquatic organisms have become increasingly used in the assessment of contamination, as both 'biomonitors' and

Abbreviations: EDXRF, Energy Dispersive X-ray Fluorescence; DL, detection limits; EDI, estimated daily intake; DW, dry weight; PCA, Principal Component Analysis; WHO, World Health Organization; TEG, Turkish environmental guidelines; USEPA, US Environmental Protection Agency; FAO, Food and Agriculture Organization; CCREM, Canadian Council of Resource and Environment Ministers; CRM, certified reference material; NOAA, National Oceanic and Atmospheric Administration; CAC, Codex Alimentarius Commission; ASTM, American Society for Testing and Materials; HCl, hydrochloric acid; ND, not detectable

* Corresponding author.
E-mail address: hasan.baltas@erdogan.edu.tr (H. Baltas).

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'bioindicators' (Rainbow, 2006; Villares et al., 2002). The mussel (*Mytilus galloprovincialis* Lamarck, 1819) is a major component of the littoral fauna in the Black Sea. Marine mussels are sedentary organisms and it is easy to collect a large number of organisms from the location at a certain period of the year (Bat et al., 2012). Mussels accumulate most of the contaminants at much higher levels than those found in the water column and they are representative of the pollution of an area and for that reason they enable the quality of coastal waters to be monitored (Chakraborty and Owens, 2014). Similarly, sea snail (*Rapana venosa*) is a useful heavy metal biomonitor and mainly feed on mussels, oysters, and other bivalves. Hence, they accumulate heavy metals from their food through nutrition. Because the sea snails are an invasive species, destructively damage the benthic ecosystem of the Black Sea (Bat and Öztekın, 2016). Moreover, mussels and sea snail not only serve as bioindicators, but also raise public health concerns because, whether cultivated or wild, they are consumed as seafood (Cardellicchio et al., 2010). Therefore, it is necessary to monitor the sea samples of the Black Sea coast regularly in terms of heavy metal analysis due to the recent population growth in the region, the filling of the sea and the fishing activities.

The aim of this review is to determine the concentration of selected heavy metals in seawater, sediment, soft tissues of Mediterranean mussel and sea snail at different sampling stations on the Eastern Black Sea coast of Turkey in 2014. Also, heavy metals transition to the sea snail through feeding was also monitored. The present results are compared with similar studies that have been carried out in the region.

The Eastern Black Sea region has rich potential in terms of a variety of mines. The mine potential of the region is reflected by the total reserves, including copper (Cu), zinc (Zn) and lead (Pb) deposits of 700 million tons and an iron reserve of 10 million tons, a manganese reserve of 260,000 tons, a gold reserve of 36 tons and a silver reserve of 1.4 million tons (Cevik et al., 2008).

The sampling stations in Giresun (3 stations), Trabzon (4 stations), Rize (3 stations) and Artvin (2 stations) provinces on the Eastern Turkish coast of the Black Sea are shown in Fig. 1. Sampling provinces, codes, locations and geographical coordinates are shown in Table 1. All seawater, mussel, sediment and sea snail samples were collected in 2014. Sampling locations were detected using GPS localization.

A total of 48 seawater samples (0.5 m depth from the seawater surface) taken from the 12 sampling stations were collected in 30-liter plastic bottles. Temperature, salinity and pH were measured for each collected seawater sample. Samples were transferred to a clean 5-liter glass beaker and were allowed to evaporate at 40–50 °C on a heater. Evaporation was continued until the residue in the bottom of the beaker. A few drops of HCl were added into the beaker to prevent the material adhering to the sides of the beaker during evaporation. About 100 g of seawater residue samples were dried in ovens at 65 °C for 48 h to a constant weight.

A further 48 surface sediment samples were collected from the same depth (~10 m) at the 12 stations with a van Veen-type grab sampler. Immediately after collection, samples were placed in polyethylene bags, refrigerated and transported to the laboratory (ASTM, 1991). The collected sediments were combined and sieved in the field and the size fractions were kept for analysis. Then they were stored in plastic cups cleaned by 1:1 HCl and HNO_3 until analysis. About 100 g of sediment samples were dried at 85 °C for 48 h (Unlü et al., 2008). After that they were put into powder by using a Spex mill for 20 min.

Mussel samples of different shell sizes were collected during each sampling season at 12 stations on the eastern Turkish coast of the Black Sea. > 300 mussel samples were collected at each location, immediately stored in bags, kept in a cooler box with ice and transported to the laboratory. Samples were classified according to their size as follows: Group A: < 5.0 cm; Group B: 5.0–7.0 cm; Group C: > 7.0 cm. About 20 mussels were selected from each group and were weighed. After the samples were classified, their tissues and shells were separated and then they were dried in ovens at 105 ± 5 °C to a constant weight (Baltas et al., 2016). The soft tissue, after the removal of the liquid, was then weighted.

The same numbers of sea snails were taken from the same sites as described above. Three shell sizes (Group A: < 4.0 cm; Group B: 4.0–6.0 cm; Group C: > 6.0 cm) were selected and performed using the same procedure as with the mussels.

To reduce the size effects of particles, the powder was sieved using a 400-mesh sieve with all the samples. The samples were kept away from metallic materials and dusty conditions to avoid contamination.

Prior to metal analysis, the dried samples were ground in a spex mill, and pressed with a hydraulic press applying a pressure of 7 tons during 20 s as pellets. The resulting pellets had a diameter of 40 mm and a uniform mass of between 2 and 3 g. Every analysis was replicated three times (Baltas et al., 2016).

An EDXRF spectrometer (Epsilon5, PANalytical, Almelo, the Netherlands) was used for the heavy metal analysis of the sediment, seawater, mussel and sea snail soft-tissue samples (Yılmaz et al., 2011). Samples were irradiated by X-rays from a Gd tube under a vacuum equipped with a liquid nitrogen cooled PAN-32 Ge X-ray detector having a Be window thickness of 8 μm. The power, current and high

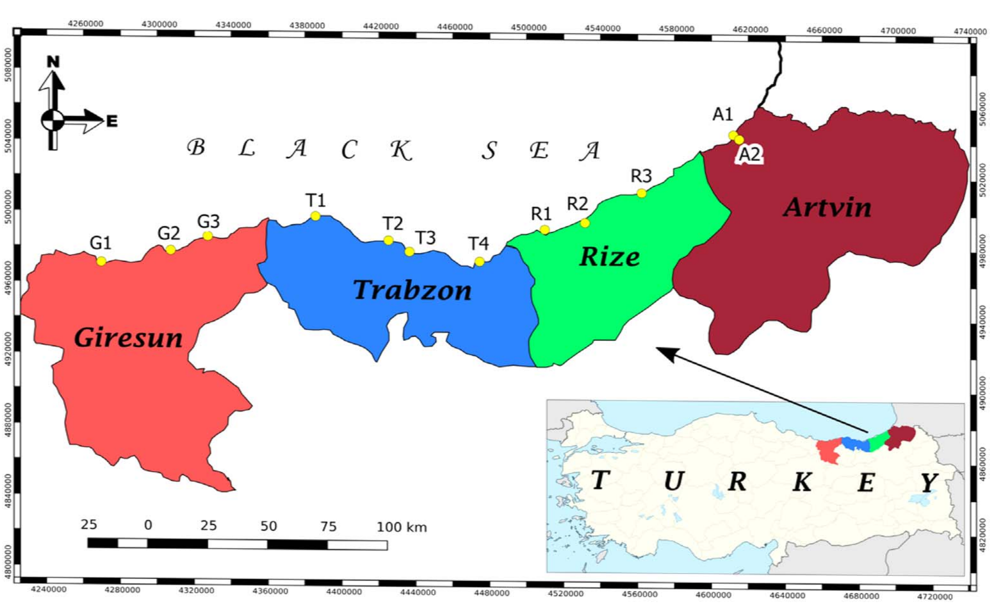

Fig. 1. Location of the sampling stations along the Eastern coast of the Black Sea.