Seasonal Accumulation of Heavy Metal in Marine Brown Algae (Phaeophyta) in the Kastamonu Coasts (Turkey)

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Abstract
This study was aimed to determine the seasonal variation of heavy metal pollution in marine brown algae (Phaeophyta) in the Kastamonu coasts (Turkey). The samples were collected two stations from Kastamonu coasts in December 2016, March 2017, June 2017 and September 2017. After that Mn, Cd, Zn, Cu, Fe, Ni and Pb concentrations of these samples were determined. After performing the necessary laboratory analyzes and statistical analyzes, the results have indicated an increase in the concentrations of heavy metal in autumn than any other season. Such revelations may be ascribed to the fact that, during the year in Turkey, the first rains take place in autumn. Besides, the air contains a great amount of pollutants and these pollutants drop down within the first rain period, the results further revealed that all the concentrations of heavy metals in Site 1 were higher than that of Site 2. The increase of the concentrations of heavy metals could be attributed to the fact that Site 1 is near to the city center and port, in which there is a high possibility of city was discharge and the city's port pollutants in the Sea, In general, the results showed a seasonal variation in heavy metal concentrations during all seasons, It can be said that heavy metal pollution in the coasts of Kastamonu has not reached a dangerous level yet. Finally, it is highly recommended that similar pollution studies should be carried out at regular intervals and reported routinely to the competent authorities.

Keywords: *seasonal, accumulation, Kastamonu, Marine brown algae*

Introduction

The problems started because of eutrophication and pollution since the 1970s. massive quantities of organic and inorganic compounds were annually discharged into the sea from rivers and waste product industry, six states have a gap at the Black Sea, however, eighteen countries use to discharge toxic wastes through the rivers flowing into the sea, Pollutants carried by rivers area unit the most supply of pollution within the Black Sea, Pollutants carried by rivers area unit the most supply of pollution within the Black Sea. (Oros et al., 2010(.The results of serious metals level within the Turkish coast of Black Sea were compared with the boundaries people independent agency and incontestible that the water is additionally contaminated than in different coastal areas Coban et al., 2009), serious metal pollution within the marine surroundings may be a drawback of a large interest at world level. The character of semi-enclosed ocean, the massive oceanography basin, and its hydrobiological options create the Black Sea a novel system, extraordinarily sensitive and exposed to those threats. Black Sea ecosystems area unit destroyed because of chemical pollution. Several pollutants come back from massive rivers, however additionally coastal activities contribute to the present development of major pollution. (Jitar et al., 2013). The investigations conducted within the NorthWestern Black Sea Danube show the importance of the distribution of serious metals in marine waters. The results show that the Black Sea is made in Cd, cobalt, copper and nickel, as compared to different regional seas (Zeri et al., 2000). The algae area unit a vital assemblage of plants that area unit classified in concerning 265 genera with over 1500 metal money, The protoctist area unit enclosed within the kingdom and area unit distinguished from different chlorophyllose plants on the premise of amphimixis. The variations between copies within the protoctist (Bold et al., 1985). The term protoctist refers to an oversized and various assemblage of organisms that contain pigment and perform oxygenic chemical change (Davis et al., 2003). Some algae species will accumulate high concentrations of serious metals in contaminated ecosystems, and as a result, they're chosen as metal biomonitors in coastal areas (Villares et al., 2002). Brown algae cell walls have sulfated fucans and process alginic acids that act as cation-exchangers, wherever cations like $Ca2+$, $K +$, $Na +$ area unit substituted by serious metal ions (Romera et al., 2006). The chemical affinity of the polyanionic polysaccharides by cations permits the utilization of non-living biomass of algae as a biosorbent material to get rid of serious metals from industrial effluent (Volesky et al., 2001). Metal quantification information obtained by atomic absorption spectrophotometry (AAS) show that (brown alga) presents the best concentrations of zinc and Cd among the protoctist found in SB (Amado Filho et al., 1996, 1999). A sequent in vitro study showed that this algae might accumulate higher amounts of zinc and Cd than all protoctist, additionally causative the metals as mineral granules into the cell walls (Andrade et al. 2004). Biosorbents area unit won't to remove/sequester serious metals from a pre-treated industrial effluent by a passive binding mechanism, and afterwards, the metals will be recovered and recycled (Andrade et al. 2010). Several studies are characterizing the physical-chemical properties of the biosorption method between completely different biomasses and serious metals (Volesky and Holan, 1995).

Materials and Methods

Study area.

The Black Sea is the world's largest interior body of water that is globally recognized for its pollution. Approximately, a third of the European continental land infiltrates into it and the Black Sea environment has experienced deterioration from the refuse from around 17 countries (Bat,Gökkurt, Sezgin, Üstün&Sahin, 2009). Study samples were collected from two sites in Kastamonu. Located in the north-western part of Turkey, the province of Kastamonu has lately been receiving national attention because of its cultural and touristic attractions (Kam et al. 2007), and they were taken 4 times in December 2016, March 2017, June 2017 and September 2017.

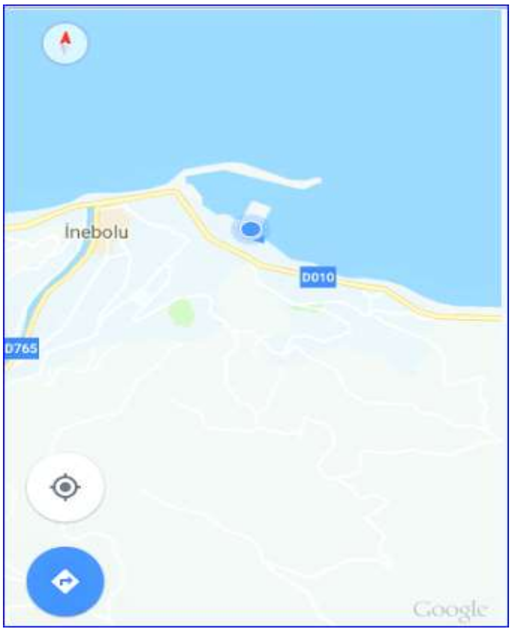


Fig. 1.Site 1

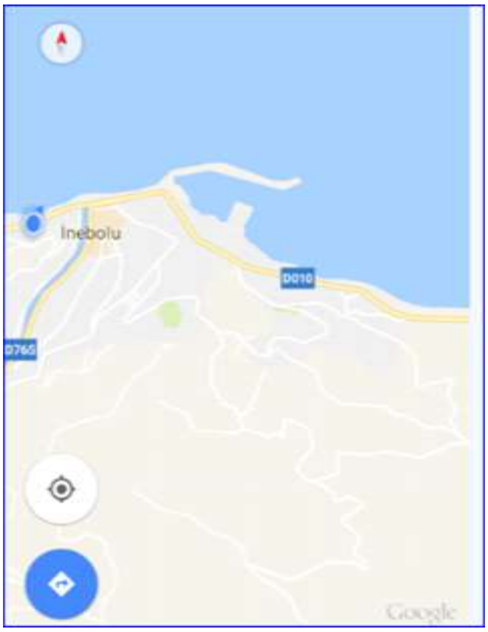


Fig.2. Site2

Sampling methods.

The brown algae samples were collected by hand from the aforementioned coastal sites. At a depth of about 1–2m. After that, they were washed with ambient water to remove clay sands, dusts, associated algae, sediments and debris. The cleaned algae were then placed separately in polythene plates. Finally, the seaweeds were shade dried for 10 days in a clean environment to prevent it from defilement **(**Kannan, 2014).

Fig .3.Image of brown algae samples

Sample analysis.

Heavy metal analyses were performed in Kastamonu University Central Research Laboratory. For brown algae samples, 0.5g of each sample was taken and HNO_3 and H_2O_2 were added. The samples were then dried under a pressure of 200°C and 45 bar for 15 minutes and then cooled to room temperature. After cooling, the samples were added to ultra-pure water and the readings were performed in ICP-OES (SpectroBlue). The ICP-OES device used performs three readings for each heavy metal and yields in ppb. There is a dilution factor 200 for all samples. Therefore, the results obtained were multiplied by 200 and all results were divided by 1000 and converted to ppm.

Statistical Analysis

For statistical analysis, Mann Whitney test and Kruskal Wallis test were applied to the data following analysis of variance (ANOVA). All statistical analyses were performed with SPSS version for Windows between heavy metals.

season	site	cu (ppm)	cd (ppm)	pb (ppm)	ni (ppm)	mn (ppm)	fe (ppm)	zn (ppm)
autumn	1	16.3554	0.6056	3.4666	7.0242	25.8116	285.69	13.9058
	1	16.0958	0.6204	3.7084	6.6794	26.5409	288.184	13.9686
	1	16.1138	0.6122	3.6128	7.0006	26.0304	287.574	13.9734
winter	1	14.0462	0.4432	2.5052	3.9038	14.8376	85.3922	12.4996
	1	14.0084	0.4274	2.362	3.4794	14.7038	83.5688	12.5519
	1	14.0328	0.4266	2.4154	3.9764	14.7008	83.309	12.5254
spring	1	18.6952	0.3388	2.3046	5.8324	6.45862	89.2262	9.6885
	1	18.5962	0.3776	2.387	5.8914	6.7476	89.1196	9.6853
	1	18.5486	0.3738	2.4144	5.4921	6.7348	88.8662	9.7528
summer	1	12.2936	0.4782	2.4136	3.6136	10.4124	77.0564	10.3958
	1	12.2248	0.4846	2.3698	3.4553	10.3754	76.5778	10.4228
	1	12.2356	0.4502	2.3484	3.5868	10.376	76.507	10.3358
autumn	2	12.8506	0.4326	2.5798	2.7314	24.4574	93.0816	16.3924
	2	13.0952	0.4298	2.5144	2.8322	24.543	92.6908	16.3664
	2	12.9704	0.4254	2.507	2.8432	24.4516	92.489	16.3354
winter	2	10.574	0.3684	2.4358	2.6646	17.3638	71.2778	12.6683
	2	10.1936	0.3347	2.4316	2.6174	17.2202	70.5318	12.462
	2	10.5289	0.3512	2.3912	2.5972	17.0856	70.1192	12.447
spring	2	9.6927	0.3339	2.2808	2.1682	13.0336	80.6068	9.3822
	2	10.1766	0.3274	2.3656	2.1368	13.058	80.9252	9.4012
	2	9.9358	0.3396	2.8439	2.1858	13.0078	80.9804	9.3692
summer	2	18.8338	0.5538	2.7086	4.4379	19.219	95.7976	19.3354
	2	17.9692	0.5557	2.7052	4.4462	19.2638	95.6004	19.4398
	2	18.5628	0.5778	2.6234	4.4116	19.2696	95.7466	19.3824

Table 2. Comparison between Cu (ppm) in the two study areas

site	samples	Mean	Std. Deviation	Std. Error Mean
1.00	12	15.2725	2.48848	.71836
2.00	12	12.8833	3.42251	.98799

The results showed that there were significant differences between the two regions where the value of the observed level of significance was (0.039) which is less than 0.05.

Fig. 4. Averages Cu (ppm) with the standard error in the two study areas

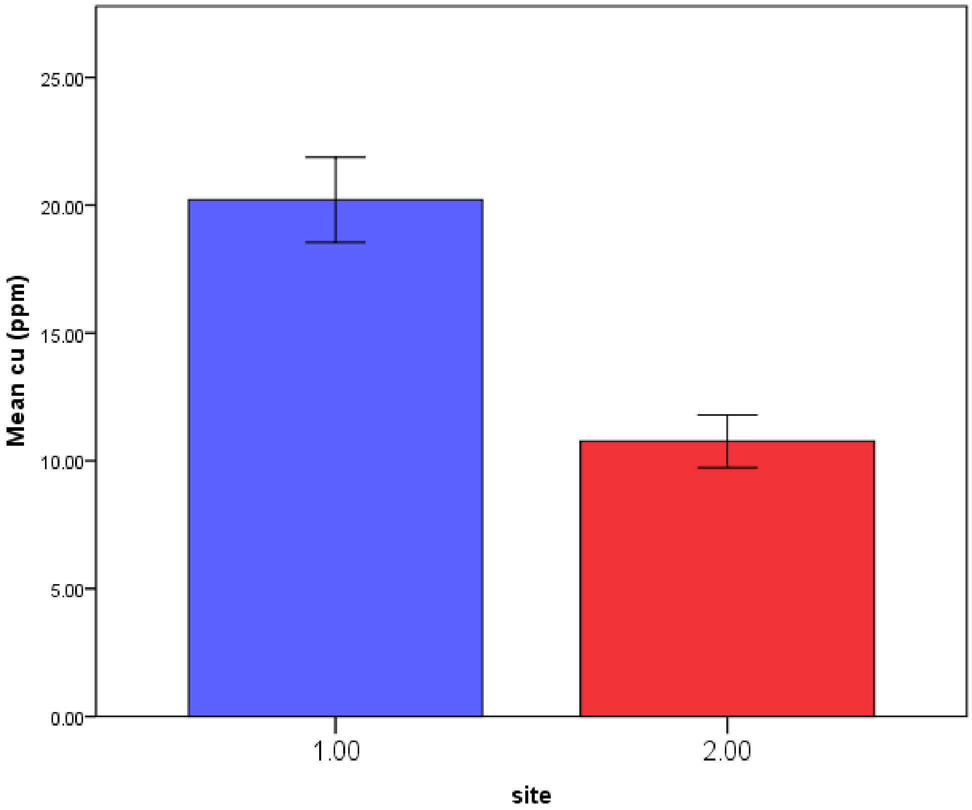


Table 3. Comparison between Cd (ppm) in the two study areas

Site	Samples	Mean	Std. Deviation	Std. Error Mean
1.00	12	.4740	.09078	.02620
2.00	12	.4208	.09350	.02699

The results showed that there were significant differences between the two regions where the value of the observed level of significance was (0.068) which is less than 0.05.

Fig. 5. Averages with the standard error of Cd (ppm) in the two study areas

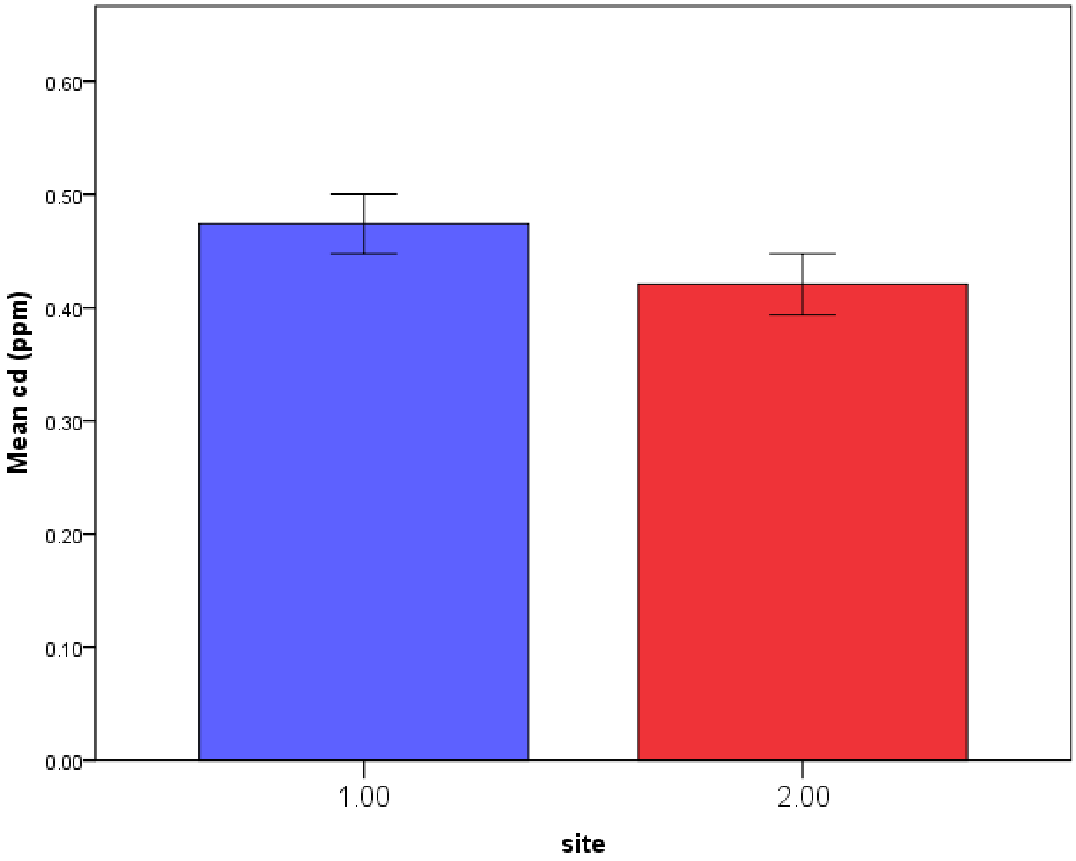


Table 4. Comparison between Pb(ppm) in the two study areas

site	samples	Mean	Std. Deviation	Std. Error Mean
1.00	12	2.6923	.54945	.15861
2.00	12	2.4985	.13414	.03872

The results showed that there were no significant differences between the two regions where the value of the observed level of significance was (0.443) which is greater than 0.05.

Fig. 6. Averages with the standard error of Pb (ppm) in the two study areas

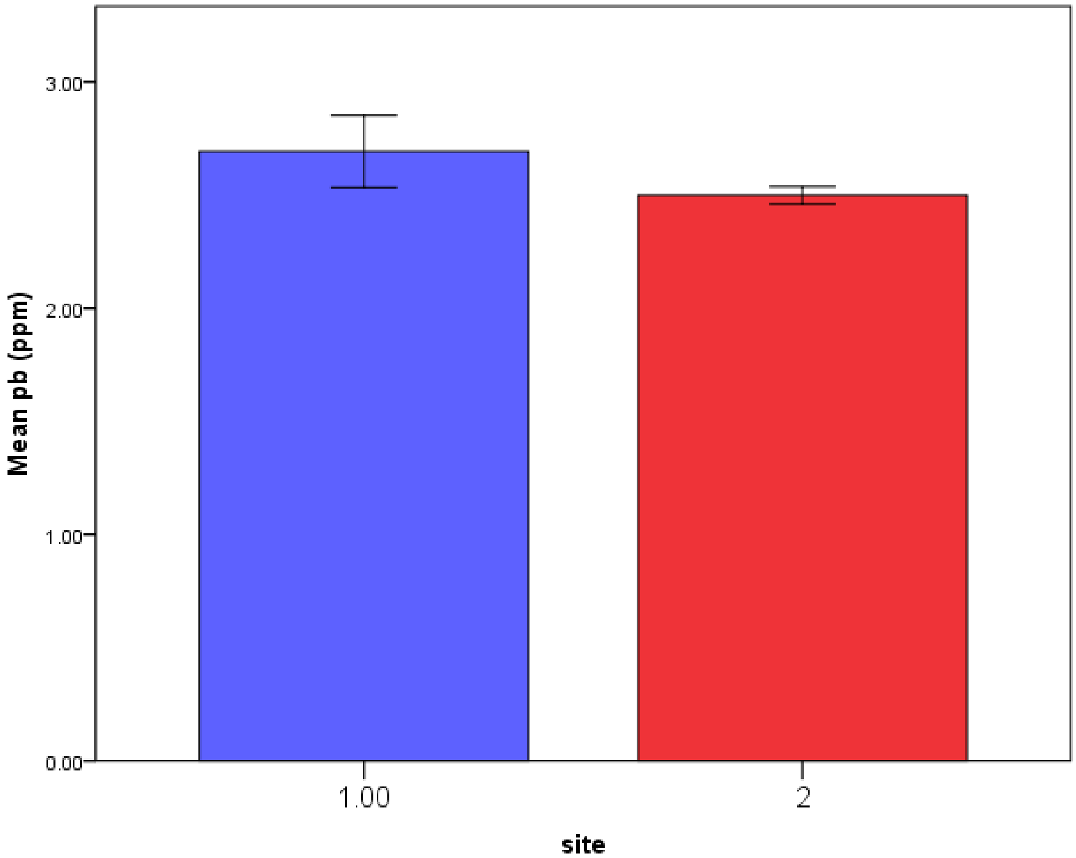


Table 5. Comparison between the Ni (ppm) in the two study areas

Site	samples	Mean	Std. Deviation	Std. Error Mean
1.00	12	5.0845	1.47394	.42549
2.00	12	3.0011	.88583	.25572

The results showed that there were significant differences between the two regions, where the value of the observed level of significance was (0.001) which is less than 0.05.

Fig. 7. Averages with the standard error of Ni (ppm)in the two study areas

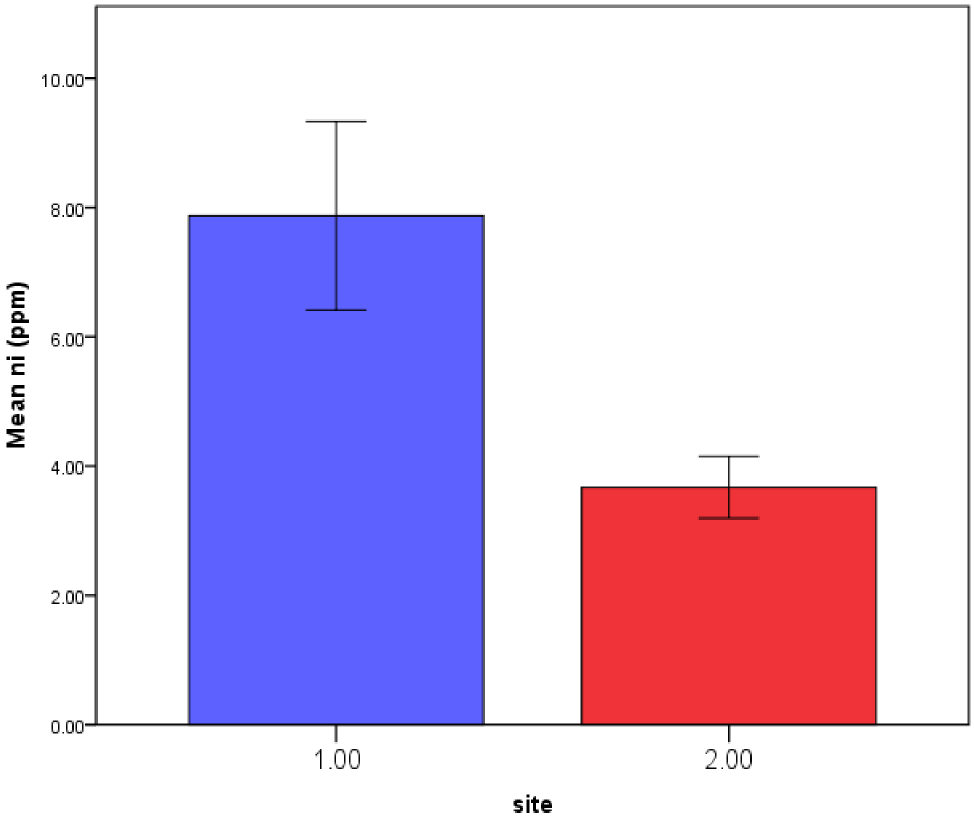


Table 6. Comparison between the Mn (ppm) in the two study areas

Site	samples	Mean	Std. Deviation	Std. Error Mean
1.00	12	14.4735	7.53708	2.17577
2.00	12	18.4978	4.30341	1.24229

The results showed that there were no significant differences between the two regions where the value of the observed level of significance was (0.128) which is greater than 0.05.

Fig.8. Averages with the standard error Mn (ppm) in the two study areas

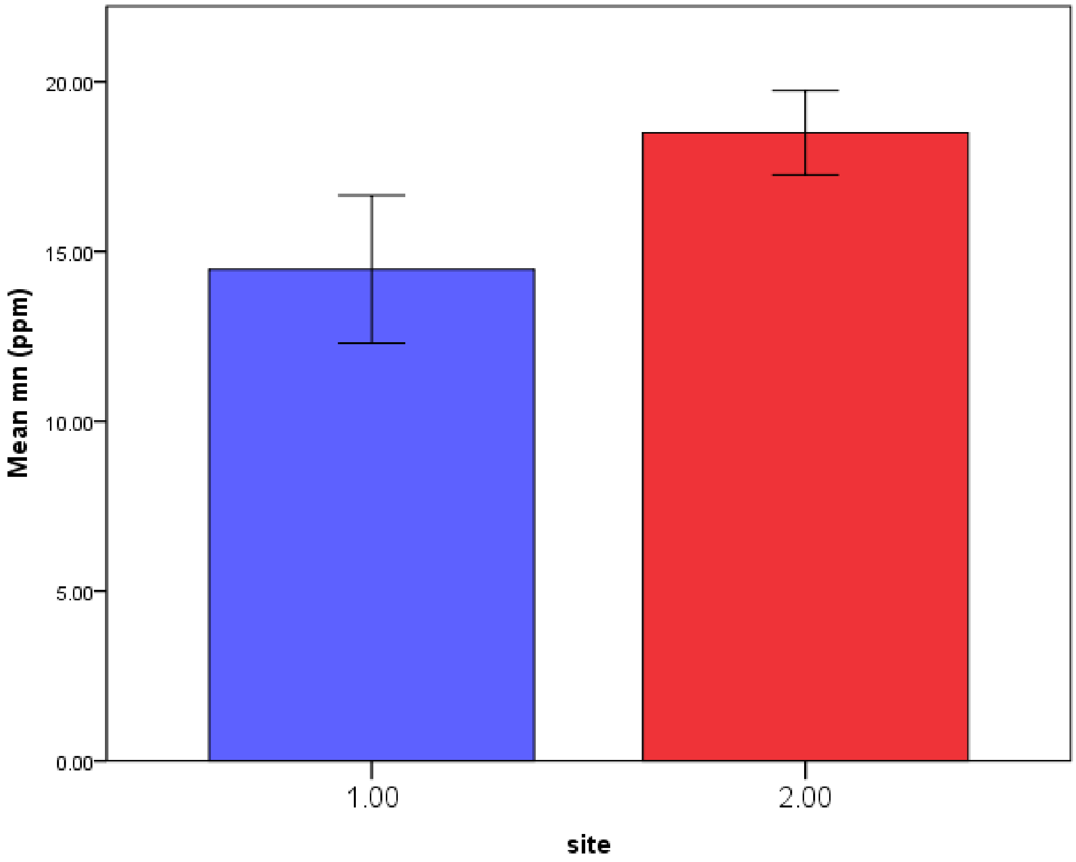


Table 7. Comparison between the Fe (ppm) in the two study areas

Site	samples	Mean	Std. Deviation	Std. Error Mean
1.00	12	134.2559	92.31551	26.64919
2.00	12	84.9873	10.42775	3.01023

The results showed that there were significant differences between the two regions, where the value of the observed level of significance was (0.603) which is less than 0.05.

Fig.9. Averages with the standard error of Fe (ppm) in the two study areas

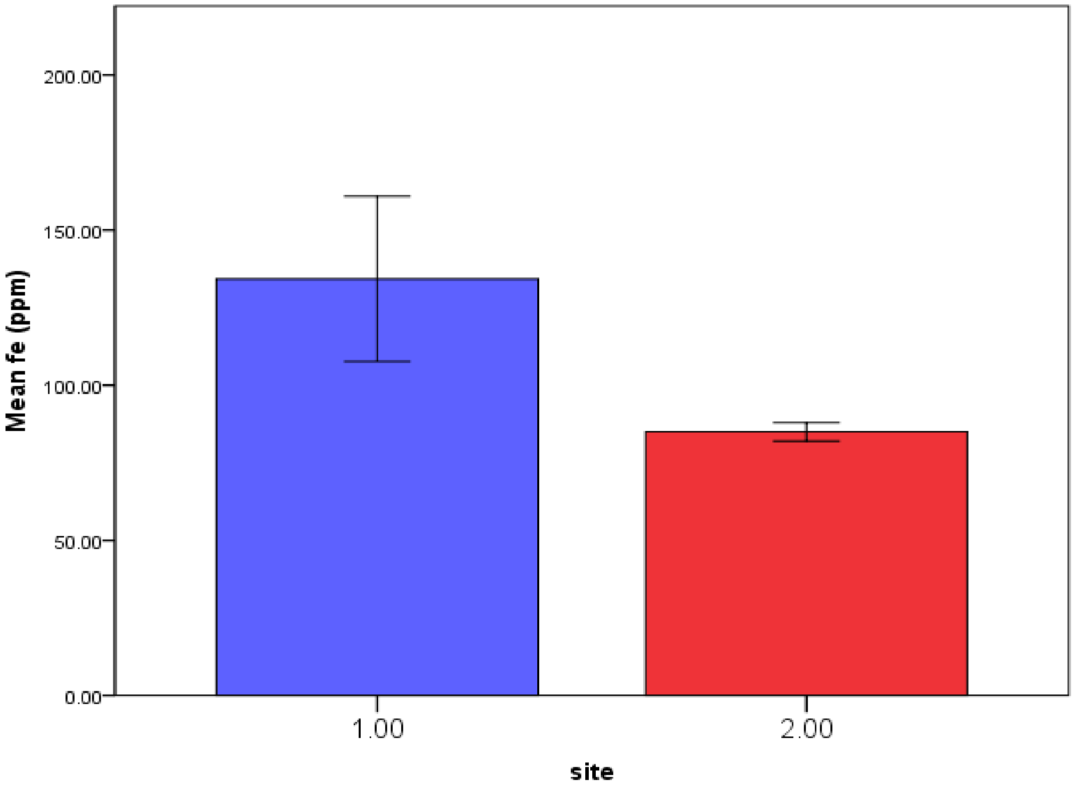


Table 8. Comparison between Zn (ppm) in the two study areas

Site	samples	Mean	Std. Deviation	Std. Error Mean
1.00	12	11.6698	1.72814	.49887
2.00	12	14.4164	3.95606	1.14202

The results showed that there were no significant differences between the two regions where the value of the observed level of significance was (0.225) which is greater than 0.05.

Fig. 10. Averages with the standard error of Zn (ppm) in the two study areas

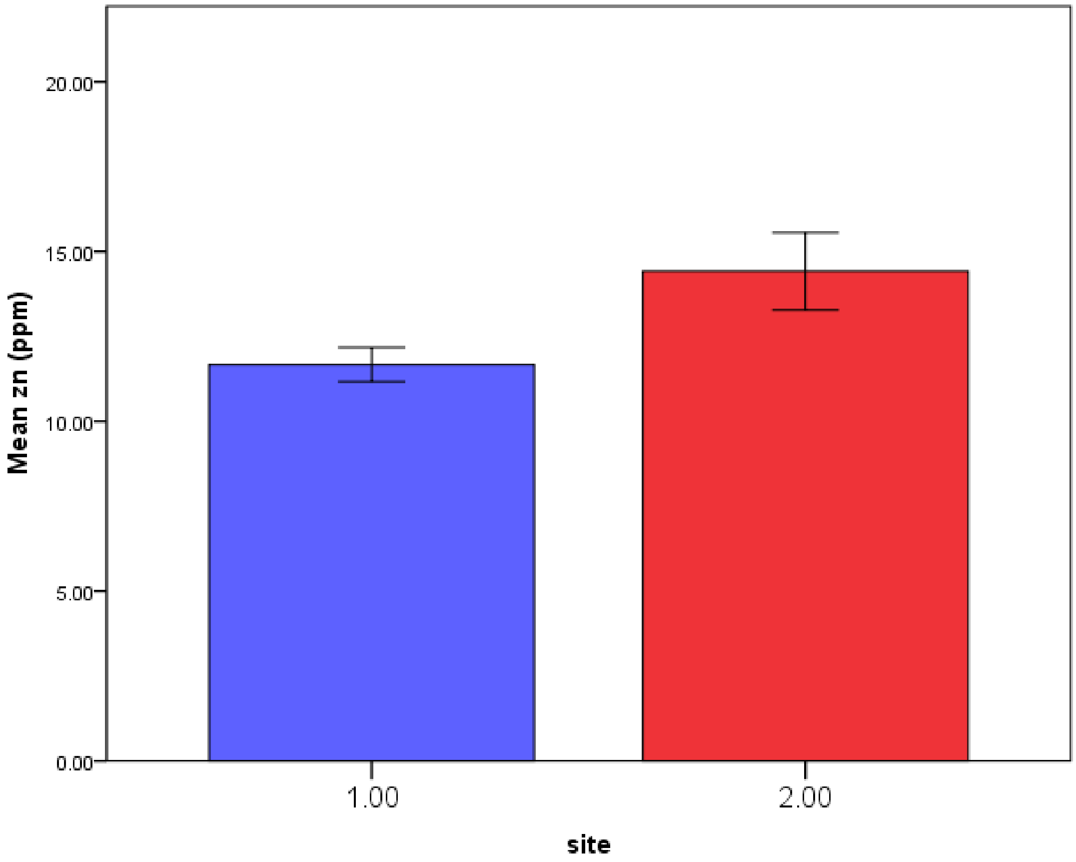


Table 9. Comparison between the of Cu (ppm) in the seasons

seasons	samples	Mean	Std. Deviation	Std. Error Mean
autumn	6	14.5842	1.76993	.72257
winter	6	12.1907	2.01786	.82379
spring	6	14.3132	4.71161	1.92351
summer	6	15.2235	3.25838	1.33023

The results showed that there were significant differences between the seasons of the year where the value of the observed level of significance was (0.655) which is less than 0.05.

Fig. 11. Averages with the standard error of Cu (ppm) in the seasons

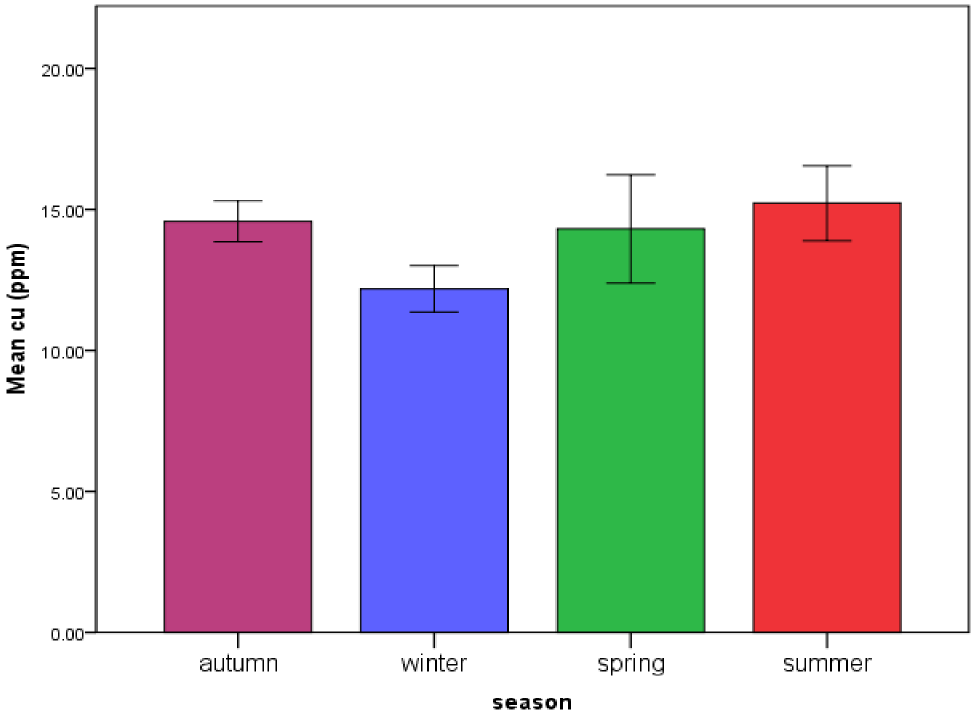


Table 10. Comparison between Cd (ppm) in the seasons

seasons	samples	Mean	Std. Deviation	Std. Error Mean
autumn	6	.5210	.10062	.04108
winter	6	.3940	.04312	.01760
spring	6	.3576	.02517	.01028
summer	6	.5169	.05228	.02135

The results showed that there were significant differences between seasons of the year where the value of the observed level of significance was P-value equal to (0.001) which is less than 0.05.

Fig.12. Averages with the standard error of Cd (ppm) in the seasons

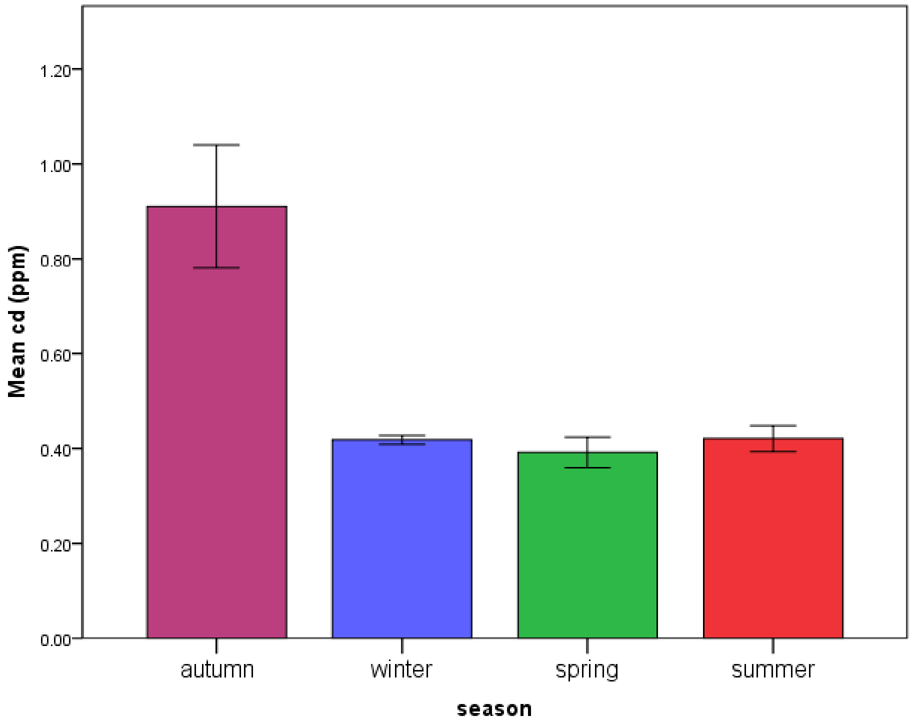


Table 11. Comparison between the of pb (ppm) in the seasons

seasons	samples	Mean	Std. Deviation	Std. Error Mean
autumn	6	3.0648	.58741	.23981
winter	6	2.4235	.04854	.01982
spring	6	2.3652	.06187	.02526
summer	6	2.5282	.16940	.06916

The results showed that there were significant differences between seasons of the year where the value of the observed level of significance was (0.009) which is less than 0.05.

Fig. 13. Averages with the standard error of pb (ppm) in the seasons

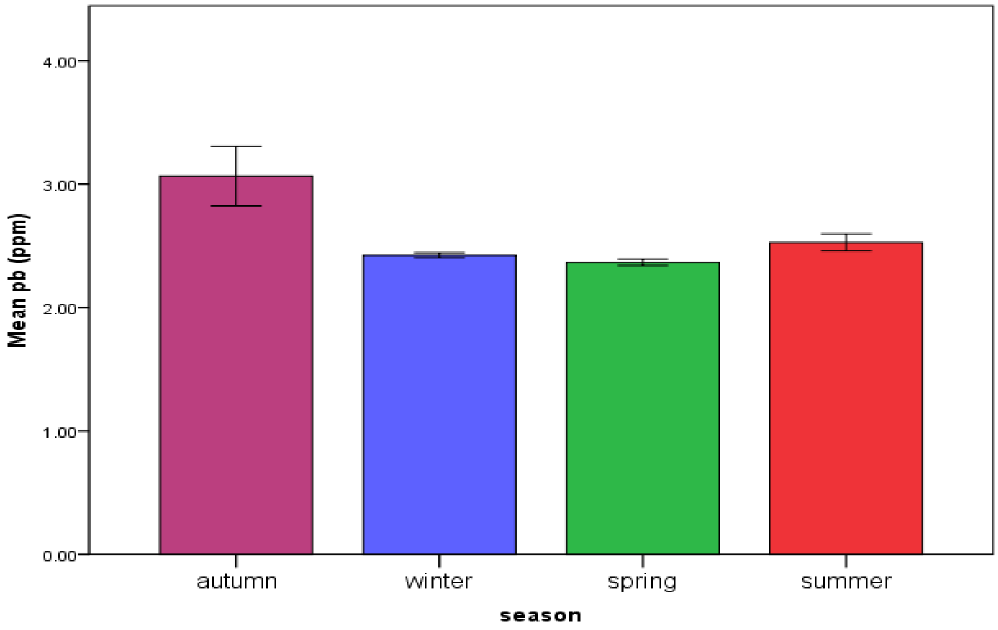


Table 12. Comparative Ni (ppm) in the seasons

seasons	samples	Mean	Std. Deviation	Std. Error Mean
autumn	6	4.8953	2.29326	.93622
winter	6	3.2589	.69564	.28400
spring	6	4.0226	2.03669	.83148
summer	6	3.9945	.45889	.18734

The results showed that there were significant differences between the seasons of the year where the value of the observed level of significance was (0.440) which is less than 0.05.

Fig. 14. Averages with the standard error of Ni (ppm) in the seasons

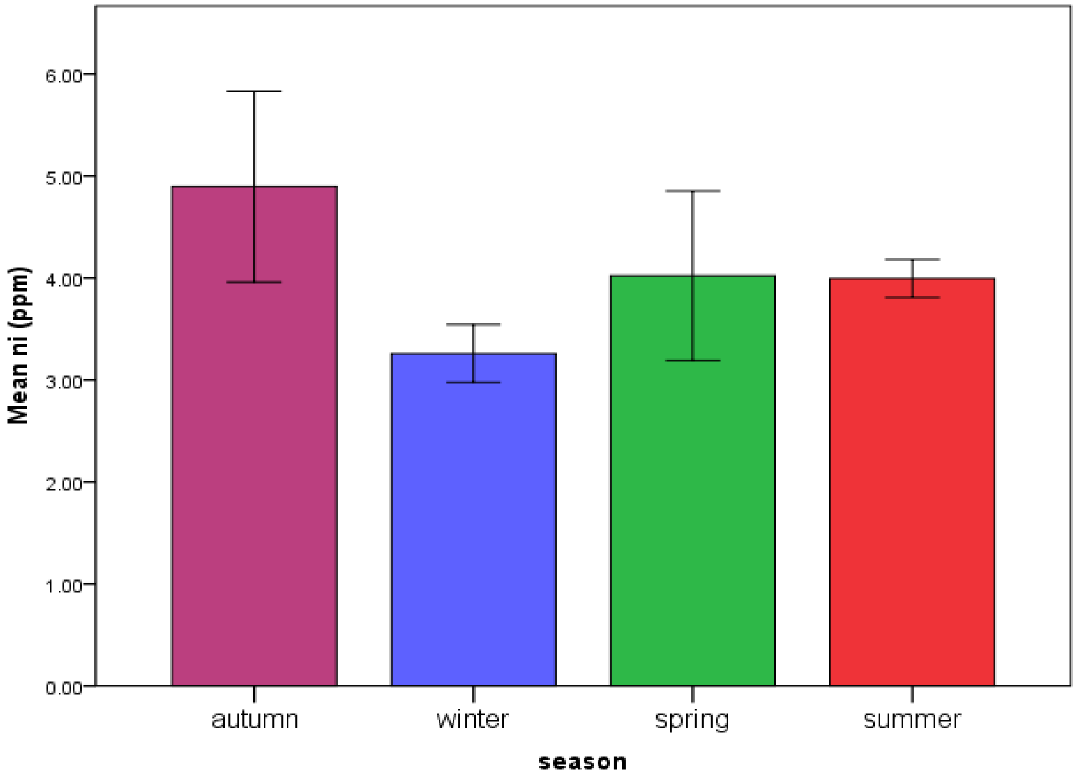


Table 13. Comparison between Mn(ppm) in the seasons

seasons	Samples	Mean	Std. Deviation	Std. Error Mean
autumn	6	25.2307	.82381	.33632
winter	6	15.9853	1.35980	.55514
spring	6	9.9073	3.42450	1.39805
summer	6	14.8194	4.85444	1.98182

The results showed that there were significant differences between seasons of the year where the value of the observed level of significance was P-value equal to (0.001) which is less than 0.05.

Fig. 15. Averages with the standard error of Mn (ppm) in the seasons

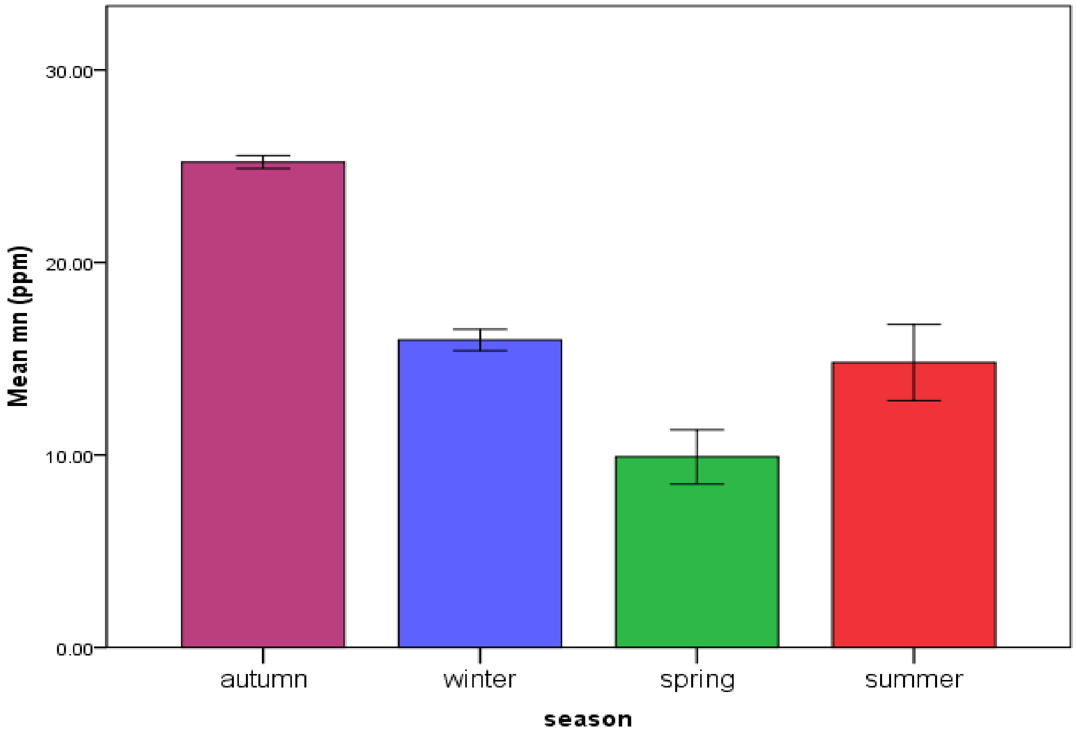


Table 14. Comparison between Fe (ppm) in the seasons

seasons	Samples	Mean	Std. Deviation	Std. Error Mean
autumn	6	189.9516	106.47816	43.46953
winter	6	77.3665	7.40949	3.02491
spring	6	84.9541	4.51283	1.84235
summer	6	86.2143	10.40927	4.24957

The results showed that there were significant differences between seasons of the year where the value of the observed level of significance was P-value equal to (0.010) which is less than 0.05

Fig. 16. Averages with the standard error of Fe (ppm) in the seasons

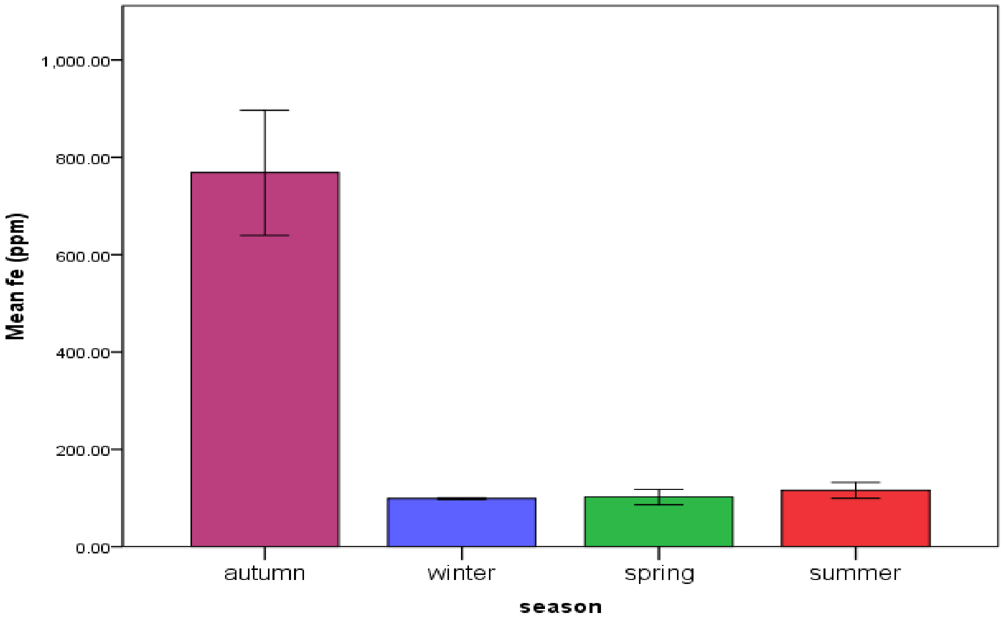
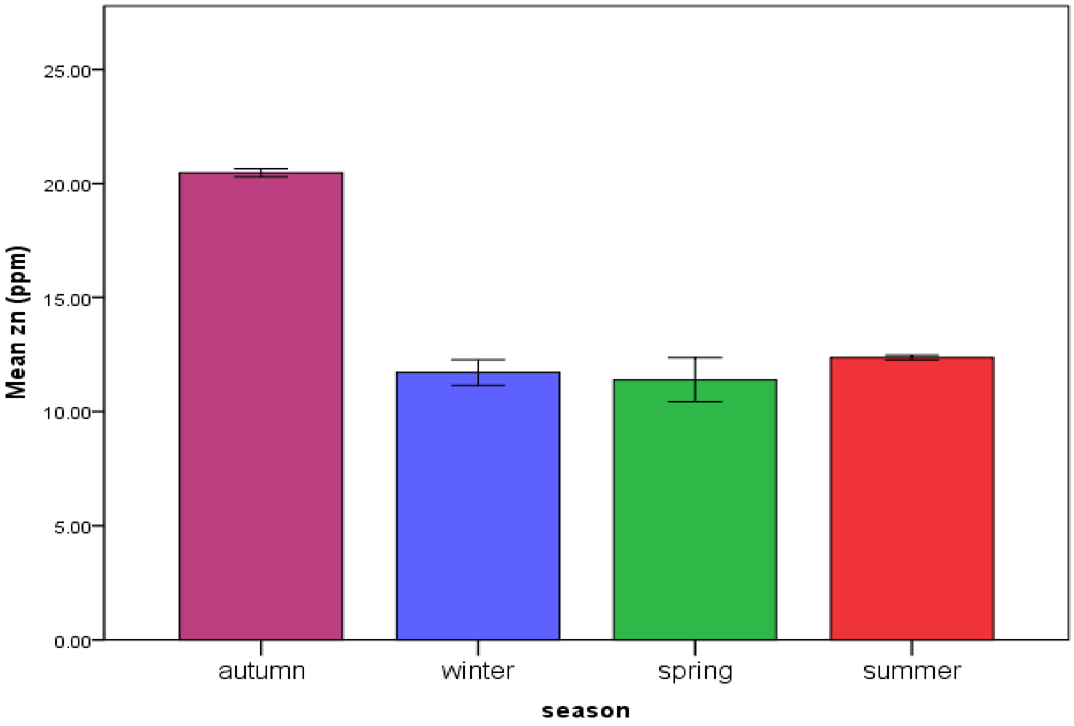


Table 15. Comparison between Zn (ppm) in the seasons

seasons	Samples	Mean	Std. Deviation	Std. Error Mean
autumn	6	15.1570	1.32334	.54025
winter	6	12.5227	.08446	.03448
spring	6	9.6072	.24839	.10141
summer	6	14.8853	4.93028	2.01278

The results showed that there were significant differences between the seasons where the value of the observed level of significance was P-value equal to (0.002) which is less than 0.05.

Fig. 17. Averages with the standard error of Zn (ppm) in the seasons



Results and Discussion

Tables (2, 3, 5 and 7) describe measures of the two study areas by making a comparison between heavy metals (Cu, Cd, Ni and Fe) in both sites. The results showed that there were significant differences between the two regions where the value of the observed level of significance was ($p<0.05$), the tables (4, 6 and 8) describe measurements of the two study areas by comparing between heavy metals (Pb, Mn and Zn), the results showed that there were no significant differences between the two regions where the value of the observed level of significance was ($p>0.05$), also the results have shown that all the concentrations of heavy metals in Site 1 were higher than that of Site 2 except the concentration of Mn, Zn. the increase of the concentrations of heavy metals could be attributed to the fact that Site 1 is near to the city centre and port, in which there is a high possibility of city waste discharge and the city's port pollutants in the Black Sea, The metal concentrations decrease in the order Fe> Mn > Cu > Zn > Ni > Pb >Cd. The high Fe and Mn contents compared to the other heavy metals where was the highest average concentration of Fe (287.14ppm) at Site 1 in autumn and the highest average concentration of Mn (25.977ppm) at Site 1 in autumn, these findings are consistent with those in the study carried out by (Strezov and Nonova, 2003) the function in the organism depends on some heavy metals, It is known that there is a correlation between the biosorption of trace elements and their role in the organism. The major part of heavy metals form relatively stable complexes with proteins, lipids and phosphates, taking part in enzyme synthesis (Fe, Mn,) and in the metabolic processes in the organisms. Fe has a great binding capability for algal lipids and was accumulated to the greatest extent in the studied macrophytes. In addition, the results showed that the Cd concentrations exhibited more decrease throughout the four seasons than that of other metals Where the lowest average concentration of Cd (0.3336 ppm) at Site 2 in spring, these results are consistent with those in the study carried out by (Su, 2013) on biological toxicity of five heavy metals on marine algae in China, also maximum uptakes of cadmium by the alga at pH value higher than 4,5. , and pH value lower than 2 the cadmium uptake capacity is almost negligible, this Confirms to the fact that pH is an important parameter, which affects sorption of cadmium by the alga (Lodeiro et al., 2004). Tables (9,10,11,12,13,14and 15) show descriptive metrics comparing between heavy metals (Mn, Cd, Zn, Cu, Fe, Ni and Pb) during the seasons of the year adopting a Kruskal Wallis test analysis. The results of heavy metals comparison show that there were significant differences in all seasons where the value of the observed level of significance was ($p<0.05$). The results have indicated an increase in the concentrations of heavy metal in autumn than any other season Such revelations may be ascribed to the fact that, during the year in Turkey, the first rains take place in autumn. Besides, the air contains a great amount of pollutants and these pollutants drop-down within the first rain period. Or coming with the flowing rivers, also the Black Sea coast receives the greatest amount of rainfall. The eastern part of that receives 2,200 millimetres annually and is the only region of Turkey that receives rainfall throughout the year (Sensoy et al., 2008). In general the results showed differences in the concentration of heavy metals in the study sites, as well as seasons these findings are consistent with those in the study carried out by) Al-Shwafi, & Rushdi, 2008 (ascribes these concentrations differences in the tendency of metals to bind to the various molecular groups found within the cells of each organism, as well as to the degree of the exposure of the organism to the metal as influenced by its metabolic characteristics and its position in the food chain. Apparently, marine algae may play a significant role in biogeochemical cycles of heavy metals in the coastal zones.

Conclusions

Toxic effects of heavy metal on algae have become one kind of safety index and an important content for environmental toxicology , By analyzing the Seven heavy metals Mn, Cd, Zn, Cu, Fe, Ni and Pb contents in Marine brown algae(Phaeophyta) that Collected from two sites in Kastamonu coasts(Turkey), Although the results obtained does not show any form of danger but the possibility of deleterious effects after long period , This is as a result of the fact that Kastamonu coasts(Turkey) receive city waste discharge and the city's port pollutants, results generally showed that metal accumulation in autumn season was higher than in the other season probably due to the first rains take place in autumn , also showed Fe and Mn concentration higher than in the other heavy metals in the two sites and all seasons, This high level accumulation could be due to the roles of these heavy metals in physiological and metabolic processes in marine organisms, this type of pollution detection studies should be done frequently, and routine reporting should also be conducted in order to take necessary measures to decision mechanisms.

REFERENCES

Amado-Filho, G. M., Andrade, L. R., Reis, R. P., Bastos, W., & Pfeiffer, W. C. (1997). Heavy metal concentrations in seaweed species from the Abrolhos reef region, Brazil. In *Proc. 8th Int. Coral Reef Symp.*, *Panamá* (Vol. 2, pp. 1843-1846).

Amado Filho, G. M., Andrade, L. R., Karez, C. S., Farina, M., & Pfeiffer, W. C. (1999). Brown algae species as biomonitors of Zn and Cd at Sepetiba Bay, Rio de Janeiro, Brazil. *Marine Environmental Research*, *48*(3), 213-224.

Andrade, L. R., Salgado, L. T., Farina, M., Pereira, M. S., Mourao, P. A., & Amado Filho, G. M. (2004). Ultrastructure of acidic polysaccharides from the cell walls of brown algae. *Journal of structural biology*, *145*(3), 216-225.

Andrade, L. R., Leal, R. N., Noseda, M., Duarte, M. E. R., Pereira, M. S., Mourão, P. A., & Amado Filho, G. M. (2010). Brown algae overproduce cell wall polysaccharides as a protection mechanism against the heavy metal toxicity. *Marine Pollution Bulletin*, *60*(9), 1482-1488.

Al-Shwafi, N. A., & Rushdi, A. I. (2008). Heavy metal concentrations in marine green, brown, and red seaweeds from coastal waters of Yemen, the Gulf of Aden. *Environmental Geology*, *55*(3), 653-660.

Bold, H. C., & Wynne, M. J. (1985). Introduction to the Algae. Englewood & Cliffs.

Bat, L., Gökkurt, O., Sezgin, M., Üstün, F., &Sahin, F. (2009). Evaluation of the Black Sea land based sources of pollution the coastal region of Turkey. *The Open Marine Biology Journal*, *3*(1).

Çoban, B., Balkıs, N., & Aksu, A. (2009). Heavy metal levels in sea water and Sediments of Zonguldak, Turkey. *Journal of the Black Sea/Mediterranean Environment*, *15*(1).

Davis, T. A., Volesky, B., & Mucci, A. (2003). A review of the biochemistry of heavy metal biosorption by brown algae. *Water research*, *37*(18), 4311- 4330.

Jitar, O., Teodosiu, C., Nicoara, M., & Plavan, G. (2013). Study of heavy metal pollution and bioaccumulation in the Black Sea living environment. *Environmental engineering and management journal*, *12*(2), 271-276.

Kam, E., & Bozkurt, A. (2007). Environmental radioactivity measurements in Kastamonu region of northern Turkey. *Applied Radiation and Isotopes*, *65*(4), 440-444.

Kannan, S. (2014). FT-IR and EDS analysis of the seaweeds Sargassumwightii (brown algae) and Gracilariacorticata (red algae). *International Journal of Current Microbiology and Applied Sciences*, *3*(4), 341-351.

Lodeiro, P., Cordero, B., Grille, Z., Herrero, R., & Sastre de Vicente, M. E. (2004). Physicochemical studies of cadmium (II) biosorption by the invasive alga in Europe, Sargassum muticum. *Biotechnology and bioengineering*, *88*(2), 237-247.

Oros, A., & Gomoiu, M. T. (2010). Comparative data on the accumulation of five heavy metals (cadmium, chromium, copper, nickel, lead) in some marine species (molluscs, fish) from the Romanian sector of the Black Sea. *Recherches Marines*, *39*, 89-108.

Romera, E., Gonzalez, F., Ballester, A., Blazquez, M. L., & Munoz, J. A. (2006). Biosorption with algae: a statistical review. *Critical reviews in biotechnology*, *26*(4), 223-235.

Strezov, A., & Nonova, T. (2003). Monitoring of Fe, Mn, Cu, Pb and Cd levels in two brown macroalgae from the Bulgarian Black Sea coast. *Intern. J. Environ. Anal. Chem.*, *83*(12), 1045-1054.

Sensoy, S., Demircan, M., Ulupinar, Y., & Balta, I. (2008). Climate of turkey. *Turkish state meteorological service*, *401*.

Su, D. (2013). Biological Toxicity of Five Metal Ions on Marine Algea. In *Applied Mechanics and Materials* (Vol. 295, pp. 17-20). Trans Tech Publications Ltd.

Villares, R., Puente, X., & Carballeira, A. (2002). Seasonal variation and background levels of heavy metals in two green seaweeds. Environmental Pollution, 119(1), 79- 90.

Volesky, B. (2001). Detoxification of metal-bearing effluents: biosorption for the next century. *Hydrometallurgy*, *59*(2-3), 203-216.

Volesky, B., & Holan, Z. R. (1995). Biosorption of heavy metals. *Biotechnology progress*, *11*(3), 235-250.

Zeri, C., Voutsinou-Taliadouri, F., Romanov, A. S., Ovsjany, E. I., & Moriki, A. (2000). A comparative approach of dissolved trace element exchange in two interconnected basins: Black Sea and Aegean Sea. *Marine Pollution Bulletin*, *40*(8), 666-673