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Original research paper

LEAD CONTAMINATION OF FISH AND WATER FROM COASTAL SEA OF BAR REGION (MONTENEGRO)

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ABSTRACT: Fish are accurate and suitable bioindicators and biomonitors for marine water pollution analyses. Depending on the diet type, the harmful and dangerous substances are accumulated in their bodies in the larger quantities than in the water column, which directly affects human health. Lead is a toxic metal whose widespread use has caused extensive environmental contamination and health problems in many parts of the world, especially in developing countries. The aim of this research was to obtain the data on lead contamination in fish and seawater samples from coastal region of Bar harbour. The highest lead concentrations have been found in muscles of *T. mediterraneus* and *M. cephalus*. The lead concentrations in water samples have varied depending on season and locality.

Key words: *fish, lead, Adriatic Sea, contamination*

INTRODUCTION

The harbour Bar is one of the most important Montenegrin port at Adriatic Sea, located in a natural bay between the old city Bar and Ulcinj. It has a wide opening to the west, but protected from the south by the hill Volujica. The total length of the operational shore is 3 km, and can host 20 ships at the same time, with the closed storage area of more than 100.000 m^2. The harbour Bar is capable for all types of goods transhipment, especially, ores, concentrates, metallurgy products, oil and its derivatives, grain and its products, fertilizers, pesticides, cement and wood.

Fish are accurate and suitable bioindicators and biomonitors for marine water pollution analyses, as the assay of their different tissue (muscle, brain, liver, fat, skin) could in appropriate time notify about the presence of the pollutants and contaminants in the water. Fish have a crucial role in marine food chains as they represent primary and secondary consumers as adult and important food resource for aquatic invertebrates and vertebrates as juvenile forms. Furthermore, a large number of fish species are usually used in human nutrition, especially in the coastal regions. Depending on the diet type, the harmful and dangerous substances are accumulated in their bodies in the larger quantities than in the water column, which directly affects human health.

Many physical, chemical, biological and environmental factors influence the marine biota accumulation of heavy metals. Essentially, the concentration of metal in the soft tissue of marine organisms is much higher than the concentration of metals in the marine water environment, and sometimes the level of metal in organism is proportional to the level of metal in the sea water (Kragulj et al., 2018). In the bioindicator program, many variables must be considered. For example, a concentration of the metal absorbed by the body is conditioned by the chemical form of metal, which varies depending on the locality and sea water depth. Other chemical factors, such as pH, temperature and salinity can also affect the bioaccumulation of metals. Apparently, it is even possible that metal contaminants interact one with another, so that one metal inhibits the accumulation of another by a particular organism (Kragulj et al., 2018).

According to Oost et al. (2003), all substances are the subject of transport and transformation processes when released into the environment. These processes, along with emission patterns, environmental parameters and substance physicochemical properties will direct their distribution and concentration in environmental compartments such as water, air, soil, sediment and biota.

Persistent pollutants and contaminants may accumulate in aquatic organisms through different mechanisms: the direct uptake from water by gills or skin (bioconcentration), uptake of suspended particles (ingestion) and the consumption of contaminated food (biomagnification) (Oost et al., 2003). Bioaccumulation of these substances in biota may be a precondition for adverse effects on different ecosystems. Oost et al. (2003) have highlighted that even without detectable acute or chronic effects in standard ecotoxicity tests, bioaccumulation should be regarded as a hazard criterion in itself, since some effects may only be recognized in a later phase of life, are multi-generation effects or manifest only in higher members of a food-chain.

Heavy metals are extremely resistant and can be toxic even when their amounts are in traces. Determining their distribution in sediment, seawater and biological material is of great importance for the environmental pollution studies. According to Purić et al. (1996), the prospected heavy elements are divided into three groups: maintaining (caesium, titanium), recycling (cadmium, chromium, nickel, zinc) and bonding (aluminium, cobalt, lead, mercury, arsenic and manganese). Depending on the seawater physical and chemical features, heavy metals can occur in a large number of different forms of chemical compounds and ions, where the toxicity of heavy metals is conditioned by their chemical forms (Kragulj et al., 2018). The most frequent forms of lead in seawater are: $PbCO_3$, $Pb(CO_3)_2^{2-}$ and $PbCl^+$.

According to WHO, lead is a toxic metal whose widespread use has caused extensive environmental contamination and health problems in many parts of the world, especially in developing countries. Lead is a cumulative toxicant that affects multiple human body systems, neurological, haematological, gastrointestinal, cardiovascular and renal systems. Children are particularly vulnerable to the neurotoxic effects of lead, and even relatively low levels of exposure can cause serious and, in some cases, irreversible neurological damage. Lead exposure is estimated to account for 0.6% of the global burden of disease, with the highest burden in developing regions. Recent reductions in the use of lead in petrol (gasoline), paint, plumbing and solder have resulted in substantial reductions in lead levels in the human blood.

Lead and its compounds are extremely toxic and pose a major threat to the animals and humans health. The human intoxication by lead is usually conducted by eating poisoned marine organisms and polluted air (Maradani et al., 2016). Lead easily penetrates the body through the skin, mouth and respiratory organs. It is stored in the human body in bones, teeth, liver, lungs, kidney, spleen and brain. Furthermore, lead can pass from the maternal to fetal blood compartments, as well as it can cross the blood brain barrier. The consequences of poisoning with lead are numerous, from anaemia to infertility in women. Lead has two rather different effects on humans, physiologically and neurologically. The most common consequences of lead poisoning are: anorexia, abdominal pain, insomnia, anaemia, irritability, mood swings, loss of coordination; and in serious situations, neurological effects such as restlessness, hyperactivity, confusion, loss of memory, mental retardation and sometimes coma and death. These changes occur when the lead concentrations in human blood are from 100 to 150 μg/dm^3 (Kragulj et al., 2018).

Considering the lead toxic effect, the aim of this research was to obtain the data on lead contamination in fish and seawater samples from coastal region of Bar harbour.

MATERIAL AND METHODS

The fish and water were sampled from three localities in Bar region: Volujica, Bar harbour and Sutomore (Figure 1), twice a year, in summer and winter. The fish were collected from the daily catch of the local fisherman by the random principal choice. The water samples were taken from the boat, at approximately depth of 0.5 and 10 m.

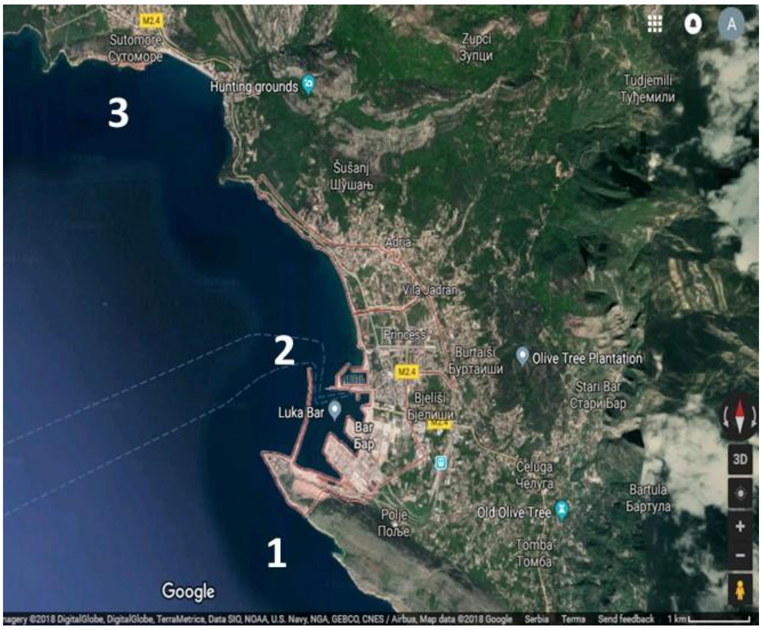

Figure 1. The sample localities: 1 – Volujica, 2 – Harbour Bar, 3 - Sutomore

The lead contamination was tested in muscle tissue, applying Atomic Absorption Spectroscopy (AAS) by the Thermo electron S2 AA System The standard metal solution (stock solution, 1000 mg/L) was made by dissolving 1 g of metal or its salt (calculated on 1,000 g of metal) in hydrochloric acid (1:1). Diluting the stock solution (with water), a series of lower concentration of metal were prepared.

RESULTS AND DISCUSSION

Seven fish species were identified (Table 1). The lad concentrations in fish and water samples are presented in Tables 2 and 3.

Table 1. Sampled fish species and their ecology (according to www.fishbase.de)

Species	Common name	Familia	Diet	Habitat type
Merluccius merluccius (Linnaeus, 1758)	European hake	Merlucciidae	Zooplankton, zoobenthos, nekton	Deep benthic, oceanic, neritic
Raja montagui Fowler, 1910	Spotted skate	Rajidae	Zoobenthos, nekton	Neritic, deep benthic
Raja miraletus Linnaeus, 1758	Brown skate	Rajidae	Zoobenthos	Neritic, deep benthic
Solea solea (Linnaeus, 1758)	Common sole	Soleidae	Zoobenthos	Neritic, coastal/supratidal
Mugil cephalus Linnaeus, 1758	Flathead grey mullet	Mugilidae	Plants, zooplankton, detritus, zoobenthos	Coastal/supratidal Neritic
Pagellus erythrinus (Linnaeus, 1758)	Common pandora	Sparidae	Zooplankton, zoobenthos, nekton	Neritic
Trachurus mediterraneus (Steindachner, 1868)	Mediterranean horse mackerel	Carangidae	Zooplankton, nekton	Oceanic, neritic

Table 2. The average concentration of lead in fish muscle tissue

Species	Pb (mg/kg)
Merluccius merluccius	0.25
Raja montagui	0.10
Raja miraletus	0.10
Solea solea	0.20
Mugil cephalus	0.78*
Pagellus erythrinus	0.10
Trachurus mediterraneus	1.12*

*concentrations above the maximum permissible concentrations (MPC) according to Official Gazette of Montenegro 81/2009 and 55/2015

The highest lead concentrations have been found in muscles of *T. mediterraneus* and *M. cephalus*. The obtained results are similar to Tepe (2009) who have found 0.11-1.15 mg/kg of lead in eight Mediterranean Sea fish species, 1.15 mg/kg in muscles of *M. cephalus* and 0.27 mg/kg in muscles of *P. erythrinus*. According to the same author, the main reasons of fish contamination by lead are fish's diet and the residues of ship waste dumped into the Mediterranean Sea. The lead contamination of fish muscle differs depending on the geographic region, as the range of 0.33–0.93 mg/kg was reported for Black and Aegean seas (Uluozlu et al., 2007), 0.01– 0.15 mg/kg for Ria de Averio, Portugal (Cid et al., 2001), and 0.11–0.89 mg/kg in muscles and 0.38–4.48 mg/kg in livers of fish from the coastal waters of Turkey (Tepe et al., 2008).

Table 3. The concentration of lead in water samples

Locality	Depth (m)	Pb (μg/dm^3)	
		Summer	Winter
Volujica	0.5	3.66	1.10
	10	6.14	2.23
Bar harbour	0.5	3.28	2.00
	10	4.11	3.01
Sutomore	0.5	1.98	0.28
	10	3.73	1.23

The lead concentrations in water samples have varied depending on season and locality. The obtained results are in accordance with Maradani et al. (2016), whose results suggested that during the summer the fish contained more heavy metals because during the summer the fish's metabolism and diet change. Cogun et al. (2006) also noted that cannier fish and fish which live in deeper waters had more heavy metals in their gills, livers, and the least amount in their muscle tissues.

Higher values of metal content in coastal water samples at the Bar region are caused by the impacts of industrial and municipal wastewaters and the drainage water from the surrounding arable land. The observed increase in metal concentration in the coastal belt can be explained by the inflow of fresh waters rich in nutrients, the discharge of industrial, agricultural and urban wastewater, and wet deposition from the atmosphere. The higher content of metals in the coastal zone in relation to the open part must be due to the impact of atmospheric precipitation, summer rainfall, waste and fresh water, as well as submarine outflows of 30.5 m (Volujica) and 40 m below the sea level (Čanj).

In some cases, the relationship between heavy metal content and body weight indicates that smaller organisms are richer in element traces than larger. The reason for this may be in exposure to an equal concentration of metal in surrounding water, so the same amount of metal is in contact with smaller and larger organisms (Kragulj et al., 2018).

Variations in metal concentration in fish at different locations can often be caused by seasonal changes in the fish weight and tissues, rather than by changes in the absolute content of metals in the body. Such weight changes can be geometric in nature, so that the reproductive cycle of the organism can, in some cases, significantly affect the concentration of metals in the overall soft tissue. The study of Lombardi et al. (2010) has shown that there is no difference in lead concentrations between male and female fish.

All these changes can be combined and obscure the interpretation of study results on the variations in heavy metal accumulation and the estimation of relative environmental pollution (Kragulj et al., 2018). According to Maradani et al. (2016), the amount of heavy metals in a fish depends on several factors: the climate that the fish lives in, what the fish eats, the fish's age, length, weight and gender.

CONCLUSIONS

At prospected localities, seven fish species were analysed and in all specimens lead concentrations were near or above the maximum permissible concentrations (MPC) according to Official Gazette of Montenegro 81/2009 and 55/2015. Fish and fish products are the dominant source of lead in food. Since all these fish species are frequently found on culinary menus in the coastal region of Montenegro, the continuous monitoring of heavy metal contamination should be conducted, not only in fish body and water, but in sediment also.

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