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5. Seasonal variations of trace metals of Eastern Black Sea streams of Turkey: a case study of Firtina, İkizdere and Çağlayan

ALKAN Nigar[1], AKIN Gökhan[1], TERZI Yahya[1], SEYHAN Kadir[1]

[1] - Karadeniz Technical University, Faculty of Marine Sciences: 61350 Sürmene, Trabzon, Turkey

Address of author responsible for correspondence: **ALKAN Nigar** - Karadeniz Technical University, Faculty of Marine Sciences: 61350 Sürmene, Trabzon, Turkey. e-mail: nalemdag@ktu.edu.tr

ABSTRACT. The main aim of this study is to determine the seasonal changes of dissolved and particulate trace metals and compere according to various quality criteria in the selected rivers of the Eastern Black Sea. In this study some Physico-Chemical parameters (Temperature, pH, Conductivity), Dissolved Oxygen, dissolved and particulate metals (Mn, Ni, Cu, Zn, As, Pb) were investigated at Fırtına, İkizdere and Çağlayan streams in the Eastern Black Sea of Turkey. To perform particulate trace metals analysis water passed through 45 micron filters. After filters digested in the closed microwave digestion system (Milestone Ethosplus, İtaly) dissolved and particulate trace metals were determined using ICP-MS (inductively coupled plasma mass spectrometry). The Collosion Reaction Interface (CRI) was used during the determination of As. Both Sc and In (50 ppb) were added to all standards, blanks and samples and acted as internal standards. The results obtained were classified regarding the criteria's of European Council Directive 98/83/EC, National Recommended Water Quality Criteria (established by US Environmental Protection Agency in 2009) and World Health Organisation (WHO, 2004). Results obtained from three streams were found to be lower than legal limits proposed by European Council Directive 98/83/EC, US Environmental Protection Agency (2009) and World Health Organisation (2004).

Key words: Black Sea rivers, pollution, trace metals

INTRODUCTION

Rivers are the most important freshwater resources used for drinking water, irrigation ,hydroelectric power plant, industrial and municipal facilities and fishing .This resource is also used as a discharged area for uncontrolled industrial, agricultural and domestic wastes [*2*].

Metals naturally occur in aquatic environments in very low concentrations, but over time, concentration levels have increased due to industrial activities as well as agriculture and mining create a potential source of metals pollution in aquatic systems.

The main trace metals reservoirs are found dissolved, particulate phase (generally these are defined as being greater than 0.45 µm in size) and bottom sediments [*1*]. Most contaminated such as trace metals tend to be trapped in suspended solid [*3*].

In the present study, seasonal trace metals concentrations in dissolved and total suspended solid (TSS) were determined and compared according to various quality criteria at Fırtına, İkizdere and Çağlayan streams in the Eastern Black Sea of Turkey.

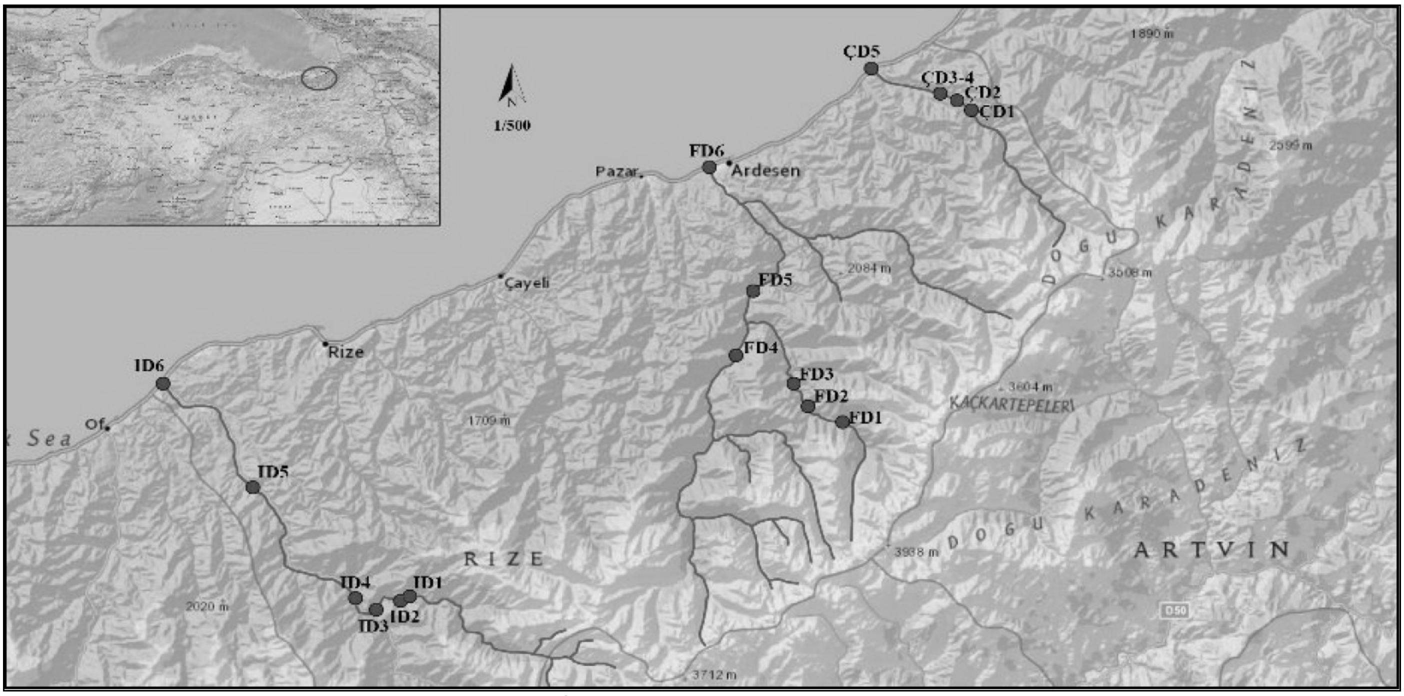

Fig. 1. Study area and sampling stations.

MATERIALS AND METHODS

Study area

Seasonaly water samples were taken from Çağlayan, Fırtına and İkizdere streams in Rize of Eastern Black Sea of Turkey between November 2013-June 2014. Water samples were taken at 5 locations in the Çağlayan, 6 locations in the Fırtına and 6 locations in the İkizdere. Nomenclatures for the rivers were as follows: Çağlayan (ÇD1, ÇD2, ÇD3, ÇD4,ÇD5,), Firtina (FD1, FD2, FD3, FD4, FD5, FD6) and İkizdere (ID1, ID2, ID3, ID4, ID5, ID6) (Fig.1).

Sampling and metal analysis

To perform trace metals analysis in the rivers, sampling was done seasonaly in specified stations. Water passed through 45 micron filters which were previously dried and brought to constant weight. Ultrapure HNO_3 added water were stored in fridges at laboratories. To perform particulate trace metals analysis dried filters digested in the closed microwave digestion system according to MILESTONE (2011) [*7*]. Dissolved and particulate trace metals were determined using ICP-MS (Varian-820 (Bruker), Australia). The Collosion Reaction Interface (CRI) was used during the determination of As. Both Sc and In (50 ppb) were added to all standards, blanks and samples and acted as internal standards.

RESULTS AND DISCUSSION

The average particule and dissolved trace metal concentrations in Çağlayan, Fırtına and İkizdere streams was given in **Fig. 2** - **Fig. 13**.

As a result particulate Mn concentration was found to be higher than other streams. This high metal concentration in suspanded solid was arised from winter and spring (**Fig. 2**). The average particulate trace manganese (Mn) concentrations were measured to be higher than dissolved Mn concentrations in all streams (**Fig. 3**).

The average dissolved nickel (Ni) concentrations in all streams were found to be higher than in particulate trace metal concentrations (**Fig. 4**). Ni was found to be higher in İkizdere than Fırtına and Çağlayan rivers. Total Ni concentration was measured as ID>FD>ÇD respectively (**Fig. 5**).

The average particulate trace copper (Cu) concentrations were measured to be higher than dissolved Cu concentrations in all streams (**Fig. 6**). Cu concentration both dissolved and particulated was measured as ID>FD>ÇD respectively (**Fig. 7**).

Generally, dissolved zinc (Zn) concentrations were measured to be higher than particulate Zn concentrations in all streams (**Fig. 9**). The highest concentration of dissolved Zn were measured during autumn in all the streams. The large proportion of the total concentrations of Zn present in dissolved form at spring and winter period (**Fig. 8**).

Dissolved arsenic (As) concentrations ware measured as İD>FD>ÇD respectively all seasons (**Fig. 11**). Investigated the seasonal variation of arsenic which the highest concentration measured in İkizdere measured as winter >spring > summer respectively (**Fig. 10**). This situation can be accounted for associated with a high level arsenic concentration in suspanted solid (TSS).

Lead (Pb) concentration was measured above one µg/L in in suspanted solid in İkizdere (**Fig. 13**). Particulate lead concentration was found to be high in İkizdere compared to other streams (**Fig. 12**).

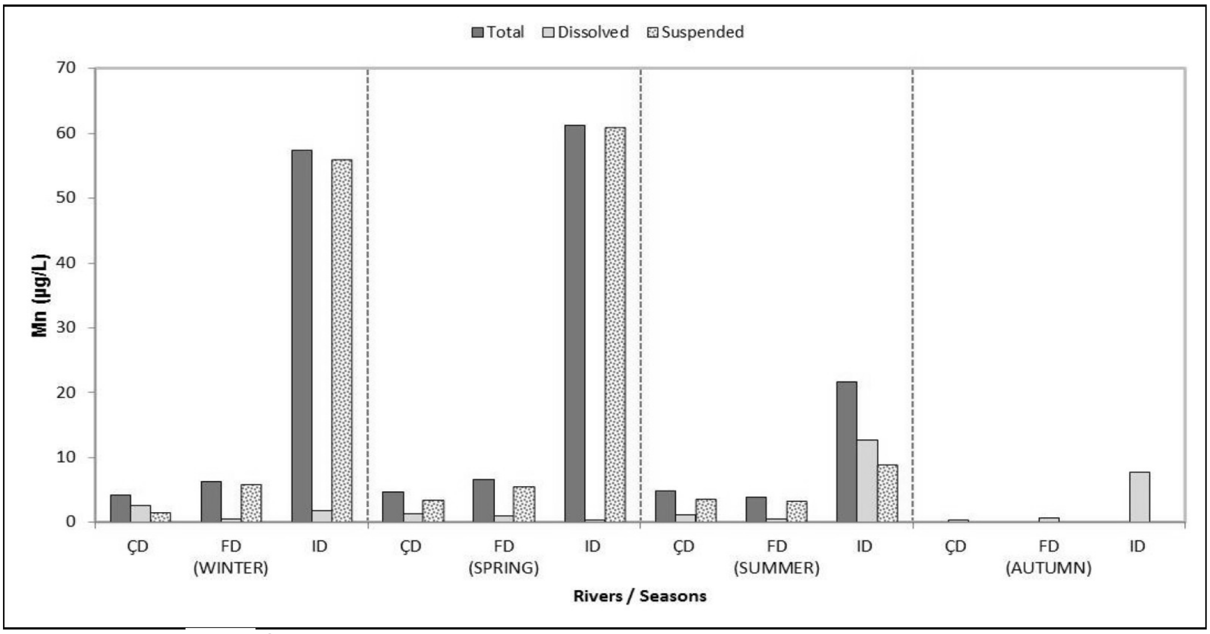

Fig. 2. Seasonal total, dissolved and suspended Mn concentrations in streams.

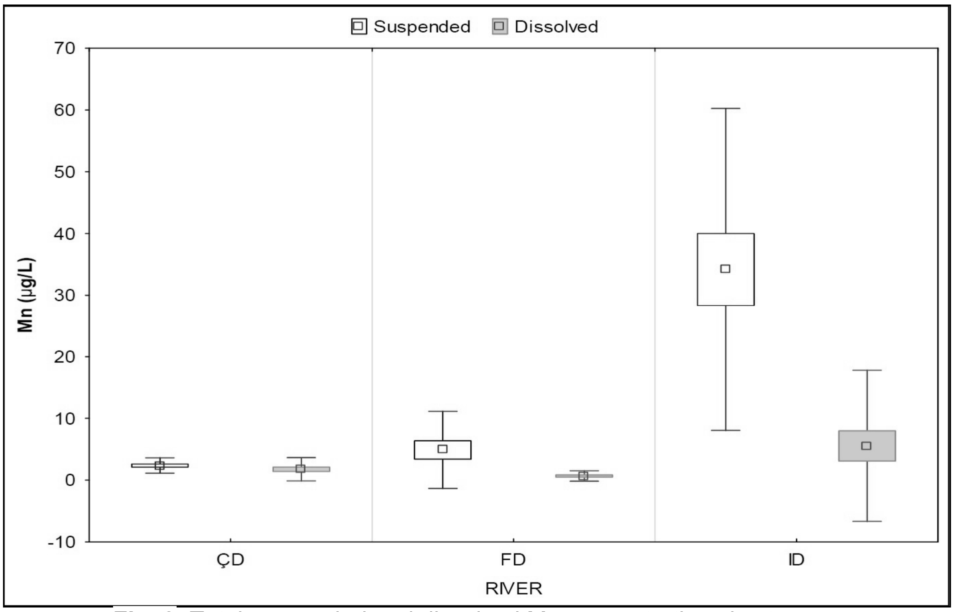

Fig. 3. Total suspended and dissolved Mn concentrations in streams

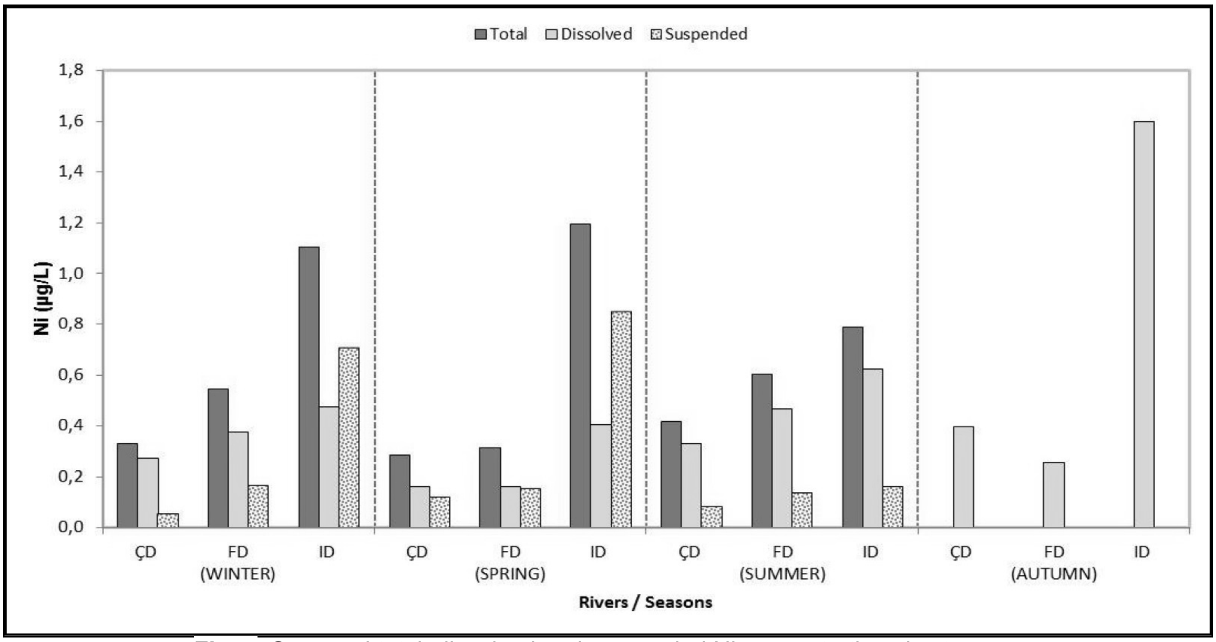

Fig. 4. Seasonal total, dissolved and suspended Ni concentrations in streams.

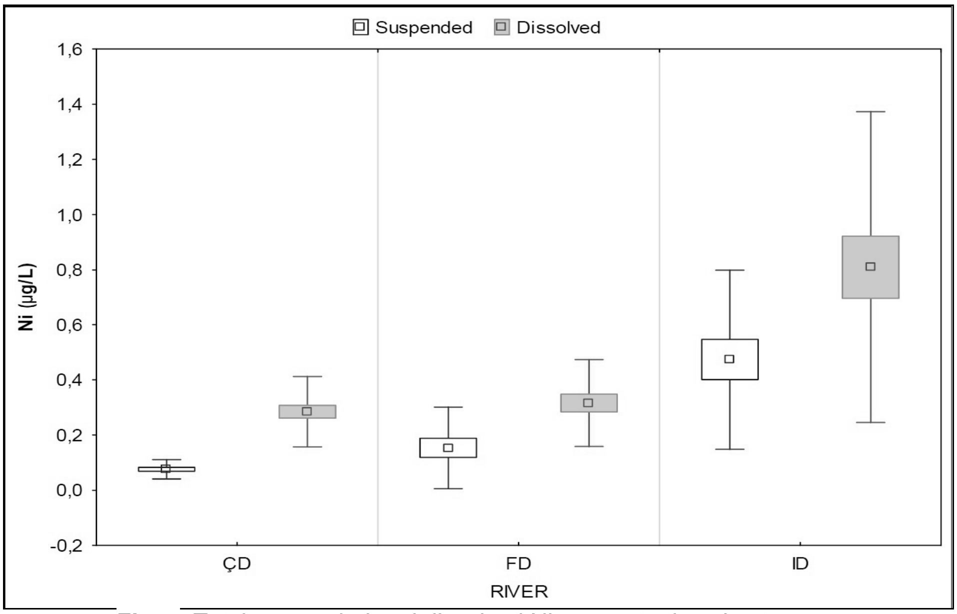

Fig. 5. Total suspended and dissolved Ni concentrations in streams.

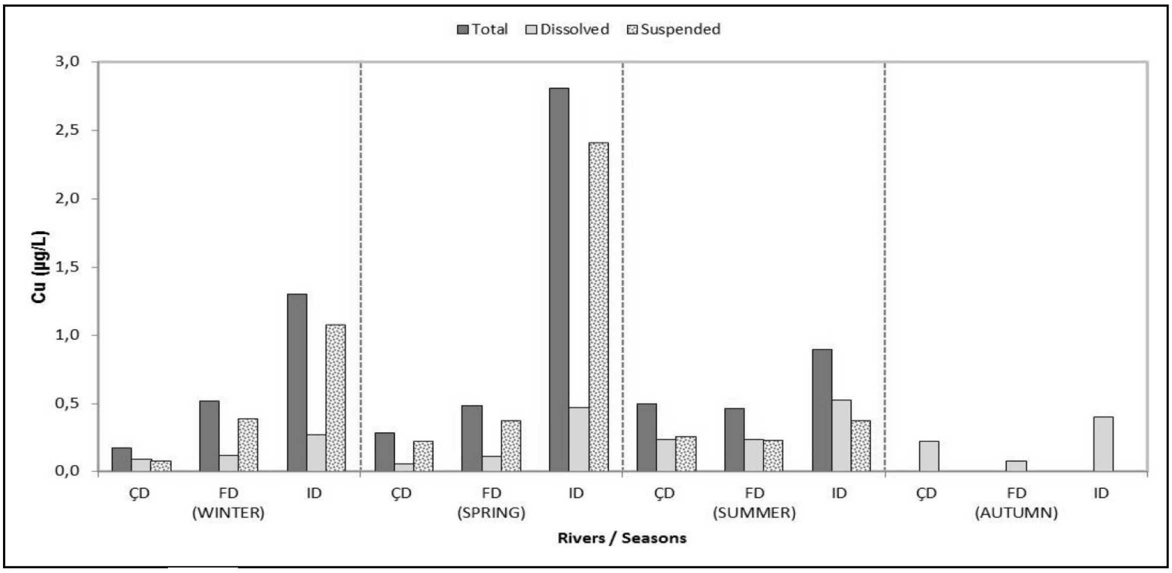

Fig. 6. Seasonal total, dissolved and suspended Cu concentrations in streams.

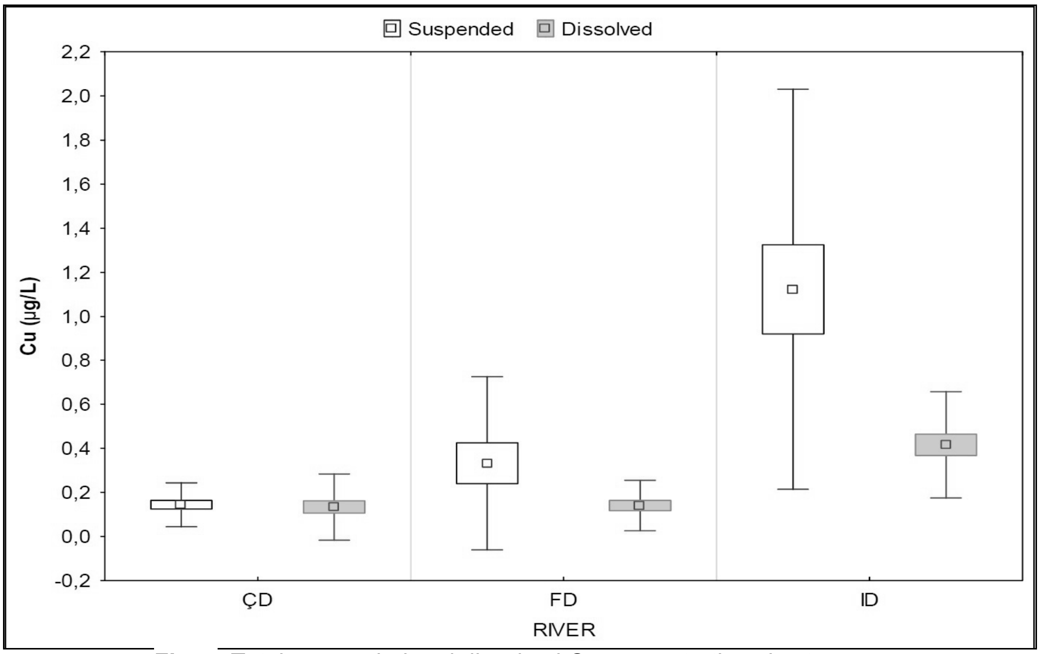

Fig. 7. Total suspended and dissolved Cu concentrations in streams.

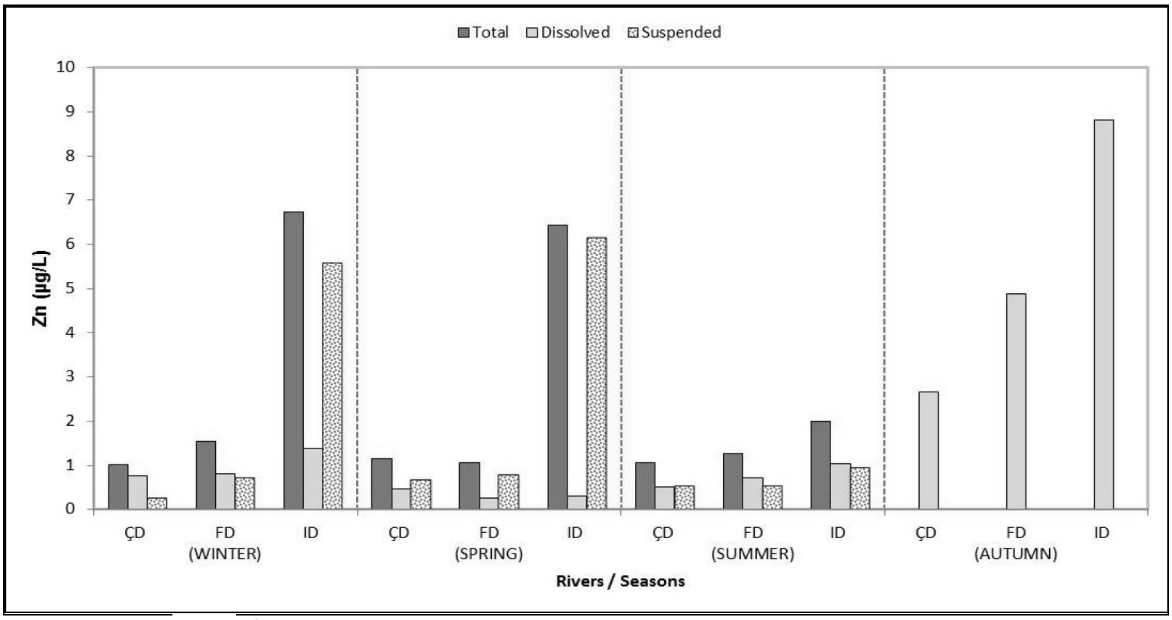

Fig. 8. Seasonal total, dissolved and suspended Zn concentrations in streams

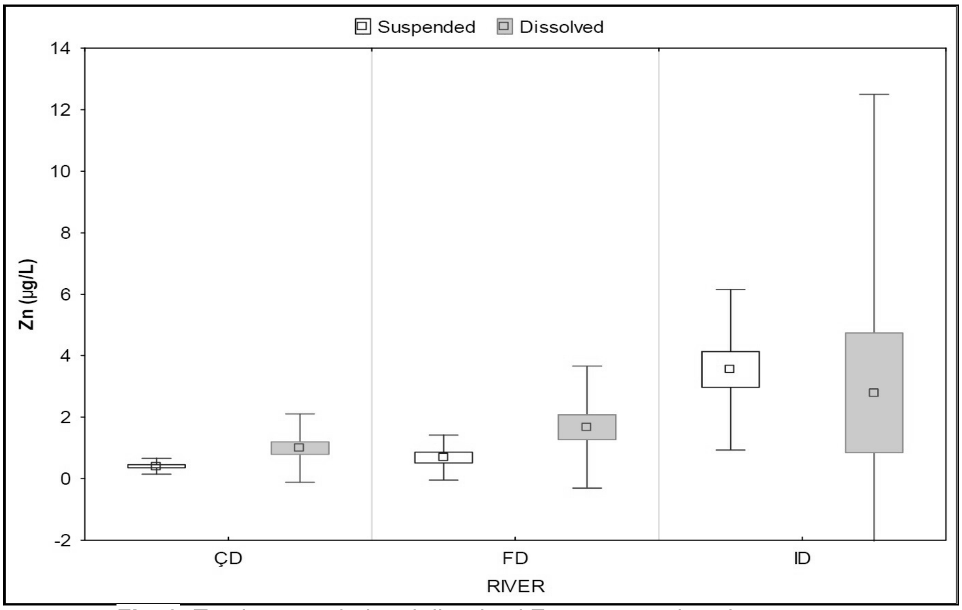

Fig. 9. Total suspended and dissolved Zn concentrations in streams.

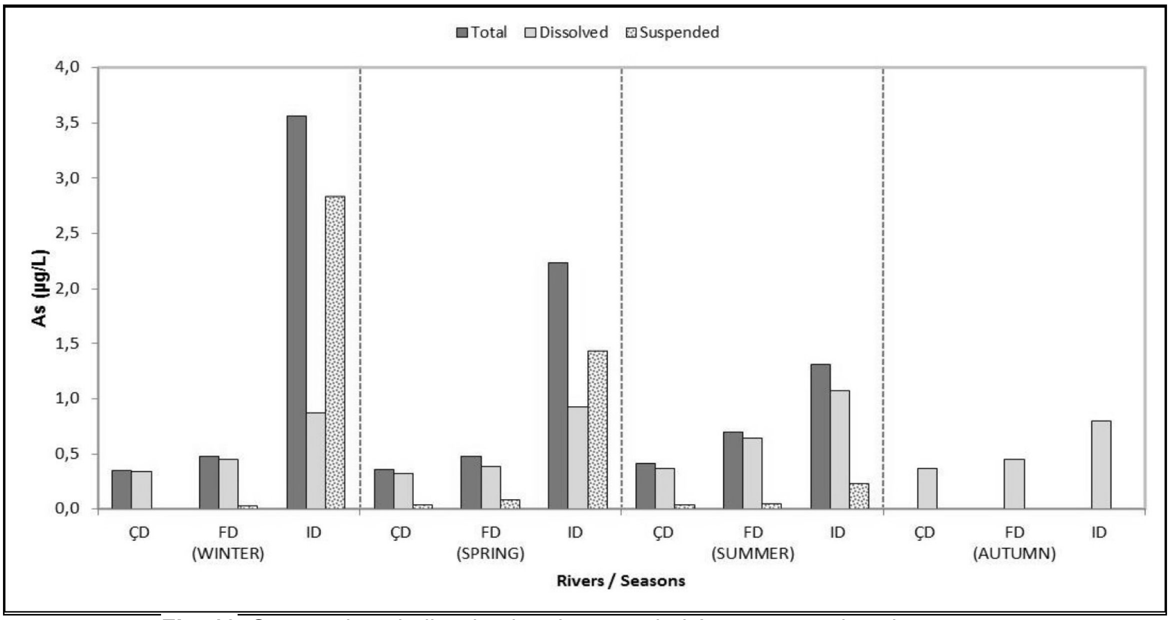

Fig. 10. Seasonal total, dissolved and suspended As concentrations in streams.

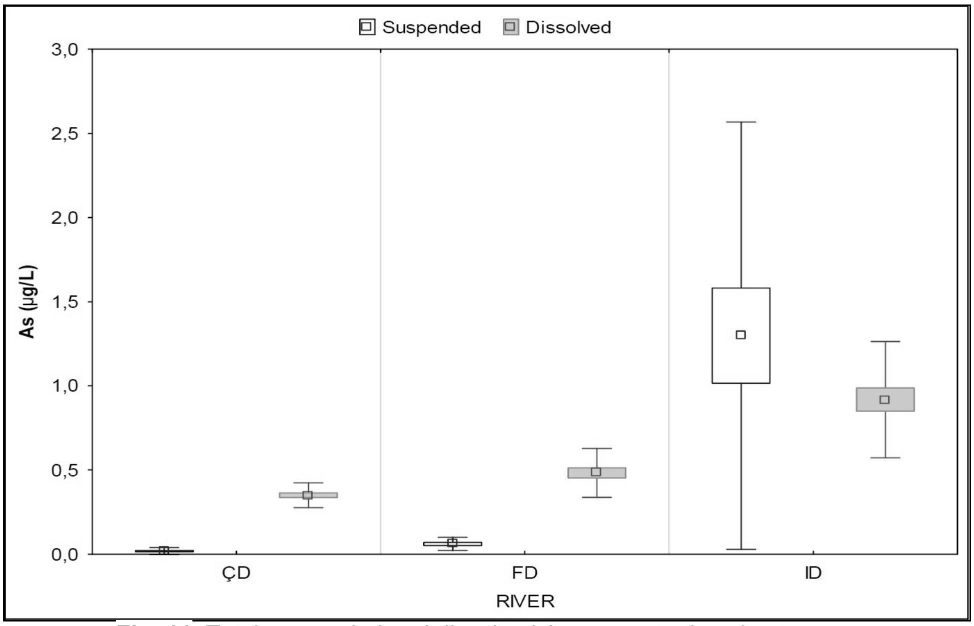

Fig. 11. Total suspended and dissolved As concentrations in streams.

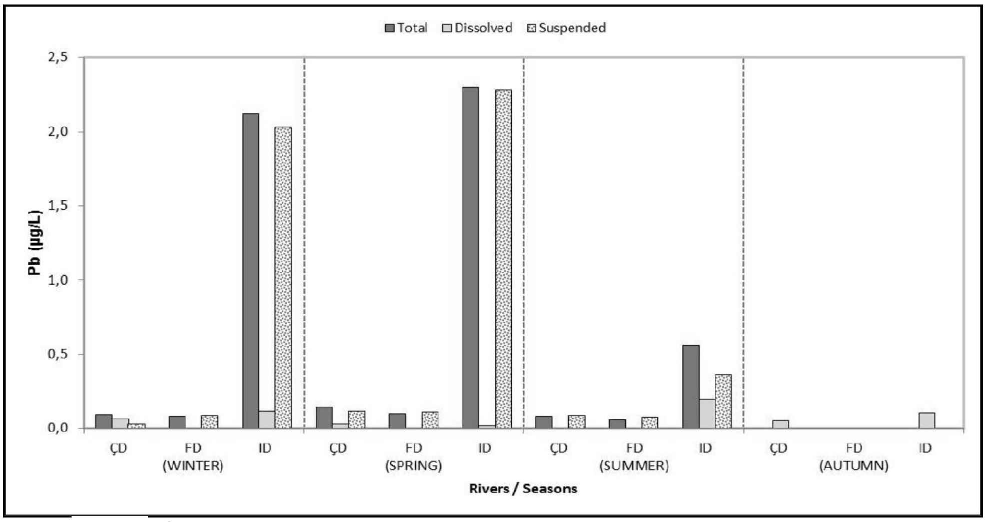

Fig. 12. Seasonal total, dissolved and suspended Pb concentrations in streams

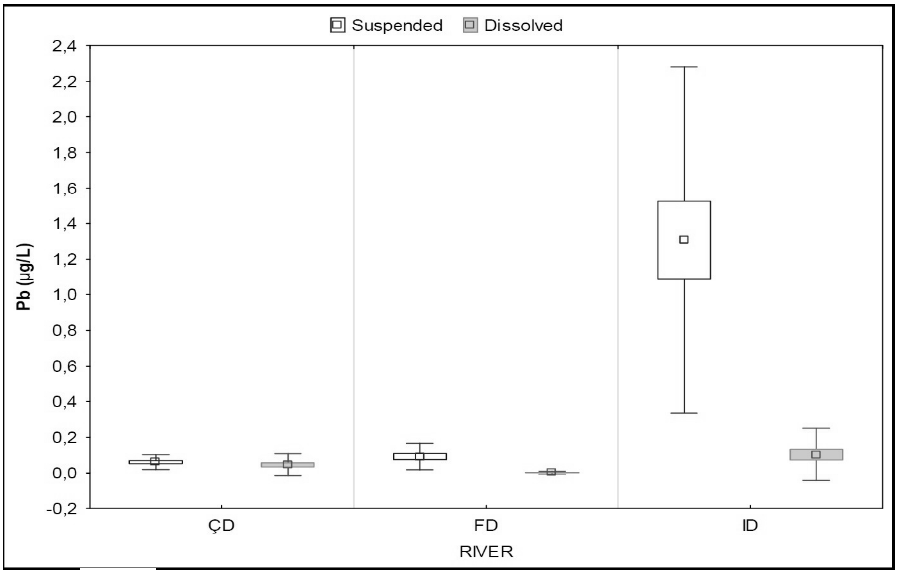

Fig. 13. Total suspended and dissolved Pb concentrations in streams

CONCLUSIONS

Metal concentrations in fresh water resources are important for human health and aquatic ecosystem. The present study shows that total concentrations were found to be high in İkizdere compared to other streams in all seasons. This is, although far away from being above the accepted level for all the concern bodies in the world, due to ongoing man made impacts on the Ikizdere stream including Hydro electricity constructions and fertilizer taken place in the Spring through Sumer time. The results obtained were classified regarding the criteria's of European Council Directive 98/83/EC [***4***], National Recommended Water Quality Criteria (US EPA) [***6***] and World Health Organisation (WHO, 2004) [***5***]. Results obtained from three streams were found to be lower than legal limits proposed by European Council Directive 98/83/EC, US Environmental Protection Agency and World Health Organisation.

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