Assessment of some heavy metals pollution in Marine Brown Algae in the Zonguldak Coasts (Turkey)

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Abstract:

The present study evaluated the concentrations of Mn, Cd, Zn, Cu, Fe, Ni and Pb in marine algae (Phaeophyta) within the Zonguldak coasts (Turkey) ,In this study, we collected the samples of Marine alga from two stations on Zonguldak Coasts (Turkey), the start of the study was autumn 2017 and also the end was summer 2018 , we selected study area depending on differences within the eco-system between stations ,for each station have individual factors which contribute to extend the pollution , the stations was distributed for 2 areas , first area near by the port and the movement of ships, another area far the port and the movement of ships about 8km, the results showed that there were no significant differences between the seasons in all the studied elements , where the value of the observed level of significance was ($p<0.05$), through the results we find there were significant differences between the two sites in all the studied elements. In general, the results showed a variation in heavy metal concentrations during all seasons, the study have shown concentrations of heavy metals all stations and seasons are within the order of Fe > Cu > Mn > Zn> Ni> Pb >Cd , Finally, we recommend should be carried pollution studies out at regular intervals and reported routinely.

Keywords: *heavy metals ,Coasts, Zonguldak, Marine brown algae.*

تقييم التلوث ببعض المعادن الثقيلة في الطحالب البنية البحرية على سواحل زنقولداك (تركيا)

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الملخص:

قيمت الدراسة الحالية تركيزات بعض المعادن الثقيلة وهي المنجنيز ، الكادميوم، الزنك، النحاس، الحديد، النيكل والرصاص بالطحالب البنيه البحرية (Phaeophyta) على سواحل مدينه زنقولداك التركية، بهده الدراسة تم جمع العينات من محطتين على سواحل زنقولداك التركية بداية الدراسة كانت خريف 2017 ونهايتها صيف 2018، تم اختيار منطقة الدراسة بناءً على الاختلافات داخل النظام البيئي بين المحطات، حيت كانت لكل محطة عوامل فردية تساهم في زيادة التلوث، وقد تم توزيعها على النحو التالي، المحطة الاولى كانت قرب الميناء وحركة السفن المحطة الثانية تبعد عن الميناء وحركة السفن بحوالي 8 كم، أظهرت النتائج عدم وجود فروق معنوية بين الفصول في جميع العناصر المدروسة حيث كانت قيمة مستوى المعنوية ($p> 0.05$)، وكدلك من خلال النتائج وجدنا فروق معنوية بين الموقعين في جميع العناصر المدروسة($p< 0.05$). بشكل عام، أظهرت النتائج تباينًا في تراكيز المعادن الثقيلة خلال جميع الفصول، فقد أوضحت الدراسة أن تركيزات المعادن الثقيلة في جميع المحطات

والمواسم تقع ضمن ترتيب Fe < Cu> Mn> Zn> Ni> Pb Cd، وأخيرًا نوصي بإجراء دراسات على التلوث بالمعادن على فترات منتظمة والإبلاغ عنها بشكل روتيني.

الكلمات المفتاحية: *المعادن الثقيلة، السواحل، الزنقولداك، الطحالب البحرية البنية.*

Introduction:

The pollution by heavy metals in marine ecosystems has been a world-wide problem within the last decades. The Black Sea ecosystem and ecological status has been damaged mainly as a result of chemical pollution(Strezov, A. 2012),Pollution of the Black Sea by chemicals such as heavy metals has been recognized as one of the major factors threat to the survival of biota especially benthic invertebrates (Bat, 2005; Bat and Arici, 2018), the Black Sea is the most important natural resource for biodiversity in Turkey (Bat et al., 2011) It still continuous the main source of fish and other seafood in the country for a long time. However, the Black Sea was subjected to a drastic pollution during the last few decades due to industrial, agricultural and sewage effluents and runoffs from major rivers along their coasts (Bat et al., 2018), Landlocked countries try to protect the marine ecosystem as much as possible and developed international laws to protect the sea. Toxicokinetics of heavy metals in the marine environment was a major concern because they pose a potential risk to flora and fauna species including humans through the food chain (Boran and Altınok,2010), its threat is potentiated by not existing chemically or biologically decomposed, once released metals can stay in the environment for hundreds of years, and therefore, they are accumulated into aquatic organisms (Noreña, 2012). some aquatic organisms have become increasingly used in the assessment of contamination, as bioindicators. Algae and molluscs are among the organisms most used for this purpose (Villares et al., 2002; Simon et al., 2008; Lavoiel et al., 2009; Topcuoğlu et al., 2010; Rajfur et al., 2010) The adsorption capacity of the algae is directly related to the presence of these sites on the alginate polymer, which itself comprises a significant component (up to 40% of the dry weight). Ion-exchange is another important concept in biosorption by brown algae (Davis, 2003; Buffle et al., 2009; Akcali and Kucuksezgin, 2011). The main advantage of bio-monitoring approach using marine organisms compared to direct measurement in water or sediment is to provide a direct and timeintegrated assessment of the metal fraction that is actually available to the organisms (Coteur et al., 2003; Danis et al., 2004; Metian et al., 2008).

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, et al 2009), Zonguldak is a coastal city located in the western Black Sea region of Turkey at latitudes 41°–27′ N and longitudes 31°–49′ E (Tecer, 2007).

Fig. 1.Site 1

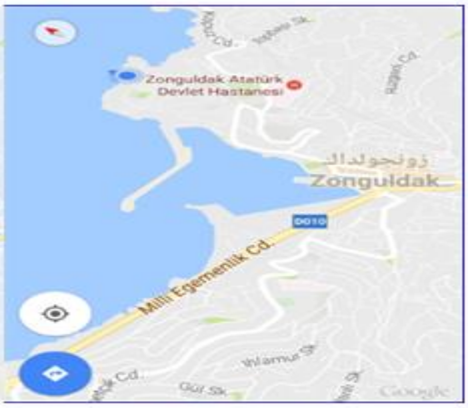

Fig.2. Site2

Sampling methods:

Algal samples were collected from two stations on Zonguldak Coasts (Turkey) using five liter polyethylene acid-washed bottles , Algal samples were collected during four seasons The samples were transferred to the laboratory in refrigerated box where they were cleaned with distilled water and identified according to previously reported protocols (Basson, 1979; Basson et al., 1989).

Analytical methods:

Heavy metal analyses were performed in Kastamonu University Central Research Laboratory. For brown algae samples, 0.5g of each sample was taken and HNO3 and H2O2 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, we used t-test and monomeric variance analysis one way ANOVA, all statistical analyses were performed with SPSS version for windows between heavy metals.

Table.1. Comparison between Cu (ppm) in the two study areas.

Site	samples	Mean	Std. Deviation	Std. Error Mean	P-value	Differences
1	12	21.3824	1.21096	.34957	0.000	There is a difference
2	12	11.3128	.62737	.18110		

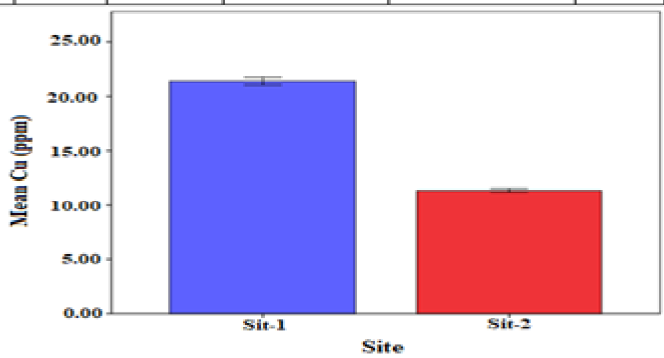

Fig.3. Averages Cu (ppm) with the standard error in the study areas.

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

Site	samples	Mean	Std. Deviation	Std. Error Mean	P-value	Differences
1	12	.7659	.20002	.05774	0.000	There is a difference
2	12	.3972	.05072	.01464		

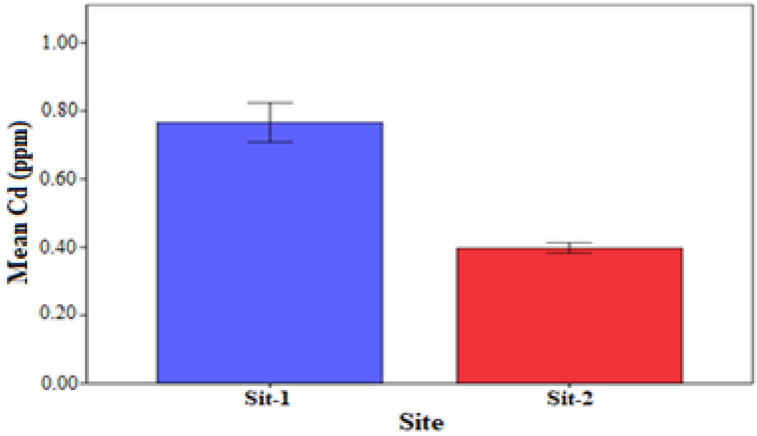

Fig.4. Averages Cd (ppm) with the standard error in the study areas.

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

Site	samples	Mean	Std. Deviation	Std. Error Mean	P-value	Differences
1	12	4.7729	1.23504	.35653	0.000	There is a difference
2	12	2.7292	.17801	.05139		

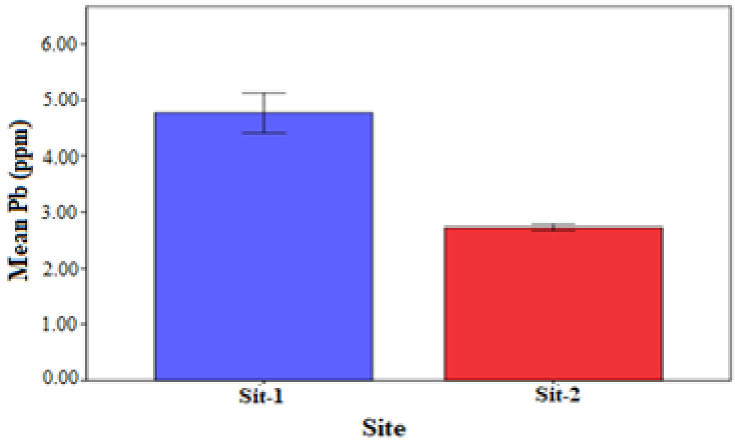

Fig.5. Averages Pb (ppm) with the standard error in the study areas.

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

Site	samples	Mean	Std. Deviation	Std. Error Mean	P-value	Differences
1	12	10.1527	1.86946	.53967	0.000	There is a difference
2	12	2.7505	.67404	.19458		

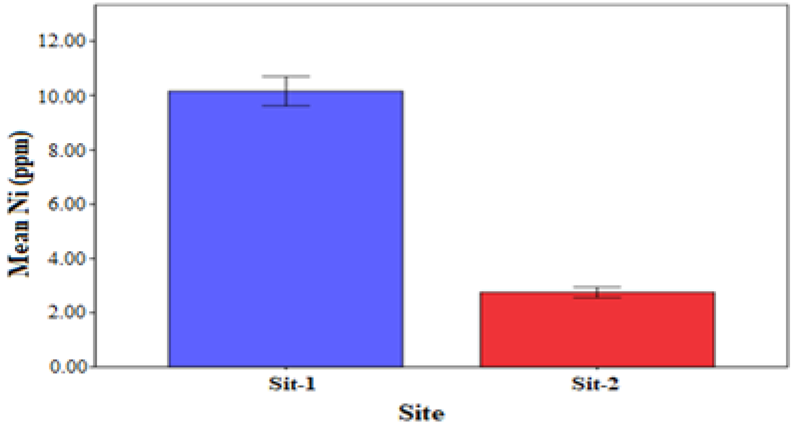

Fig.6. Averages Ni (ppm) with the standard error in the study areas.

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

Site	samples	Mean	Std. Deviation	Std. Error Mean	P-value	Differences
1	12	40.3125	16.83732	4.86052	0.000	There is a difference
2	12	16.1084	2.79990	.80826		

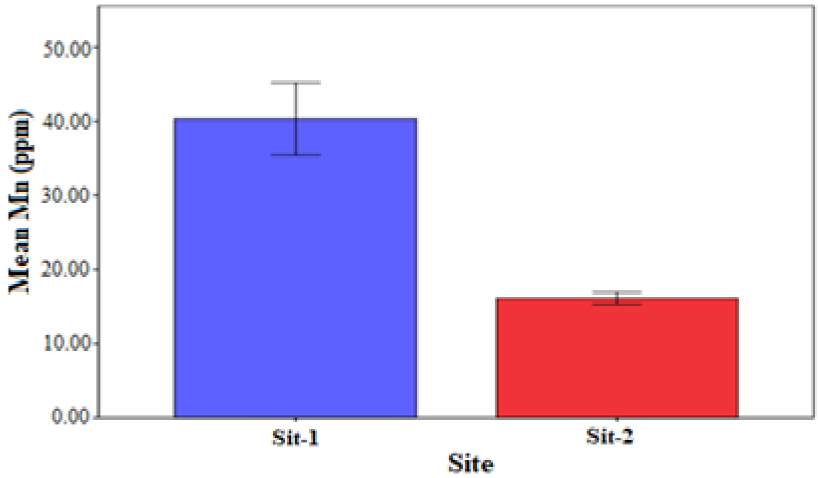

Fig.7. Averages Mn (ppm) with the standard error in the study areas.

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

Site	samples	Mean	Std. Deviation	Std. Error Mean	P-value	Differences
1	12	535.4120	251.77557	72.68135	0.000	There is a difference
2	12	111.7407	27.77504	8.01796		

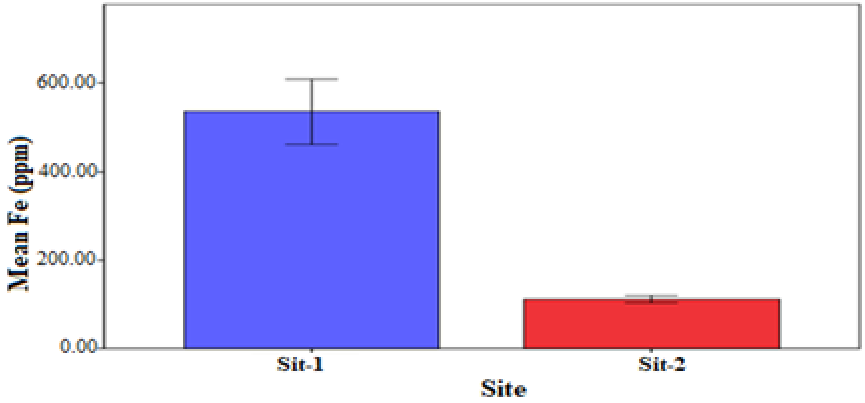

Fig.8. Averages Fe (ppm) with the standard error in the study areas.

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

Site	samples	Mean	Std. Deviation	Std. Error Mean	P-value	Differences
1	12	16.3605	2.45755	.70943	0.000	There is a difference
2	12	11.1750	1.26439	.36500		

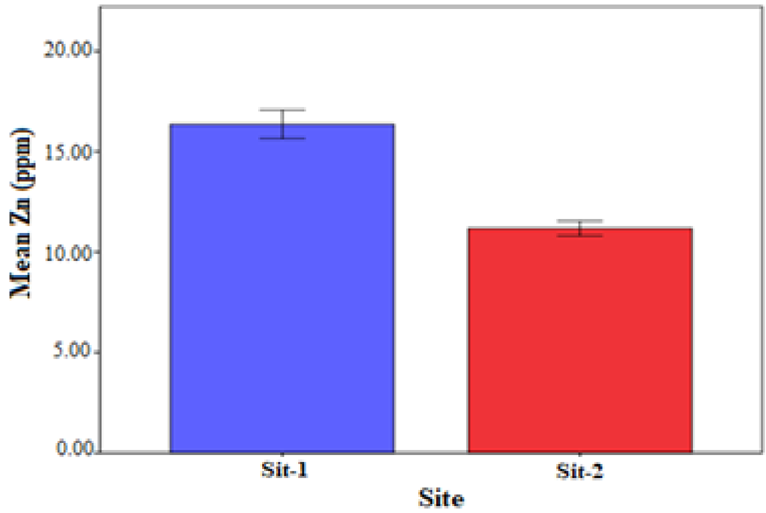

Fig.9. Averages Zn (ppm) with the standard error in the study areas.

Table. 8 . Comparison between the of Cu (ppm) in the seasons.

seasons	samples	Mean	Std. Deviation	Std. Error Mean	P-value	Differences
autumn	6	16.0277	5.43117	2.21727	0.896	There is not a difference
winter	6	15.5154	5.20326	2.12422		
spring	6	16.0348	5.41257	2.20967		
summer	6	17.8126	6.02100	2.45806		

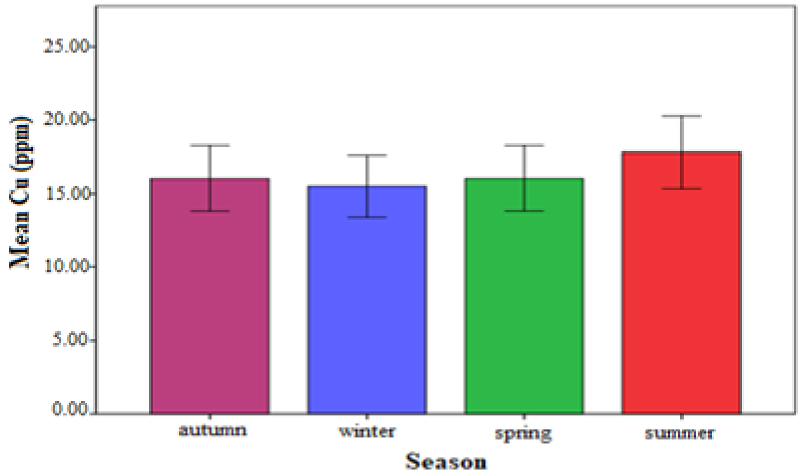

Fig.10 . Averages with the standard error of Cu (ppm) in the seasons.

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

seasons	samples	Mean	Std. Deviation	Std. Error Mean	P-value	Differences
autumn	6	.4762	.01694	.00692	0.403	There is not a difference
winter	6	.6446	.27775	.11339		
spring	6	.5235	.20200	.08247		
summer	6	.6819	.32306	.13189		

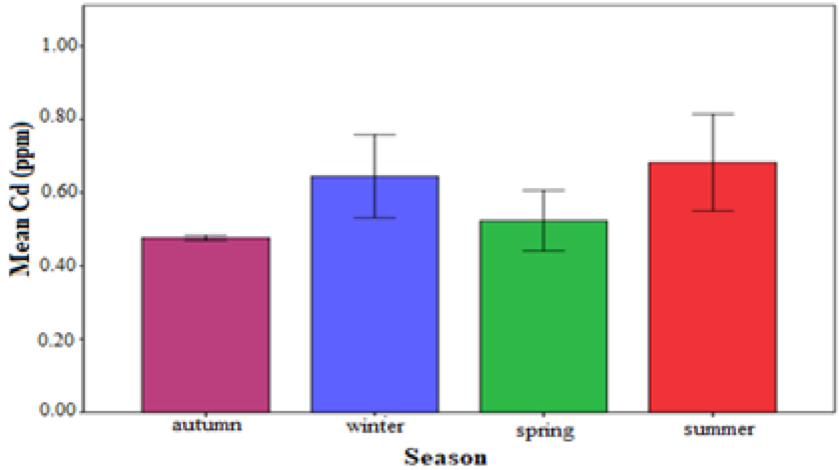

Fig.11 . Averages with the standard error of Cd (ppm) in the seasons.

Table.10. Comparison between the of Pb (ppm) in the seasons.

seasons	samples	Mean	Std. Deviation	Std. Error Mean	P-value	Differences
autumn	6	3.1009	.18002	.07349	0.274	There is not a difference
winter	6	3.6074	1.05696	.43150		
spring	6	3.6695	1.17009	.47769		
summer	6	4.6264	2.11172	.86210		

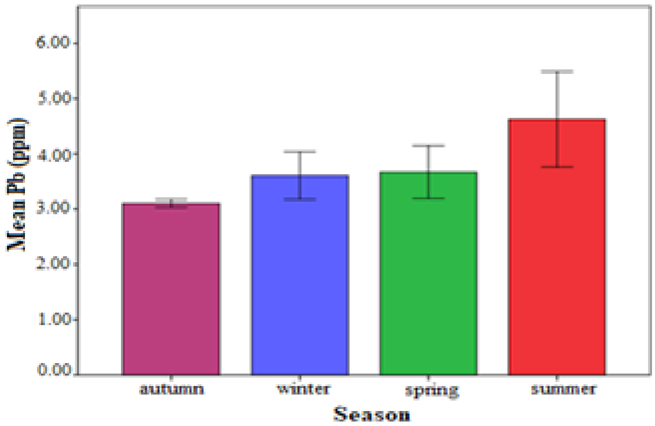

Fig.12. Averages with the standard error of Pb (ppm) in the seasons.

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

seasons	samples	Mean	Std. Deviation	Std. Error Mean	P-value	Differences
autumn	6	5.4554	2.08973	.85313	0.923	There is not a difference
winter	6	6.5165	3.61793	1.47701		
spring	6	6.8608	5.24349	2.14065		
summer	6	6.9737	5.26925	2.15116		

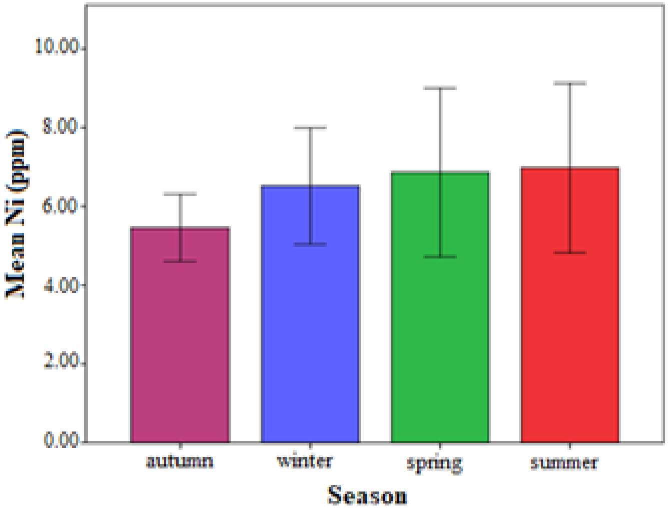

Fig.13. Averages with the standard error of Ni (ppm) in the seasons.

Table.12 . Comparison between the of Mn (ppm) in the seasons.

seasons	samples	Mean	Std. Deviation	Std. Error Mean	P-value	Differences
autumn	6	16.9255	3.88873	1.58757	0.297	There is not a difference
winter	6	32.8099	18.56017	7.57716		
spring	6	28.9254	15.49554	6.32603		
summer	6	34.1811	22.86121	9.33305		

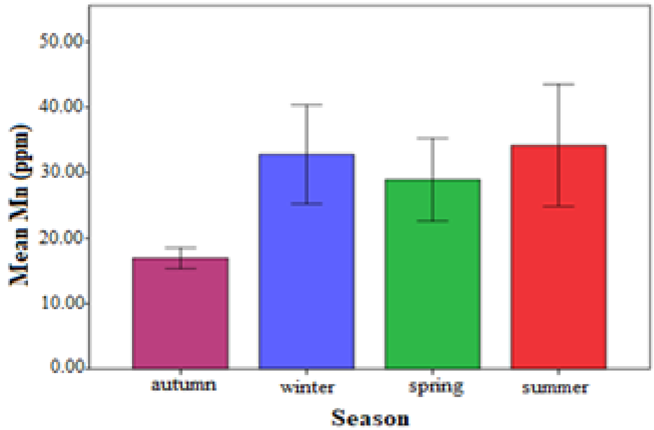

Fig.14 . Averages with the standard error of Mn (ppm) in the seasons.

Table.13. Comparison between the of Fe (ppm) in the seasons.

seasons	samples	Mean	Std. Deviation	Std. Error Mean	P-value	Differences
autumn	6	173.1677	54.22959	22.13914	0.288	There is not a difference
winter	6	331.9910	263.55139	107.59440		
spring	6	302.1619	167.59244	68.41933		
summer	6	486.9848	442.99132	180.85045		

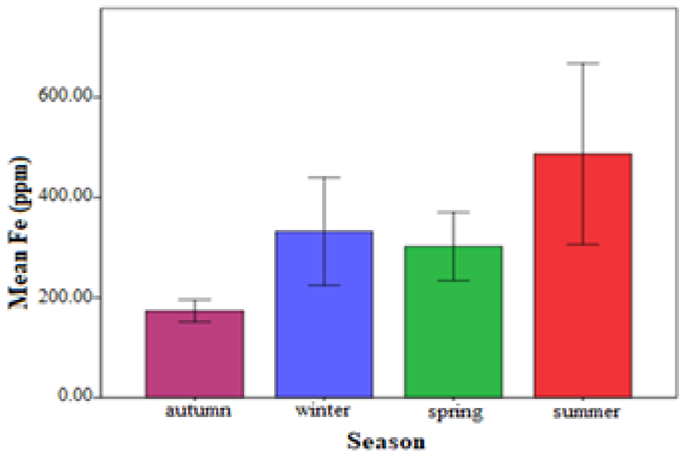

Fig.15. Averages with the standard error of Fe (ppm) in the seasons.

Table.14. Comparison between the of Zn (ppm) in the seasons.

seasons	samples	Mean	Std. Deviation	Std. Error Mean	P-value	Differences
autumn	6	.06727	.16478	12.2332	0.523	There is not a difference
winter	6	1.78811	4.37997	14.4520		
spring	6	1.73673	4.25409	13.4640		
summer	6	1.05408	2.58195	14.9219		

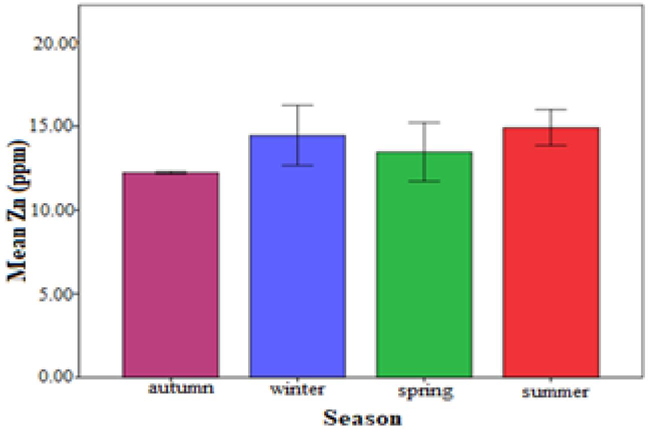

Fig.16. Averages with the standard error of Zn (ppm) in the seasons.

Results and Discussion:

Tables (1, 2,3, 4, 5,6 and 7) describe measures of the two study areas by making a comparison between heavy metals Mn, Cd, Zn, Cu, Fe, Ni and Pb by means of the t-test of the two independent samples , through the results presented in the tables we find there were significant differences between the two sites in all the studied elements, where the value of the observed significance level (0.000) was less than 0.05 , the results have shown the concentrations of heavy metals in Site 1 higher than that of Site 2 the reason may be that Site 1 is so nearby to the port and the ship traffic,where these results are in agreement with the study by(Dobaradaran et al.,2018) where showed that ballast water has the long-term possibility to change the chemical quality in marine environments and may also affect the marine ecosystem as ships discharge ballast water in sea. Samples results at all stations and seasons within the order of Fe> Cu> Mn> Zn> Ni> Pb> Cd, the highest Fe concentration (897.35 ppm) at Site 1 and the lowest concentration(82.1824 ppm) at Site 2, the most Samples have shown Accumulation of Fe was high in which might be due to high rates of photosynthesis in coastes or Iron element is absorbed by plankton and marine plants for use in biological processes (Chakraborty et al.,2014) (Morrissey and Bowler, 2012). tables (8, 9,10, 11, 12,13, and 14) describe measures of the seasons by making a comparison between heavy metals Mn, Cd, Zn, Cu, Fe, Ni and Pb By means of a monomeric variance analysis One way ANOVA ,the results showed that there were no significant differences between the seasons in all the studied elements , where the value of the observed level of significance was ($p>0.05$), The results have shown a slight increase in the concentrations of some elements during the autumn season this may be attributed to the fall the heavy metals with the first rain, where the air contains a great amount of pollutants and these pollutants drop down within the first rain period, these results are in agreement with the Chinese study by(Li & Zhang, 2010), where it have shown minimum total concentration of heavy metals was found in spring, and most variables tended to higher levels in the rainy season and many factors may influence the bioavailability of metals in algae including pH, salinity, temperature (Wai-Yin and Wen-Xiong, 2001), (Jothinayagi and Anbazhagan, 2009). In addition, the results showed a decrease in the cadmium concentrations compared to the other elements in all seasons the lowest concentration of cadmium was recorded in spring season (3.6695 ppm) 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).

Conclusions:

Marine Brown Algae can be used as bioindicators for monitoring of eco-toxicological state of the Black Sea environment, this study have shown a seasonal variation in heavy metal concentrations during all seasons, the results Seemingly depend on biological specificity of the algae , Although that the results obtained do not show any form of danger but the possibility of deleterious effects after long period. generally the results showed Fe and Mn concentration Relatively higher than other heavy metals also showed that concentrations of heavy metals in autumn season Relatively higher than other seasons .Finally, a special attention is required for treatment of industrial waste of Turkey before disposal into the coast ,In addition monitor and control ships ballast water discharge to meet the internationally accepted procedures for environmental impact and risk assessment to manage human impact on coastal environments, 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:

Akcali, I., & Kucuksezgin, F. (2011). A biomonitoring study: heavy metals in macroalgae from eastern Aegean coastal areas. *Marine pollution bulletin*, *62*(3), 637-645.

Basson, P. W. (1979). Marine algae of the Arabian Gulf coast of Saudi Arabia (second half). *Botanica Marina*, *22*(2), 65-82.

Basson, P. W., Mohamed, S. A., & Arora, D. K. (1989). A survey of the benthic marine algae of Bahrain. *Botanica marina*, *32*(1), 27-40.

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).

Bat, L. (2005). A review of sediment toxicity bioassays using the amphipods and polychaetes. *Turkish Journal of Fisheries and Aquatic Sciences*, *5*(2), 119-139.

Bat, L., & Arici, E. (2018). Heavy metal levels in fish, molluscs, and crustacea from Turkish seas and potential risk of human health. In *Food Quality: Balancing Health and Disease* (pp. 159-196). Academic Press.

Bat, L., Sezgin, M., Satilmis, H. H., Sahin, F., Üstün, F., Özdemir, Z. B., & Baki, O. G. (2011). Biological diversity of the Turkish Black Sea coast. *Turkish Journal of Fisheries and Aquatic Sciences*, *11*(4), 683-692.

Bat, L., Şahin, F., & Öztekin, A. (2018). Toxic metals in Nereis diversicolor Müller, 1776 from inner shores in Sinop peninsula of the Black Sea as bio-indicator species. *Pakistan Journal of Marine Sciences*, *27*(1), 11-20.

Boran, M., & Altınok, I. (2010). A review of heavy metals in water, sediment and living organisms in the Black Sea. *Turkish Journal of Fisheries and Aquatic Sciences*, *10*(4), 565-572.

Buffle, J., Wilkinson, K. J., & van Leeuwen*, H. P. (2009). Chemodynamics and bioavailability in natural waters.

Chakraborty, S., Bhattacharya, T., Singh, G., & Maity, J. P. (2014). Benthic macroalgae as biological indicators of heavy metal pollution in the marine environments: A biomonitoring approach for pollution assessment. *Ecotoxicology and environmental safety*, *100*, 61-68.

Coteur, G., Gosselin, P., Wantier, P., Chambost-Manciet, Y., Danis, B., Pernet, P., ... & Dubois, P. (2003). Echinoderms as bioindicators, bioassays, and impact assessment tools of sediment-associated metals and PCBs in the North Sea. *Archives of environmental contamination and toxicology*, *45*(2), 190-202.

.**Danis,** B., Wantier, P., Dutrieux, S., Flammang, R., Dubois, P., & Warnau, M. (2004). Contaminant levels in sediments and asteroids (Asterias rubens L., Echinodermata) from the Belgian coast and Scheldt polychlorinated biphenyls and heavy metals. *Science of the Total Environment*, *333*(1-3), 149-165.

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.

Dobaradaran, S., Soleimani, F., Nabipour, I., Saeedi, R., & Mohammadi, M. J. (2018). Heavy metal levels of ballast waters in commercial ships entering Bushehr port along the Persian Gulf. *Marine pollution bulletin*, *126*, 74-76.

Jothinayagi, N., & Anbazhagan, C.(2009). Heavy metal monitoring of Rames waram by some Sargassum species. American-Eurasian Journal of Scientific Research,4(2),73.

Lavoie, M., Le Faucheur, S., Fortin, C., & Campbell, P. G. (2009). Cadmium detoxification strategies in two phytoplankton species: metal binding by newly synthesized thiolated peptides and metal sequestration in granules. *Aquatic toxicology*, *92*(2), 65-75.

Lee, W. Y., & Wang, W. X. (2001). Metal accumulation in the green microalga Ulla fasciata: effects of nitrate, ammonium and phosphate. Science of the Total Environment, 278(1-3), 11-22.

Li, S., & Zhang, Q. (2010). Risk assessment and seasonal variations of dissolved trace elements and heavy metals in the Upper Han River, China. *Journal of Hazardous Materials*, *181*(1-3), 1051-1058.

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, Sargassummuticum. *Biotechnology and bioengineering*, *88*(2), 237-247.

Metian, M., Giron, E., Borne, V., Hédouin, L., Teyssié, J. L., & Warnau, M. (2008). The brown alga Lobophora variegata, a bioindicator species for surveying metal contamination in tropical marine.

Morrissey, J., & Bowler, C. (2012). Iron utilization in marine cyanobacteria and eukaryotic algae. Frontiers in microbiology, 3, 43.

Noreña-Ramirez, D. A. (2012). Heavy metals (Cd, Pb and Ni) in fish species commercially important from Magdalena river, Tolima tract, Colombia. *Revista Tumbaga*, *2*(7).

Rajfur, M., Kłos, A., & Wacławek, M. (2010). Sorption properties of algae Spirogyra sp. and their use for determination of heavy metal ions concentrations in surface water. *Bioelectrochemistry*, *80*(1), 81-86.

Simon, D. F., Descombes, P., Zerges, W., & Wilkinson, K. J. (2008). Global expression profiling of Chlamydomonas reinhardtii exposed to trace levels of free cadmium. *Environmental Toxicology and Chemistry: An International Journal*, *27*(8), 1668-1675.

Strezov, A. (2012). Sustainable environment–Monitoring of radionuclide and heavy Metal accumulation in Sediments, algae and Biota in Black Sea Marine ecosystems. *Environmental Contamination*, 51.

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.

Tecer, L. H. (2007). Prediction of SO2 and PM concentrations in a coastal mining area (Zonguldak, Turkey) using an artificial neural network. environments. *Journal of Experimental Marine Biology and Ecology*, *362*(1), 49-54

Topcuoğlu, S., Kılıç, Ö., Belivermiş, M., Ergül, H. A., & Kalaycı, G. (2010). Use of marine algae as biological indicator of heavy metal pollution in Turkish marine environment. *J. Black Sea/Mediterranean Environment*, *16*(1), 43-52.

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.