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MONITORING CHEMICAL CONTAMINATION LEVELS IN KARASU RIVER BASED ON THE USE OF ENOCHRUS SPP. (HYDROPHILIDAE) AND CHONDROSTOMA REGIUM (CYPRINIDAE)

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ABSTRACT

Introduction
Existing literature indicate that elements are present in varying concentration in all ecosystems but anthropogenic activities increase the level of this pollutants.
Aim of the study
To find out concentration of some heavy elements (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Sr, Pb) as heavy element pollution in Erzurum (Turkey), accumulation level of Hydrophilidae (Coleoptera) and *Chondrostoma regium* species and to assess the health status of Erzurum wetlands.
Material and methods
Water, sediment, fish and insect samples were collected in Karasu River (Erzurum, Turkey). Heavy elements levels in insects and abiotic samples were analyzed by Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometer. Fish tissues, from the same habitat were measured by ICP-MS.

Results
The elements concentrations were found to increase from fish tissues to insects (fish tissues< sediment < water <insects). It can be said that insects accumulate more heavy elements than fish tissues thus insects can be one of the source of contamination of the fish. All results were well below the limits for fish proposed by national and international standards and did not pose a health concern for fish consumers.

Conclusions
Based on the analyses of fish samples, heavy element concentrations in fish from studied areas of Erzurum are low. Although levels of heavy element are not high, residue of Pb, Cd and Hg in food may cause health problem for future.

Keywords: Aquatic insects, fish, EDXRF, ICP-MS, health hazard.

INTRODUCTION

Heavy elements are natural constituents of the earth's crust, but geochemical levels of heavy elements in the environment have been increased, especially at the industrial and agricultural fields. Some elements like Fe, Cu, Zn, Se are required in minute quantities by organisms. But, excessive amounts of these elements can become harmful to organisms. Besides, heavy elements such as Pb, Cd, Hg, and As do not have any beneficial effect on organisms and they are very harmful to biota (1, 2). Heavy elements considered as most dangerous anthropogenic pollutants due to their toxicity, accumulation, persistence and enrichment in the environment, and also affect the distribution and biodiversity of organisms (3, 4). The enrichment of heavy elements in the environment is important due to their toxicity to human health and nature (5). Besides, these elements are nonbio-degradable and causing cytotoxic, carcinogenic and mutagenic effects in animal (6).

Earth, known as “Blue Planet” is covered in water. Almost of that water (97%) is saltwater. That means freshwater constitute less than three percent of earth's water, and it is the source of all drinking water. As it stated in the literature, freshwaters have rich biodiversity and are vulnerable to the impacts of environmental changes (7, 8). The pollution of these aquatic environments by heavy elements and their toxicological impact on organisms has gained attention in recent years (1, 2, 4).

Biomonitoring of pollution by using biota are gaining popularity in the assessment of environmental pollution. Generally, biological monitoring or biomonitoring are used for determining and evaluating the quality of the environment and level of heavy element pollution. Analyzing only water or sediment cannot give strong evidence on quality of environment. Use biota gives an indication of past and current status of the environment (9). Today, there are many biomonitoring studies in the literature that are used certain species or communities to evaluate the quality of the environment and how it change over time (10, 11, 12). The terms of biological indicators or bioindicator and biological monitor or biomonitor are quite different each other, but many researchers use as synonyms. Bioindicators reflect qualitatively of the environmental stress and biomonitors on the other hands give quantitative information of the environment (13, 14).

A lot of aquatic invertebrates have been used for assessing the health of freshwater due to their abundance, easily identifiable, well-known life history, body size, found in all types of water and habitats and reflects local conditions over time. Aquatic insects are a group of arthropods that spend their part of life in the different type of water bodies (15). These organisms uptake these chemicals via food, water and sediment. The dietary uptake of elements is an important

exposure route and this may cause biomagnifications up tropic levels in insects. By taking up these substances aquatic organisms are not excreted but accumulated in the organism's tissues. Beetles are the most numerous group of insects throughout the animal kingdom and aquatic insects are one of the most important invertebrate groups in freshwater ecosystems. Also, they are an important food source for fish.
Hydrophilidae are mostly known as water scavenger beetles and spend their part of life in a variety of water bodies (16). The genus Enochrus belongs into Hydrophilidae which is one of the largest families of Coleoptera. The water scavenger beetle genus *Enochrus* Thomson, 1859 is divided into six subgenera and contains 223 described species throughout the world (17). Fishes have a significant impact on the food web as well as human diet. *Chondrostoma regium* (Heckel 1843), also called kingnase, belongs into Cyprinidae. It has a worldwide distribution, including Anatolia. It has not economical value, but it is consumed by local people (18). The objective of the present study was to analysis and compares the heavy element concentration level in insects and fish tissues. With this study, heavy element contamination levels of water and sediment were investigated and assessed.

MATERIALS AND METHODS

Sampling sites
Erzurum province is located in eastern Anatolia in Turkey and is at the junction of the Coruh, Aras and Euphrates basin. Karasu River is one of the two sources of Euphrates and its length of about 450 km. The present study was conducted at Karasu River, which situated at 65. km Erzurum-Bayburt Highway and the coordinates are 38º 22' 33N, 36º 58' 26E. Water, sediment, fish and insect samples were collected in Karasu River (Erzurum, Turkey). The Cement Factory is one of the biggest industry in Erzurum. In this sites source of heavy elements are highway transportation, industrial activities of the Cement Factory, fossil fuels and municipal pollutions. Sampling location is shown in Figure 1.

Figure 1. The map of the study area and sampling location in Erzurum province.

Collection and Preparing of samples

All samples were collected from Karasu River in Erzurum, on June to August 2015. For insect samples, the study area was disturbed by the foot, thus insects which live in the gravel or sediment drifted into the sieve. Then the insects were collected via 1 mm mesh aperture sieve and mouth aspirator. The collected samples were stored in 70% alcohol and labeled separately in the field and then carefully cleaned with a small paint brush in the laboratory before identification. For the species identification, firstly the insect samples humidified 1-2 h in Petri dish, and then, male genitalia was dissected with a dissecting needle, under a stereo microscope. The aquatic insects, which belong to family Hydrophilidae (Coleoptera), were identified with the aid of (19) taxonomical key to the species level. These insects were identified by the first author and certified by the second author. Two insect species belonging to genus *Enochrus* Thomson, 1859 were determined. Determined species are given; *Enochrus* (Lumetus) *fuscipennis* (Thomson 1884) and *Enochrus* (*L.*) *bicolor* (Fabricius 1792). Sediments were taken via plastic shovel from 30 cm depth benthic zone, then stored in a glass bottle and noted describing information of station. Before taking the water samples the glass bottles washed 4-5 times with water which situated study area. Then the glass was plunged to upstream 0.5 m depth and filled with water that there was no space between the cap and the bottle. Until analysis, the samples were kept in the refrigerator. In the study site, ten fishes were caught with the help of using gill net. The living fish were carried to the laboratory in water tanks. Total body length and wet weight of fishes were measured. Liver, muscle and gill samples were quickly removed, rinsed with distilled water, and stored at -18 °C prior to analysis. All procedures were performed in compliance with the relevant laws and institutional guidelines, and that the appropriate institutional committees approved them.

Elemental analysis

The concentration of fourteen heavy elements in insect samples and their associated sediment and water were analyzed by Energy Dispersive X-ray Fluorescence spectrometer (EDXRF). EDXRF can analyze all kind of environmental samples simultaneously and quantitatively of a wide range of elements from Aluminum (Al) to Uranium (U) in the concentration range from 100% down to the ppm level (20). All measurements were carried out under vacuum. Insect samples were dried at 80˚C during 36 h. Dried insects were pulverized and then cellulose was added as a binder for gain a better shape. Five tons of pressure applied to make 13 mm diameter pellets of each species. Water samples were done by using an Al sample holder with Mylar films on both sides. Sediment samples were put in a plastic sample holder and it has Mylar window for emitting photons. Samples were irradiated by 59.5 keV photons, emitted by 1 Ci ^{241}Am radioactive source. X-ray spectra were collected with HPGe detector which uses Genie-2000 software (Canberra) program. HPGe detector resolution is ~180 eV. Measurement time for water and sediment samples was 4 h and insect samples were 24 h. The concentration of elements in each sample was determined by Win AXIL software, which uses Fundamental Parameters Method (FPM) for quantitative analysis. Fish tissues, from the same habitat were measured by ICP-MS. Most elements in the periodic table can be quantitatively measured with this system. Stored frozen fish tissues were allowed to thaw at +4 °C. All plastic containers were washed with 10% HNO_3 and then rinsed with ultrapure water. Weighed 0.1 g (wet weight) tissue samples were put in a teflon bomb which has high pressure and concentrated 3 ml HNO_3, 0.5 ml $HClO_4$ and 1 ml of H_2O_2 were added. The mixtures in the teflon bomb was heated in a microwave at 90 °C/15 sec, 120°C/sec15 to 140 °C/60 sec 150 °C/60 sec, (Temperature/sec) respectively. After cooling to room temperature, these solutions are taken into a volumetric flask and adjusted with 10 ml 18.2 MΩ cm ultrapure water. The accuracy of analytical procedure was checked by analyzing the certified reference material (DORM-3).

RESULTS

Elements tend to accumulate in water and sediment move up through the food webs and adversely affect living things. Thus to monitor the level of heavy elements in the environment and determine potentially hazardous levels for human are necessary. In this investigation, the concentration of fourteen heavy elements (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Br, Pb) in water, sediment, two species of genus *Enocrus* spp. and twelve heavy elements (Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, Hg, Pb) in fish tissues have been determined.

All insects collected in the contaminated river and were elevated whole-body heavy element concentrations. The results showed that Mn, Fe, Ni, Zn, As, Br and Pb were detected in all samples, but Br was not measured in fish tissues and Pb concentration was not detected in fish muscle. In water, the highest heavy element concentration was Ti and in all samples, Co measured only in water. Se, Cr, Sr were not measured in water. In sediment, the highest heavy element concentration was V, and Cu, Co was not measured in sediment. *E. bicolor* is the best heavy element accumulator for certain elements than *E. fuscipennis*. The highest concentration of Cr was measured in *E. fuscipennis* but V and Co were not measured in this species. The highest concentration of Mn, Fe, Ni, Cu, Zn, As, Se, Br and Pb were measured in *E. bicolor* but Ti and Co were not measured in this species. The element concentration showed a general trend of Ti>V>Mn>Fe>Pb>Co>Ni> Zn=Br>As>Cu>Sr=Se=Cr in water; and V>Fe>Mn>Cr>Ni>Sr>Se>As>Br>Zn>Pb> Ti>Co=Cu in sediment.

In insects Al, Cd, and Hg; in fish tissues Ti, V, Co, Se, Sr and Br were not measured. The results were compared with national and international standards. The observed heavy elements concentrations in fish, water and sediments were below the recommended limits. Mean concentration of water, sediment and insect samples were given in Table 1; in fish tissues were given in Table 2.

Table 1. Heavy Element Content of (Mean ± SD) in Water, Sediment and Insect Samples (ppm).

Heavy Element	Water	Sediment	*Enochrus fuscipennis*	*Enochrus bicolor*
Ti	802±4	0.3±0.07	0.1±0.05	0±0
V	150±1.5	775±2.2	0±0	0.6±0.01
Cr	0±0	10±0.9	45±5	0.1±0.01
Mn	10±0.5	64±4	15±0.2	470±1.7
Fe	5±0.8	308±15	20±2	760±5
Co	2±0.9	0±0	0±0	0±0
Ni	0.9±0.6	5.1±0.3	0.8±0.1	25±1.4
Cu	0.3±0.05	0±0	0.4±0.1	15±0.3
Zn	0.3±0.1	1±0.3	0.5±0.2	8.5±0.5
As	0.3±0.2	2.2±0.5	0.7±0.2	12±0.1
Se	0±0	2.3±0.3	0.3±0.2	17±0.1
Br	0.3±0.1	1.7±0.5	0.7±0.1	28±1
Sr	0±0	3.1±0.5	0.2±0.1	3.1±0.5
Pb	3.5±0.2	0.8±0.4	5±0.2	110±2.7

Table 2. Mean heavy element concentrations in tissues of *Chondrostoma regium* (μg/g).

Heavy Element	Liver	Muscle	Gill
Al	1.5±0.1	1.4±0.02	1.08±0.1
Cr	0.02±0.01	0.04±0.01	0.4±0.09
Mn	0.76±0.04	0.7±0.06	2.7±0.1
Fe	11.06±0.91	3.1±0.08	6.2±0.1
Ni	0.19±0.02	0.03±0.01	0.1±0.03
Cu	2.83±0.26	0.1±0.03	0.1±0.01
Zn	2.68±0.34	1.9±0.13	3.6±0.08
As	0.05±0.01	0.05±0.02	0.04±0.01
Cd	0.002±0.001	0.001±0.01	0±0
Hg	0.08±0.01	0.04±0.001	0.05±0.01
Pb	0.001±0.001	0±0	0.003±0.001

DISCUSSION

Thus this research attempted to assess the health status of wetlands in Erzurum. If a pollutant enters in an environment the organism living in, it will take up the pollutant via food, water or sediment and bioaccumulate it in its body. According to Table 2 liver is the most heavy elements accumulator than the muscle, suggesting that the primary target organ of the heavy elements is liver followed by the gill and muscle. Studied samples concentrated these elements with different levels. As it seen Table 1 and Table 2 generally, the elements concentrations were found to increase from fish tissues to insects (fish tissues< sediment < water <insects).

CONCLUSION

Fish are at the top of the aquatic food chain, thus, they can accumulate these elements from food, sediment and water (6). It can be said that insects accumulate more heavy elements than fish tissues thus, insects can be one of the source of contamination of the fish. The data presented in the paper showed that the *Enochrus fuscipennis* and *Enochrus bicolor* are capable of accumulate the elements in their habitats with different levels. All results were well below the limits for fish proposed by national and international standards and did not pose a health concern for fish consumers. Although levels of heavy element are not high, but residue of Pb, Cd and Hg in food may cause health problem for future. These results will constitute a reference to future studies on the evaluation of contamination in studied station of Erzurum. Karasu River and its environment should be monitored periodically. This is important for conservations of Erzurum's wetlands.

Competing Interests
All authors hereby have declared that no competing interests exist.

Authors Participations
ZA participated in the study design, writing the protocol, data collection, managing the analyses of the study, determine the species, and writing all versions of the manuscript. Üİ participated in the study design, certified the determined species and evaluate the results. TŞ participated in the managing the analyses of the fish samples and evaluate the results. AG performed in the study design, managing the analyses of the study, and evaluates the results. All authors read and approved the final manuscript.

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