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A Study on Heavy Metal Content of Sardine (Sardina Pilchardus) Caught in the Dardanelles

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Abstract

Sardine (Sardina pilchardus) is one of the most important species among Turkish fisheries and is broadly distributed along Turkey's Saros Bay waters. In this study, the amount of heavy metal content of sardine, which is a fish abundantly consumed and caught in the Dardanelles has been determined between November and December of 2013. The effects of heavy metals, which are found especially in fisheries, on human health and on the environment arouse great interest. Toxic contaminants particularly such as lead, cadmium and mercury are found in the water as a result of industrial and agricultural activities and mining. The high concentration of these metals affects not only aquatic environments but also fish species negatively. In this research, the amount of heavy metal in two sardine samples (R1/R2) taken from Çanakkale fish market is analyzed. ICP-AES (Inductively Couple Plasma Atomic Emission Spectroscopy) is used in the analysis for Zn, Cr, Cd, Pb, Fe, Cu, and Ni. According to the results obtained, the average heavy metal amount of the two samples are found at the levels: 47,81001 for Zn, 0,163543 for Cr, 0,047545 for Cd, ND for Pb, 19,60705 for Fe, 1,385225 for Cu and 0,174258 for Ni. Pb is below the limits of the detection of ICP device, and no figures have been obtained. Other obtained figures have been observed to be below the acceptable amount in comparison to the figures of EPA standards.

Keywords: the dardanelles, sardine, sea pollution, metal, toxic substance

1. Introduction

Worldwide production of sardine is 965,431 tons/year (FAO, 2011), which makes, Sardine an important fish species of great economic importance to Turkey, as well as to many other countries (Finney et al., 2002, Moutopoulos, and Stergiou, 2002, Williams 2003). In Turkey it is approximately 34 708,6 tons/year (DIE, 2012) and most of the yield comes from the Saros Bay (8,350 tons/year). Contaminating factors which upset the natural balance may be grouped as organic substances, industrial waste, petroleum products, artificial agricultural fertilizers, detergents, inorganic salts, artificial organic chemicals and waste heat. According to this classification, heavy metals are included in industrial waste and reach to a level that they threaten the natural balance. Water, which is vital for all the creatures on Earth and an irreplaceable element of ecological balance, is in a constant cycle known as water cycle or hydrologic cycle. Industrial development, and environmental pollution which increases day by day all over the world threaten nature by accumulating ever-increasingly in earth, air and aquatic ecosystems. Numerous domestic and industrial wastes show up during the industrialization period. Contaminants which come into the marine environment through various ways affect the lives of living beings in the ecosystem negatively (Egemen and all., 1997). Heavy metals are one of the main toxic substances that pollute the natural environment.

Heavy metals pose a common threat to all organisms in the ecosystem by forming an ever-increasing accumulation through food chain. When lead (Pb) goes over the allowable limit in the setting in which it exists, firstly it affects physiological activities of creatures, and then it accumulates in the organs and tissues and could result in death. With the wastes which contains heavy metals produced by most of the industrial institutions, there happen serious pollutions in aquatic environments. The need for researching the effects of increasing metal pollution in fish which creates an important ring of biological cycle, and which is also consumed as an important protein source have shown up. For this reason, in aquatic environments, significant studies over heavy metals accumulations in fish and other organisms have been performed (Akgün M., 2006). In this study, heavy metals in sardine, a pelagic fish kind which is found and consumed plentifully in Çanakkale, are going to be measured.

Heavy metals are metals which are found in solid-state under normal circumstances except mercury; conduct heat and electricity; can become plate and wire; have metallic colour shine; can transmute to ionic-state with "+" valance by chemically electron donating; can replace with [H]+ which is found in acids; cannot form compound between each other but can form with non-metals and whose density is more than 5,0 g/cm^3 (Ciminli, 2005). Primary sources that cause heavy metals to mix in the nature are mines, waste waters of several metal and paper industries, fertilizers, fossil fuels, pesticides, various chemicals and domestic wastes (Kalay and all., 2004).

As a result of the use of water resources such as sea, lakes and rivers as receiving environment for waste, heavy metals whose concentrations are growing constantly are taken by aquatic organisms into their structures. Thus, it reaches to all creatures through food chain. Heavy metals accumulate in active tissues and organs via food chain and this accumulation causes functional and structural disorders at cellular and molecular levels. Heavy metal accumulation in aquatic organisms shows changes according to the species, metal properties and concentration, effect period of the metal, staying period of the metal in the environment, which growth phase the living is in and chemical and physical properties of the environment (Güner, 2008). Toxic substances affect one's health and cause diseases and death, even when they are found at low concentrations (e.g.: 1 mg/1) in the water (Katalay and all., 2005).

Metals which are found in marine environment at different concentrations accumulate in the structures of marine species. The accumulation mechanism takes place as follows:

1. By ions', which are bonded with organic molecules or are found soluble in sea water, being taken with water
2. With the consumption of foods in which heavy metals accumulation occurred.
3. Via sestons which adsorb (Note 1), heavy metals on their surfaces.
4. Through absorption emerging from the gravity between toxic metal ions and some substances that organisms produce (Uslu and all., 1999)

Some of the heavy metals are highly toxic. These elements are usually transitional metals. Along with the essential elements like iron, heavy metals also include toxic metals such as cadmium and mercury. Substances showing toxic effects are harmful to human health even if they are found at low concentrations in the water; and they can even cause to deaths and diseases (Alhas E., 2007). (Repetition of the same thing stated in the previous paragraph).

Human actions affect geologic and ecologic dispersal of heavy metals via air, water and earth pollution. Just as mines, foundries, and product and vehicle emissions whose primary anthropogenic sources of heavy metals are point source and coal burning plants (Rahman A., 2009). With the waste containing heavy metals that most of the industrial corporations produce, serious contamination in aquatic environments takes place. The need to research the effects of increasing metal pollution in fish which creates an important ring of biological cycle and also consumed as an important protein source have shown up. (Too much repetititon of the same sentences). In this respect, significant studies on the heavy metal accumulation in fish and other organisms in aquatic environments have been conducted. Also a lot of fish species and water products living in Turkish seas have been researched in terms of heavy metal accumulation (Akgün, 2006). Determined by Turkish Food Codex, acceptable consumption amounts for Cu, Zn, Pb, and Cd in fresh fish are 20 mg/kg, 50 mg/kg, 1 mg/kg and 0.1 mg/kg, respectively.

Previous Studies

In his 2006 study named "Food Composition and Heavy Metal Contents of Fishes Consumed in Fishing Season in Northeastern Mediterranean (Adana/Karataş) Region", Ersoy determined the heavy metal rates in red-eyed sardine (*Etrumeus teres*). In the month of February, Zn value was measured as 11.36 mg/kg. In the study "Levels of Heavy Metals in Canned Bonito, Sardines, and Mackerel Produced in Turkey" by Mol Suhendan, Zn, Cu, Sn and Hg values in the sardines which had been analyzed were determined to be within the allowed limits. On the contrary, values for Fe, Cd and Pb were determined to be above of the allowed limits. These high values of heavy metals pose danger for human health. In the study "*Heavy Metal Contents of Different Fish Species' Liver and Muscle Tissues*" by Canlı and Atlı in 2003, values below were obtained from the muscle and tissues of *Sardina pilchardus*. In the study, Cd, Cr, Cu, Fe, Pb and Zn values were examined.

Table 1. Heavy Metal Contents in Sardina Pilchardus

	Cd	Cr	Cu	Fe	Pb	Zn
Muscle	0.55	2.22	4.17	39.60	5.57	34.58
liver	2.99	17.16	29.26	225.47	39.43	73.22

Note. Chandrasheaker and Deosthale (1993) stated that 4.7-51.14 mg of Ca, 29-54.3 mg of Mg, 0.5-1.8 mg of Fe, 1.1-3.2 mg of Zn, 22-106.9 µg of Cu, 9.7-79.7 µg of Mn and 15.8-69.3 µg of Cr had been found in 100 gr of muscle tissues of 17 sea and 3 fresh water fish in India. In their study, named "*Assessment of Heavy Metals and Nonessential Content of Some Edible and Soft Tissues*", Ahdy and all. (2007) examined the heavy metal levels in many fish species. Values received are converted to the table below.

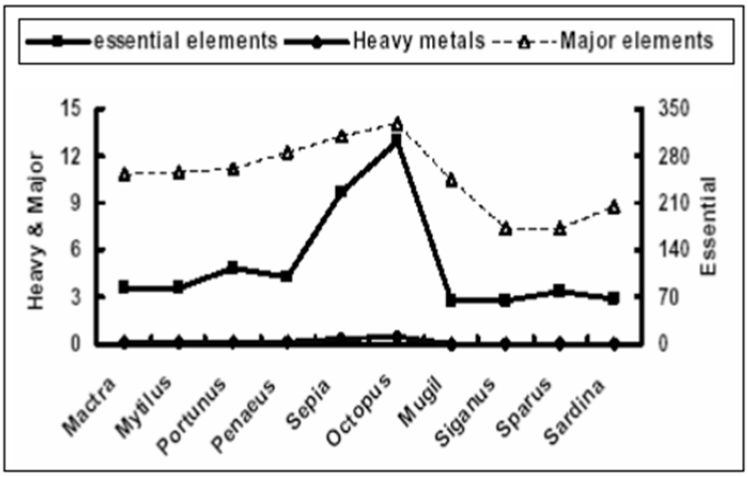

Figure 1. MPI in Marine Organism

2. Material and Method

The two fish examined in the study are taken from Çanakkale fish market. The location where they had been caught was around Babakale. They were brought to laboratory on the same day; pieces were taken, and weights were noted on the same day.

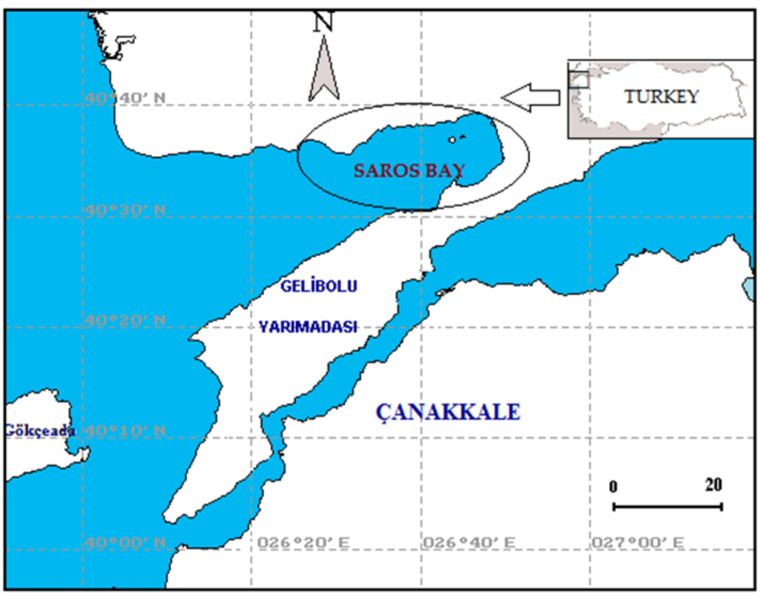

Figure 2. Location Map of Sampling Locations

The equipment used for the analysis included a, bistoury for separating the tissues from the body, glass slide and precision scales during the measurement of dry weights, a drying-oven to dry the tissues and nitric acid in order to solubilize the tissues . When samples were completed, they were put in a volumetric flask and then passed through a roughing filter. ICP-AES (Inductively Couple Plasma Atomic Emission Spectroscopy) device is used in order to determine the heavy metals.

Table 2. Sample of R1 and R2 Lam Weight (gr)

Sample code	Lam	Lam + wet weight	Lam + dry weight
R1	4,555	7,370	5,300
R2	4,545	8,555	5,510

After the tissue samples taken from the fish were dried in the drying-over, their dry weights were scaled. Lam weight was also measured. The samples were kept in the drying-oven at 70 ^{o}C for 2 days.

Table 3. Results of ICP-AES analysis (mL / L) ND: Not detected

	Zn	**Cr**	**Cd**	**Pb**	**Fe**	**Cu**	**Ni**
R1	50,94601	0,203514	0,049565	ND	24,2971	1,59343	0,254722
R2	44,674	0,123571	0,045525	ND	14,917	1,17702	0,093793
Average	47,81001	0,163543	0,047545	ND	19,60705	1,385225	0,174258

The samples, whose dry weights were already known, went through a decomposition process; the samples in the beaker were put in the volumetric flask and the outer surfaces were completed to 25 millimeters. By being passed through roughing filter, they were sent to the ICP device in order to be read. Values for Zn, Cr, Cd, Pb, Fe, Cu and Ni were measured. The values were then compared with EPA (Environment Protection Agency) values which have international validity.

3. Findings

3.1 Dry, Wet and Lam Weight Values of Samples

In order to analyze the samples, firstly wet weights then dry weights were obtained. With the help of a bistoury, pieces were taken from the samples and the dry weights were determined. Lam weights are also measured and noted.

Figure 3. Sardine Sample from Soros Bay

After these values were noted, the samples were left to dry in the drying-oven at 70 ^{o}C for 2 days.

3.2 Wet Decomposition Analysis

At the end of 2 days, dried samples were taken and their weights were measured (Table 1). The samples whose dry weights were discovered were added 5 millimeters of nitric acid. The reason for this was to prevent metals from sticking on the beaker face during evaporation (Kovancı A, 2008). Each of them was added 5 ml of nitric acid. The samples in the beaker were then put in the volumetric flask and the outer surfaces were completed to 25 millimeters. Afterwards, the samples that were completed with nitric acid were burned in the Hot Plate

(Magnetic Stirrer) until they became liquefied (Image 2). After the burning process was complete, the samples were left to cool.

Figure 4. Boiling samples in the ICP device

3.3 ICP-AES (Inductively Couple Plasma Atomic Emission Spectroscopy) Analysis

ICP results of the samples were received. In the analysis, values for Zn, Cr, Pb, Fe, Cu and Ni were examined (Table 2). ICP analysis results for these metals were multiplied by the amounts whose upper surface was completed. Then the results were divided by dry weight and thus heavy metal results were received.

Table 4. ICP-AES Analyze Results (ml/L) ND: undeterminable

	Zn	Cr	Cd	Pb	Fe	Cu	Ni
R1	50,94601	0,203514	0,049565	ND	24,2971	1,59343	0,254722
R2	44,674	0,123571	0,045525	ND	14,917	1,17702	0,093793
R.ort	47,81001	0,163543	0,047545	ND	19,60705	1,385225	0,174258

Since the Pb value was below the sub limits (detection limits) of ICP-AES device's element determining, no measurements were taken for these elements. The value for Pb was 0,084.

4. Comparison of Heavy Metal Results

A Comparison was made by calculating the medium of R1 and R2 values. When the results of measurement were examined, heavy metal values in the samples were conformed with those of Turkish standards.

The obtained values were compared with EPA (Environmental Protection Agency)'s internationally accepted heavy metal values.

Table 5. Comparison of Sample Values with EPA values (ml/L)

Heavy Metal	R. Average	EPA
Zn	4,781	5.000
Cr	0,163	0,050
Cd	0,047	0,010
Pb	ND	0,300
Fe	1,960	ND
Cu	1,385	0,020
Ni	0,174	ND

5. Conclusion and Evaluation

In this study, tissue samples from the sardine *(Sardina pilchardus)* caught in the Dardanelles between November and December 2010 were examined. Heavy metals like cadmium chromium, copper, iron, nickel, lead and zinc were analysed in the ICP-AES device. The values obtained were as follows: 47.81001 for Zn, 0.163543 for Cr, 0.047545 for Cd, No values for Pb, 19.60705 for Fe, 1.385225 for Cu and 0.174258 for Ni.

When the findings of heavy metal analysis on the sardine *(Sardine pilchardus)* samples which were caught around Çanakkale province, the following results were reached:

- The figure for Zn (zinc), which is a trace element, drew close to the critical limit.

- Pb (lead) values could not be measured since they were below the measurement precision of ICP device.

- When the numbers obtained were compared with EPA's acceptable heavy metal values, it was seen that the results were below of the sub limits. In terms of human health, any risk in fish meat was not found.

- It was all in all observed that the determined metal values were within the acceptable limits and they did not pose any risk with regards to food security.

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Note.

Note 1. Adsorbtion: molecules' sticking to a solid surface and forming a surface course which is formed of a single molecule course (Karol and all., 2004).