



## Analysis of heavy metals content in water, sediments and fish from the Gorgan bay, southeastern Caspian sea, Iran

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### ABSTRACT

The heavy metals concentrations including Zinc, Copper, Lead and Cadmium (Zn, Cu, Pb and Cd) in water and sediments in Gorgan Bay and their accumulation in *Rutilus frisii kutum*, *Acipenser persicus*, *Rutilus rutilus caspicus* and *Cyprinus carpio* organs (gills, muscle, kidney and liver) were investigated. There was substantial increase in concentration of heavy metals ingoing from the water to the sediment samples. In water and sediments, The concentration of heavy metal was in the order Pb > Cd > Zn > Cu. Fish samples were collected from Gorgan bay and analyzed for heavy metal content of liver, muscle, kidney and gills tissues. The maximum and minimum of heavy metals concentration were recorded in liver and muscle, respectively. The order of heavy metals concentration in different organs of fish samples was liver > gills > kidney > muscle and the order of heavy metals level in muscle, gills, kidney and liver was Pb>Cd>Zn>Cu. According to the results, heavy metal concentrations in fish species tissues were well within the limits set by the FAO/WHO recommendations and showed that the fish from investigated region are safety for consumers.

**Keywords:** *Rutilus frisii kutum*, *Acipenser persicus*, *Rutilus rutilus caspicus*, *Cyprinus carpio*, Heavy metal, sediment, water

### INTRODUCTION

The freshwaters pollution with contaminants has become a matter of great concern over the last decades. Some heavy metals are necessary to living organisms and usually found in natural waters, although these

heavy metals can reach a level of toxic concentration that can potentially demolishes the ecological environment (Agusa et al., 2005, 2007; Hajeb et al., 2009; Kiyani et al., 2013). Heavy metals enter into aquatic ecosystems from different anthropogenic and natural sources including domestic or industrial sewage, leaching from dumpsites/landfills, atmospheric deposits and storm runoff (Forstner and Wittmann, 1983). Heavy metals discharge into aquatic environments can change both ecosystems and diversity of aquatic species, because of their accumulative behavior and toxicity (Heath, 1987; Allen, 1995). Many of the sediments in oceans, lakes and rivers have been polluted by contaminants. Some toxic sediments kinds kill benthic organisms and decrease the food availability for larger animals such as fishes. In a process called bioaccumulation, some pollutants in the sediments are taken up by benthic organisms. When larger organisms eat these polluted organisms, these toxins transfer to the food chain (Begum et al., 2009). Fishes perform an important role in nutrition of human and so need to be routinely and cautiously screened to make certain that there are no high heavy metals levels being transferred to man by way of consumption (Adeniyi et al., 2008). The accumulation region of heavy metals within fishes varies with heavy metals, uptake route, and fish species. Fishes are considered as biomonitors in aquatic ecosystems for assessment of the heavy metal contamination and hazardous potential of human consumption (Peakall and Burger, 2003; Marcovecchio, 2004; Dalman et al., 2006). Few reports are available on metal levels in some food fishes indicated that some heavy metals are concentrating at various levels in the sampled fish (Wijesinghe et al., 1999; Allinson et al., 2002; Anil and Pathiratne 2002; Silva and Shimizu 2004; Witharana et al., 2005; Indrajith et al., 2006; Manage et al., 2006). If many perilous chemical elements released into the environment, they gather in the soil and water body sediments. The some aquatic organisms take up and transfer them by way of the food chain to higher levels of trophic such as fishes. The free bivalent ions of many metals could be absorbed directly by gills of fish from the water in the acidic conditions. Therefore, heavy metals concentrations in the fish organs are determined initially by the pollution level in the food and water. In particular conditions, chemical components gathered in the silt and water bodies sediments can move back into the water, so silt can be a secondary source for contamination of heavy metal (Varol and Şen, 2012).

The Gorgan Bay with an area about 400 km<sup>2</sup> is located at the southeast of the Caspian sea. Oil extraction and transportation throughout the sea is one of the main pollution sources in this bay and Caspian sea. Many industries and cities which are surrounded the Caspian sea is another pollution source. Cities and industries pollution enter the Caspian sea and Gorgan bay either directly or through rivers (Ganjidoust, 2001). Because of the shallow depth, lack of heavy waves and clayey bed, the Gorgan Bay is an appropriate habitat for benthic communities. It is the important fish stock rehabilitation site in the southern of Caspian sea. It is a rich source of different aquatic living organisms such as crustaceans and fishes. The fish species of this bay are *Rutilus frisii kutum*, *Acipenser persicus*, *Rutilus rutilus caspicus* and *Cyprinus carpio*. So, the purpose of this study was to provide information and evaluate the levels of four heavy metals viz Zinc (Zn), Copper (Cu), Lead (Pb) and Cadmium (Cd) in water, sediments and *R. frisii kutum*, *A. persicus*, *R. rutilus caspicus* and *C. carpio* organs (muscle, gills, kidney and liver) collected from Gorgan Bay, Southeastern Caspian sea, Iran.

## MATERIALS AND METHODS

Water samples and Sediment samples were collected from October to November 2013 from 5 sampling sites (Fig. 1). Sediments samples were collected by a polyethylene corer in accord with standard methods. Then samples were digested in acid-cleaned Teflon microwave vessels with 2ml ultrapure hydrofluoric acid and 5ml of ultrapure nitric acid and they were digested at 200°C for 30 min. After allowing at least 2h for cooling, the vessels were opened and for dissolving the fluoride precipitates, 0.8g boric acid was added and then they were detected via Atomic Absorption Spectrometer. A YSI 33 model portable

conductivity meter were used for measuring of pH and salinity. At this study, 16 fish samples for each species were collected from October to November 2013 in Gorgan bay (Southeastern Caspian sea, Iran). The preparations of samples and analysis were performed according to the protocol that described by American Public Health Association (APHA) [2005] and United Nations Environment Programme (UNEP) [1984]. The fish dissected to separate organs (gills, muscle, kidney and liver) according to Food and Agriculture Organization of the United Nations (FAO) method. These organs were putted in petri dishes and dry at 120 °C until reaching a stable weight. Then the separated organs were putted into digestion flasks and ultrapure Conc. After that H<sub>2</sub>O<sub>2</sub> (1:1 v/v) and HNO<sub>3</sub> was added. Until dissolution, the digestion flasks were heated to 130 °C. Afterwards, the samples diluted with distilled water and analyzed by atomic absorption Spectrometer for concentration of heavy metals.

### Statistical analysis

All data were analyzed as a completely randomized design with three replications. Data were expressed as means ± standard error (SE). One-way analysis of variance (ANOVA) was calculated using SPSS v. 11.5 (IBM SPSS, New York, USA) and differences between various organs of fishes were compared using Duncan's multiple range test at  $P < 0.05$ .

## RESULTS AND DISCUSSION

The analysis of water and sediments samples showed that the concentration of heavy metal was in the order Pb > Cd > Zn > Cu. (Table 1, 2). In sediment samples, Heavy metals showed a similar pattern of concentration as its abundance in water. The results of heavy metals analysis in various organs (gills, muscle, kidney and liver) of *R. frisii kutum*, *A. persicus*, *R. rutilus caspicus* and *C. carpio* showed that Fig. 2: A, B, C and D. In this research, we observed the trend that different metals are accumulated at various concentrations in different organs of fishes. The maximum and minimum of heavy metals concentration were recorded in liver and Muscle, respectively. The order of heavy metal concentration in different organs was liver > gills > kidney > Muscle. Also the results showed that the Order of heavy metal level in muscle, liver, gills and kidney was Pb > Cd > Zn > Cu. The results showed that the heavy metal concentrations in fish organs (muscle, gills, kidney and liver) are closely depend on heavy metal content of water and sediments. A remarkable relationship between concentrations of heavy metals in aquatic organisms, water and sediments were reported by Ibrahim et al. [2000] and Ibrahim and El-Naggar [2006]. The fish *A. persicus* has shown higher values of Pb (6.6 µg kg<sup>-1</sup>) in the muscle. The liver and gills (9.1 and 8.9 µg kg<sup>-1</sup>) of *R. frisii Kutum* and *C. carpio* exhibited elevated levels of Pb. The highest concentration of Pb (7.4 µg kg<sup>-1</sup>) in kidney was recorded in *R. frisii kutum*.

The highest concentrations of Zn (2.5 µg kg<sup>-1</sup>) in muscle and liver (3.9 µg kg<sup>-1</sup>) were recorded in *A. persicus* and *R. frisii kutum*, respectively and the highest concentration of Zn in gills (3.4 µg kg<sup>-1</sup>) were measured in *R. frisii Kutum* and *C. carpio*. The highest of Zn (3.2 µg kg<sup>-1</sup>) concentration in kidney were observed in *C. carpio*. The maximum concentration of Cd (6.3 µg kg<sup>-1</sup>) in muscle was measured in *A. persicus*. The highest concentration of Cd were observed in liver (8.8 µg kg<sup>-1</sup>), gills (8.5 µg kg<sup>-1</sup>) and kidney (7.4 µg kg<sup>-1</sup>) in *R. frisii kutum*. The *R. frisii kutum* has shown higher values of Cu (2.3 and 2.6 µg kg<sup>-1</sup>) in the muscle and kidney, respectively. The liver and gills (3.5 and 3.4 µg kg<sup>-1</sup>) of *R. frisii kutum* and *C. carpio* showed elevated levels of Cu. The many studies on metal accumulation in fish living showed that considerable amounts of different metals might be deposited in fish tissues without causing its mortality. Different metals are accumulated in various amounts in fish body. The differences in the accumulation levels in different organs of a fish can chiefly be depend on the differences in the

physiological role of each organ. Other parameters like behavior, regulatory ability and feeding habits may play an important role in the accumulation differences in the various organs (Marzouk, 1994). The results of many research indicated that metals exhibit various affinity to different organs. The major total body part of loads accumulated at various metals concentrations in the water and at different exposure times are found in kidney, liver and gills (Al-Mohanna, 1994; Kock et al., 1998; Giguere et al., 2004). Irrespectively of the uptake route, liver accumulates high level of metals. The liver is introduced as a good water pollution monitor. In the liver, Metal levels rapidly rise during exposure and it remains high for a long time of purification, when other organs are previously cleared. Concentrations of metal in the kidneys increase slower than in liver and it prevalently reach slightly lower values; hence the kidneys might be considered as a good pollution indicator too. In purification period, levels of kidney metal remain high or may even rise for some time, which is depend to the kidneys role as organs of excretory (Jeziarska and Witeska, 2006). Accumulation of metals in fish depends on contamination and it may be different for various fish species living in the same water (Jeziarska and Witeska, 2001). Kidwell et al., [1995] reported that the benthivores contained more zinc and cadmium but predatory fish species accumulated more mercury. Ney and Van Hassel [1983] expressed that concentrations of zinc and lead were higher in benthic fish. Overall, the higher concentration of metals in the environment, the more might be taken up and accumulated by fish. Relationship between concentrations of metal in water and in the fish was reported in many studies (Moiseenko et al., 1995; Linde et al., 1996; Yamazaki et al., 1996; Zhou et al., 1998). The physiochemical properties of sampling station showed in table 3. The water pH value of study region varies between 6.3 to 6.8. The reactions of Acid base are significant in water due to their influence on the ion chemistry and pH. In acidic conditions, there are sufficient hydrogen ions that they occupy many of the negatively charged surfaces and little space is left to bind heavy metals, therefore, majority of heavy metals are in the soluble phase (Chapman, 1992). It is thought that the soluble form of heavy metals is more harmful because it is more readily available to aquatic organism and more easily transported. The data comparison about metal concentration in fish from different lakes shows that the cadmium and lead concentrations, but not zinc, are significantly higher in the fish of acidified lakes (Grieb et al., 1990; Haines and Brumbaugh, 1994; Wiener et al., 1990; Horwitz et al., 1995).

## CONCLUSION

In conclusion, Heavy metals accumulate in various tissues of fish with different amount. Overall, accumulation of metals in muscle was lower than liver, gills and kidney. The results present new information on the distribution of these metals in liver, gills, kidney and muscle of *R. frisii kutum*, *A. persicus*, *R. rutilus caspicus* and *C. carpio*. Generally, this research showed that concentrations of heavy metal in the Gorgan bay were so far significantly lower than effects range low (ERL) and lower than the maximum permissible concentration for various countries. According to the fish samples analyses, concentrations of heavy metal in fish species tissues were well within the limits set by the FAO/ World Health Organization (WHO) [1984] recommendations and showed that the fish from investigated region are safety for consumers.

## Conflict of interest

The authors declare no financial or other conflicts of interest.

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**Table 1.** Heavy Metal Concentrations in water samples in the different station. Values are mean of  $\pm$  SE of three replicates

| station | Heavy metal concentration in water sample( $\mu\text{g/L}$ ) |                 |                 |                 |
|---------|--|-----------------|-----------------|-----------------|
|         | Cu   | Zn              | Cd              | Pb              |
| 1       | $2.48 \pm 0.05$  | $5.4 \pm 0.3$   | $4.7 \pm 0.6$   | $7.1 \pm 0.6$   |
| 2       | $2 \pm 0.3$  | $6.2 \pm 0.7$   | $3 \pm 0.8$     | $5 \pm 0.6$     |
| 3       | $1.03 \pm 0.02$  | $1.18 \pm 0.04$ | $1.07 \pm 0.04$ | $2.1 \pm 0.7$   |
| 4       | $1.15 \pm 0.06$  | $1.33 \pm 0.09$ | $1.01 \pm 0.01$ | $1.06 \pm 0.03$ |
| 5       | $0.2 \pm 0.1$  | $1.24 \pm 0.08$ | $1 \pm 0.6$     | $0.96 \pm 0.03$ |

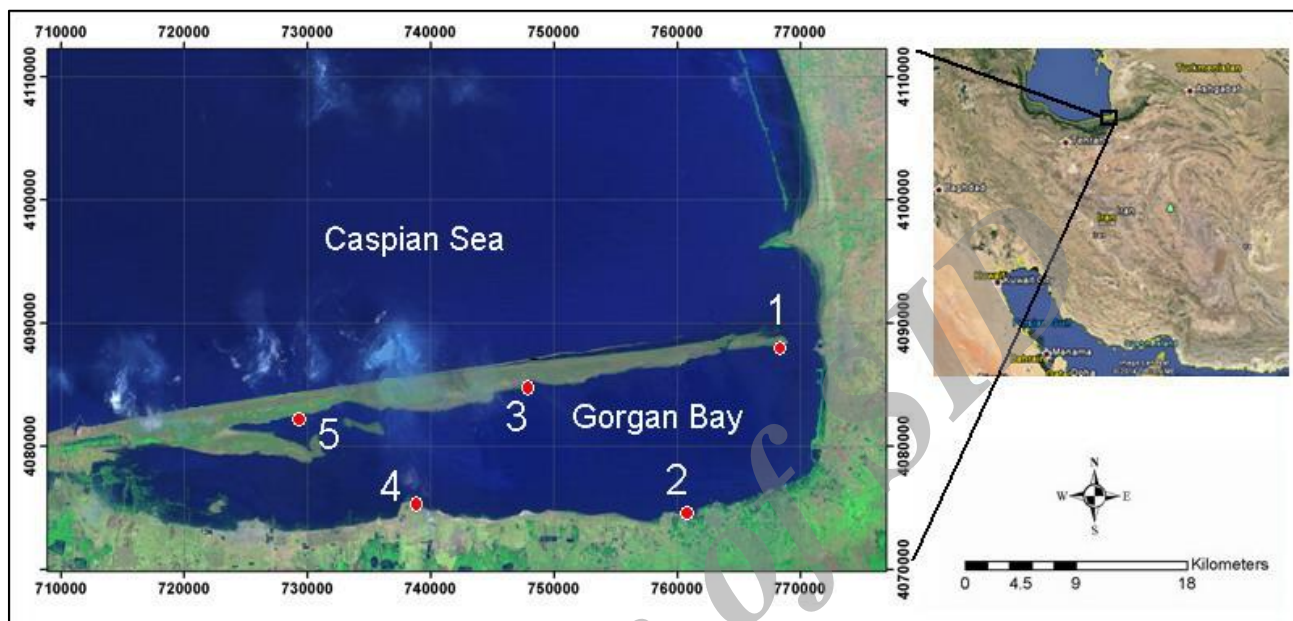
**Table 2.** Heavy Metal Concentrations in sediment samples in the different station. Values are mean of  $\pm$  SE of three replicates.

| station | Heavy metal concentration in sediment sample( $\mu\text{g/kg}$ ) |                 |                 |                 |
|---------|--|-----------------|-----------------|-----------------|
|         | Cu   | Zn              | Cd              | Pb              |
| 1       | $2.5 \pm 0.09$   | $6.55 \pm 0.06$ | $5.38 \pm 0.04$ | $7.8 \pm 0.5$   |
| 2       | $2.2 \pm 0.2$  | $6.4 \pm 0.4$   | $3.95 \pm 0.08$ | $5.62 \pm 0.04$ |
| 3       | $1.9 \pm 0.04$   | $1.7 \pm 0.08$  | $1.48 \pm 0.04$ | $2.82 \pm 0.02$ |
| 4       | $1.6 \pm 0.12$   | $1.72 \pm 0.02$ | $1.45 \pm 0.04$ | $1.51 \pm 0.05$ |
| 5       | $0.7 \pm 0.2$  | $1.64 \pm 0.04$ | $1.47 \pm 0.03$ | $1.09 \pm 0.02$ |

**Table 3.** The physiochemical properties of sampling station.

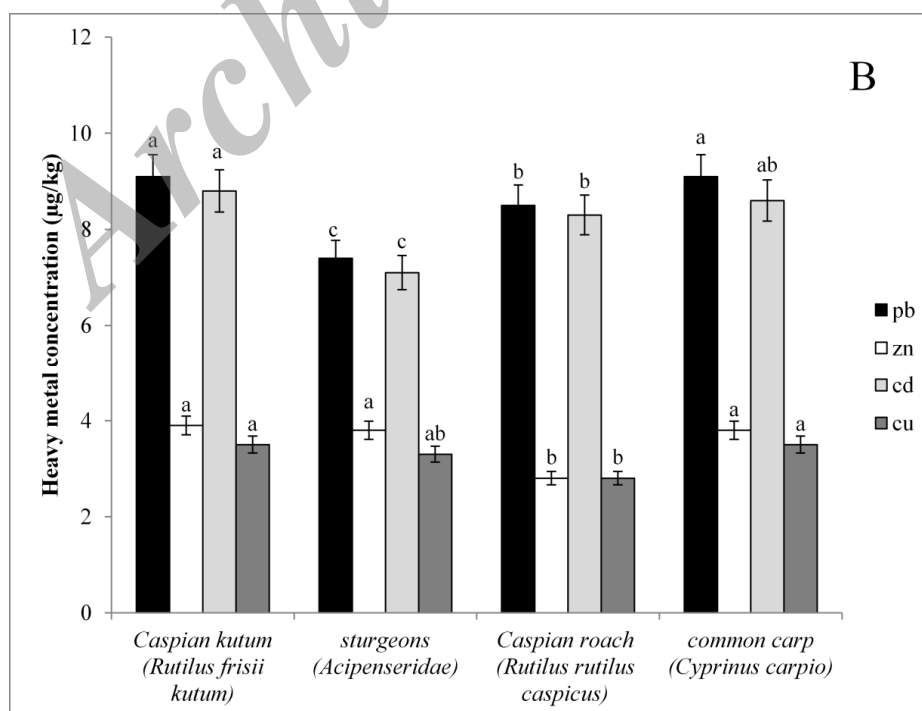
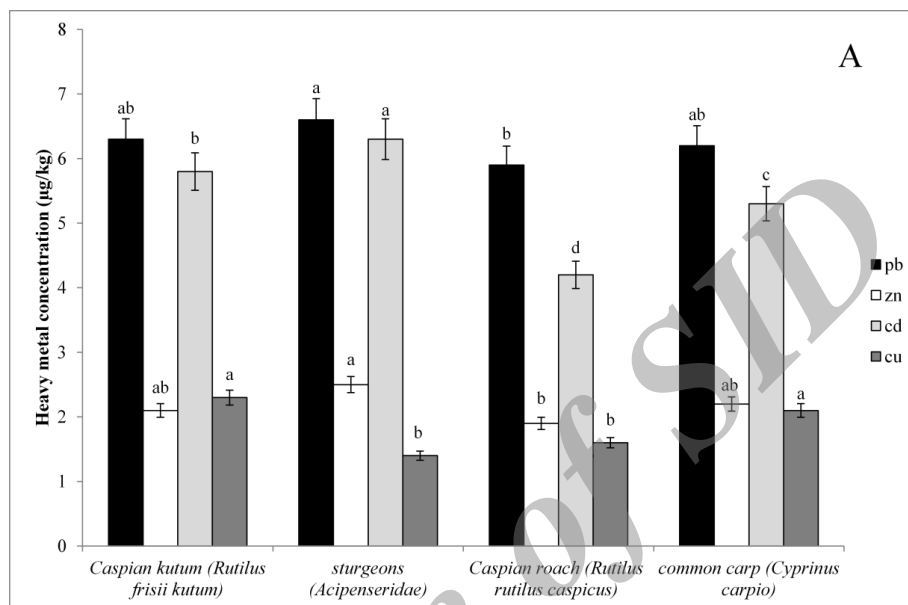
| Station | Temperature ( $^{\circ}\text{C}$ ) | pH  | Salinity (ppt) | DO (mg/l) |
|---------|------------------------------------|-----|----------------|-----------|
| 1       | 31.1                               | 6.2 | 13             | 5.7       |
| 2       | 31                                 | 6.5 | 12.8           | 6.3       |
| 3       | 30.9                               | 6.8 | 13             | 6.8       |
| 4       | 30.6                               | 6.8 | 13.2           | 6.4       |
| 5       | 30.7                               | 6.9 | 12.9           | 5.6       |

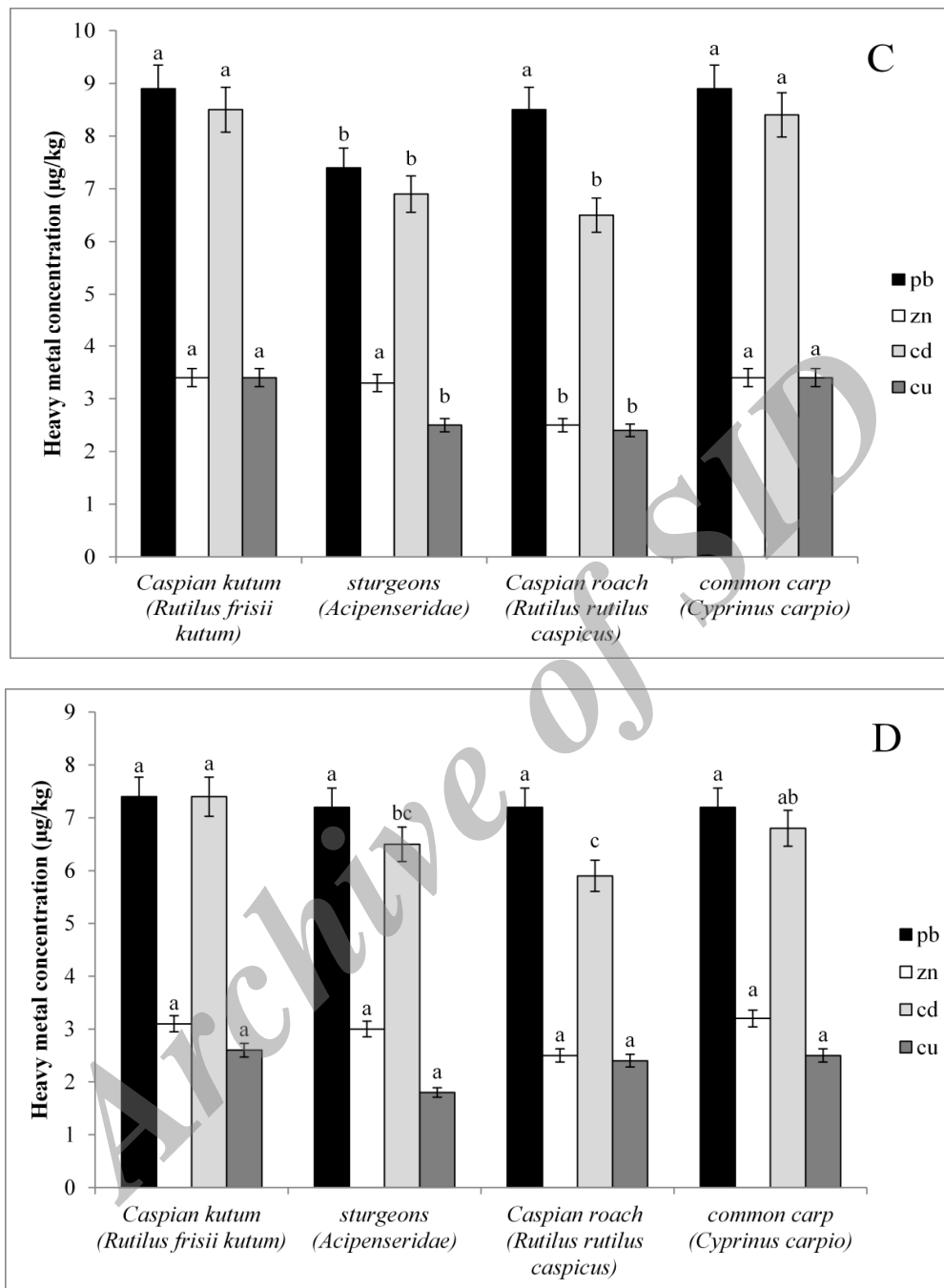




**Fig 1.** Location of sampling sites on the Gorgan bay, southeastern Caspian sea, Iran

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**Fig 2.** Heavy Metal concentration in the Fish Species organs (A: muscle; B: Liver; C: Gills and D: Kidney) collected from Gorgan Bay, Southeastern Caspian Sea, Iran. different letters indicate significant differences according to the Duncan's test ( $P < 0.05$ ) between different fishes. Error bars indicate standard error (SE).