Heavy metal pollution in Inebolu and Bartin Ports, Black Sea, Turkey

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The study was conducted in Inebolu and Bartin ports located in Black Sea region of Turkey between August 2013 and July 2014. Sea water, sediment, and Mytilus galloprovincialis samples were collected from both ports and the amounts of 11 heavy metals (Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) in each sample were determined. When the results for sediment samples were compared with the limit values of US EPA, it was found that the port of Bartin was very polluted in terms of Ni, and moderately polluted in terms of Cr and Cu, while the port of Inebolu was very polluted in terms of Cu and moderately polluted in terms of Cr and Ni. Pollution was found in sea water in both ports. When the data of Mytilus galloprovincialis was compared with the meat quality standards of European Commission (EU), it was determined that As, Cd, Cu, and Zn values were high in Inebolu post and As, Cd, and Zn values were high in Bartin port. It was observed that the load diversity, ships, shipyard, submarine maintenance and repair facility, runoffs and rivers and port activities were responsible for the pollution.

Keywords: Heavy metals; Sediment; Sea water; Mytilus galloprovincialis; Inebolu port; Bartin port

Introduction

Ships are used to transport 80% of the world's burden due to the high load-bearing capacities1. For this reason, human and industrial activities and population have increased significantly in the areas where ship traffic is intense, resulting in environmental pollution in port areas. It was pointed out that the biodiversity was quite diminished in Sydney harbor, the largest harbor in the world, as a result of dense population and intensified human activities2.

Heavy metals, one of the major pollutants affecting the ports, are non-biodegradable and damage the metabolism by the way of their accumulation in organisms3. For instance, accumulation of Cd changes gill structure, deteriorates neural activities, and inhibits growth and nephrotoxicity4. As a result, ports are subjected to many studies focused on determining heavy metal pollution5-11.

There are many factors that can lead to heavy metal pollution in ports. For example, the loads are significant heavy metal sources and the accidents during the handling of loads lead to heavy metal pollution. Additionally, river inputs to the port areas and human activities cause many different pollutants to enter the ports12,13. As a matter of fact, both Inebolu and Bartin ports have two river inputs and there are no treatment plants in both regions.

This study was aimed to determine the heavy metal pollution status of Inebolu and Bartin ports located in Black Sea. As a result of this study, the anthropogenic sources causing heavy metal pollution in the ports were identified and the precautions to be taken against metal pollution were suggested.

Material and Methods

The study was conducted at Inebolu and Bartin ports located in Black Sea Region of Turkey between August 2013 and July 2014. Sea water, sediment and Mytilus galloprovincialis samples were collected during the study period. The amounts of Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn were determined.

Study areas

Inebolu and Bartin ports are located in Black Sea region of Turkey (Fig. 1). Sea water and sediment samples were collected monthly from six different stations (Figs 2 and 3). Mytilus galloprovincialis samples were gathered only in August and November 2013 due to bad weather conditions.
In 2012, 453.688 tonnes of cargo were handled at Inebolu port and 60 vessels traded, while 1.317.819 tonnes of cargo were handled at Bartin port and 476 ships traded.

**Sediment samples**

During the study period, 1 kg sediment samples were collected monthly by using van Veen grab. At the same time, physico-chemical parameters were measured with a multimeter (Table 1).

Samples were put into plastic bottles sterilized with dilute acidic water and brought to the laboratory quickly. After the samples were dried at room temperature (approximately 25 °C) for 24 hr, they were passed through a 100 mesh (micron) sieve to prepare them for extraction.

The extraction process was done according to the standard methods of US EPA 3051a 14. The heavy metal concentrations in the samples were determined with Spectro SpectroBlue ICP-OES instrument and CPI International Peak Performance Certified Reference Materials, Certified by ICP against NIST SRM3151 reference matter was used to calibrate ICP-OES (Table 2).

**Sea water samples**

Samples were gathered monthly from each station with Nansen bottle (from 4-5 m depth) and put into the 1 L plastic bottles sterilized with dilute acidic water. After the samples were taken, 3 ml of nitric acid was added and the samples were brought to the laboratory. After the samples were homogenized by using magnetic stirrer, they were put into 100 mL volume plastic bottles; and heavy metal amounts were measured directly with ICP-OES.

**Mytilus galloprovincialis samples**

Due to feeding by filtering the sea water and having high heavy metal accumulation capacity, *M. galloprovincialis* which is one of a mussel species was chosen as a bioindicator to assess the heavy metal pollution in the study. *M. galloprovincialis* samples were collected by scuba diving. The samples were brought to the laboratory with cold chains. After length, width and weight of the samples were measured (Table 3), their contents were removed using sterile dissection sets. The contents were then dried at 105 °C throughout 24 hr. The extraction process was carried out according to US EPA 3052 standard method 15.

**Statistical analysis**

Kolmogorov Smirnov Test was applied to each data set to determine the normal distribution of amounts of the heavy metals obtained from sediment, sea water and *M. galloprovincialis* samples from both
ports and as a result it was determined that the data are normally distributed\textsuperscript{16}. Independent samples t-test was applied to the samples to show whether the sediment, sea water and \textit{M. galloprovincialis} samples differed between ports according to the means\textsuperscript{16}. SPSS v22 software was used for statistical calculations.
Results

The study was conducted at Inebolu and Bartin ports in the Central Black Sea region of Turkey between August 2013 and July 2014. Sea water and sediment samples were collected monthly during the study. *Mytilus galloprovincialis* samples were gathered only two times due to bad weather conditions and lack of a diver who can dive in the port area. In the sample sets, Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, and Zn ratios were determined to evaluate the pollution status of the ports.

The heavy metal concentrations in the sediment samples obtained monthly from Inebolu and Bartin ports is given (Table 4). The pollution level in Inebolu port was significantly higher than in Bartin port in terms of Al, As, Co, Cu, Fe, and Zn (12782.61±3449, 10604.12±286.7, 34.32±1.87, 452.04±20.88, 35608.71±112.16 and 0.104±0.006 mg/kg dry weight, respectively) (p<0.05). For other metals, the differences between ports were not important (p>0.05). When the results were compared with the limit values of US EPA, it was found that Inebolu had high pollution in terms of Cu (452.04±20.88 mg/kg dry weight) and moderate pollution in terms of Cr and Ni (53.36±13.58 and 44.92±9.94 mg/kg dry weight, respectively) and Bartin port had high pollution in terms of Ni (488.45±39.28 mg/kg dry weight) and moderate pollution in terms of Cr and Cu (32.56±6.59 and 49.04±8.82 mg/kg dry weight, respectively). There was no pollution in terms of other metals.

The comparison of sea water samples of Inebolu and Bartin ports is given in Table 5. It was determined that heavy metal pollution in Bartin port was significantly higher than Inebolu port in terms of Al, Fe and Mn (6.64±0.50, 0.214±0.029 and 0.0065±0.0008 ppm, respectively) (p<0.05). There were no differences between the ports for As and Zn (p>0.05). On the other hand, the amounts of heavy metals did not exceed the limit values of US EPA.

The Mytilus galloprovincialis samples were compared between the ports (Table 6), it was found that amounts As (9.89 mg/kg, dry weight) and Pb (0.88 mg/kg, dry weight) obtained form Bartin port were significantly higher than Inebolu port (6.38 and 0.83 mg/kg, respectively). The Co concentration (0.64 mg/kg, dry weight), Cu concentration (39.50 mg/kg, dry weight) and Fe concentration (458.66 mg/kg, dry weight) were importantly higher than the Bartin port (0.16, 7.05, and 409.84 mg/kg, dry weight, respectively) (p<0.05). The differences between the ports for other heavy metals were not significant (p>0.05). When the heavy metal concentrations were compared with the limit values of the meat quality values determined by EU Commission, As, Cd, Cu and Zn in Inebolu port and As, Cd and Zn concentrations of *M. galloprovincialis* in Bartin port exceeded the limit values, clearly suggesting pollution in terms of these heavy metals.
Discussion
In both the ports, Cr, Cu and Ni pollution in terms of sediment and As, Cd, Cu and Zn pollution in terms of *Mytilus galloprovincialis* were determined. It was suggested that the main factors in achieving these results were loads in the ports, shipyard and submarine maintenance and repair facility, ships, and river inputs. For instance, loads such as copper, pyrite, marble, stone charcoal, potato, chipboard, fertilizer, wood, coal, urea fertilizer and methanol were being handled in the port of Inebolu and mainly profile and ingot iron bars, citrus, diatomite mine, gypsum, cement, kaolin and kaolin clay, ingot iron, logs and coal in Bartin port. Copper mine is the main load in Inebolu port and this explained why Cu pollution was high in the sediment in Inebolu port.

Similarly, the transport of the profile and ingot iron bars caused high Ni pollution in Bartin port. In addition, the dock is washed with pressurized water after each loading and unloading process at the port of Bartin. This meant that the waste left from every loading and unloading process in the port is discharged directly into the sea. Other loads such as coal and fertilizer contained significant amounts of the heavy metals.

In addition to the loads, shipyard and submarine maintenance and repair facilities were also considered to have contributed significantly to the heavy metal pollution in both ports. Engine maintenance and other repairs were carried out at the submarine maintenance and repair facility. In Inebolu shipyard, all works except shipbuilding were done. Indeed, both facilities were significant heavy metal pollution sources.

Especially in shipyards, wastes released after some processes such as bilge and ballast waters, protective dyes, blasting, dismantling and repair were among the most serious pollutant sources. The operations in Inebolu port were conducted in floating dry dock. Therefore, antifouling dyes containing high amounts of Cu and Zn were discharged directly into the sea. As a result, the findings reported high Cu pollution in Inebolu port.

### Table 5 — Comparison of sea water samples of Inebolu and Bartin ports, ppm

<table>
<thead>
<tr>
<th></th>
<th>Inebolu Port</th>
<th>Bartin Port</th>
<th>p values</th>
<th>t values</th>
<th>US EPA Guidelines</th>
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<tr>
<td><strong>Al</strong></td>
<td>0.032±0.0002</td>
<td>0.116±0.016</td>
<td>0.009*</td>
<td>-4.225</td>
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<tr>
<td><strong>As</strong></td>
<td>0.004±0.0004</td>
<td>0.005±0.0004</td>
<td>0.246</td>
<td>-1.166</td>
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<tr>
<td><strong>Cd</strong></td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
<td>40</td>
</tr>
<tr>
<td><strong>Co</strong></td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
<td>1100</td>
</tr>
<tr>
<td><strong>Cr</strong></td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
<td>4.8</td>
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<tr>
<td><strong>Cu</strong></td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
<td>74</td>
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<tr>
<td><strong>Fe</strong></td>
<td>0.067±0.005</td>
<td>0.21±0.029</td>
<td>0.009*</td>
<td>-3.988</td>
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<tr>
<td><strong>Mn</strong></td>
<td>0.002±0.0002</td>
<td>0.006±0.0008</td>
<td>0.009*</td>
<td>-4.093</td>
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<tr>
<td><strong>Ni</strong></td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
<td>210</td>
</tr>
<tr>
<td><strong>Pb</strong></td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
<td>8.1</td>
</tr>
<tr>
<td><strong>Zn</strong></td>
<td>0.005±0.0006</td>
<td>0.004±0.0007</td>
<td>0.669</td>
<td>0.429</td>
<td>90</td>
</tr>
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</table>

The p values marked with * indicate that the differences are significant.

### Table 6 — Comparison of samples of *Mytilus galloprovincialis* in Inebolu and Bartin ports, mg/kg dry weight

<table>
<thead>
<tr>
<th></th>
<th>Inebolu Port</th>
<th>Bartin Port</th>
<th>p values</th>
<th>t values</th>
<th>European Commission</th>
</tr>
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<tr>
<td></td>
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<td></td>
</tr>
<tr>
<td><strong>Al</strong></td>
<td>214.17±16.13</td>
<td>210.23±12.54</td>
<td>0.336</td>
<td>0.237</td>
<td></td>
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<tr>
<td><strong>As</strong></td>
<td>6.34±0.39</td>
<td>9.90±2.57</td>
<td>0.001*</td>
<td>-6.730</td>
<td>1</td>
</tr>
<tr>
<td><strong>Cd</strong></td>
<td>1.03±0.08</td>
<td>1.04±0.09</td>
<td>0.297</td>
<td>-0.13</td>
<td>0.1</td>
</tr>
<tr>
<td><strong>Co</strong></td>
<td>0.64±0.09</td>
<td>0.16±0.04</td>
<td>0.000*</td>
<td>4.085</td>
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<tr>
<td><strong>Cr</strong></td>
<td>20.81±7.83</td>
<td>14.15±3.99</td>
<td>0.232</td>
<td>0.680</td>
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<tr>
<td><strong>Cu</strong></td>
<td>39.83±4.73</td>
<td>7.08±0.36</td>
<td>0.000*</td>
<td>6.123</td>
<td>20</td>
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<tr>
<td><strong>Fe</strong></td>
<td>457.23±44.54</td>
<td>410.72±25.45</td>
<td>0.036*</td>
<td>0.851</td>
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<tr>
<td><strong>Mn</strong></td>
<td>16.30±1.22</td>
<td>17.98±1.39</td>
<td>0.269</td>
<td>-0.737</td>
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<tr>
<td><strong>Ni</strong></td>
<td>11.11±3.85</td>
<td>8.44±2.33</td>
<td>0.222</td>
<td>0.532</td>
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<tr>
<td><strong>Pb</strong></td>
<td>0.83±0.11</td>
<td>0.88±0.07</td>
<td>0.002*</td>
<td>-0.365</td>
<td>1</td>
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<tr>
<td><strong>Zn</strong></td>
<td>197.46±12.90</td>
<td>235.05±11.66</td>
<td>0.982</td>
<td>-1.90</td>
<td>50</td>
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</table>

The p values marked with * indicate that the differences are significant.
In ships, another factor causing the heavy metal pollution in both ports, the antifouling dyes containing Cu and Zn components lose their function over time and thus their Cu and Zn are components spread in to the sea water. These components cause serious pollution especially in relatively small areas such as harbors, marinas, bay and gulf. It is reported that 3.86 tonnes of Cu per year from a marina with 876 vessels consisting of sailing and motorboats and average 15 $10^6$ kg Cu per year from around the world is spread in to the sea water. There is also an anchoring area at the port of Inebolu where 85 fishing boats are anchored all year round. Therefore, this effect became more important in the port of Inebolu.

In addition, there were river inputs to the ports of Inebolu and Bartin, with no wastewater treatment plants in both regions. Therefore, wastewater discharged directly in to the rivers increased the pollution load of the rivers. As a matter of fact, it is stated that many kinds and amounts of pollutants from cities reached the sea by river inputs.

When the pollution was evaluated in terms of *M. galloprovincialis* samples, As, Cd, Cu and Zn pollution for Inebolu port and As, Cd and Zn pollution for Bartin port were determined. In many studies, the mussels were used as bioindicator organisms to evaluate the pollution due to their unique characteristics, including their civility to live on hard substances, exhibiting high resistance to variable environmental conditions (temperature, salinity, oxygen concentration, pollution, etc.), living for long, producing metal binding proteins, feeding by filtration of the sea water, and accumulating high amounts of pollutants. It is reported that there is a direct correlation between the heavy metal amounts and the human activities in *M. galloprovincialis* samples. Which is compatible with our study. It was observed that metals with high concentration in sediment and seawater were also high in *M. galloprovincialis* samples obtained from the ports of Inebolu and Bartin.

**Enrichment factor (EF)**

The aim of the study was to determine heavy metal pollution in Inebolu and Bartin ports. To achieve this aim, we examined our findings using different approaches such as EF and I-Geo index. We used EF to determine whether the metal concentrations found in sediment were geochemically usual or unusual. Aluminum and Fe metals, which are common in the earth's crust, are used for the calculation of the EF. According to the EF, if the EF value is between 0.5 and 1.5, it is considered that the heavy metal accumulation in the region is caused by natural events (wind, rain, flood, erosion, etc.). When the EF value is higher than 1.5, it is understood that the metal accumulation in the region is from point or non-point sources. Sediments containing high organic matter, clay and fine grains are dominant especially in the river estuaries. In clay minerals, Fe element is abundant. Because of the river inputs to the Inebolu and Bartin ports, Fe was used to calculate the EF. Indeed, in other studies also, the Fe element was used successfully in EF calculations. The EF was calculated according to the formula:

$$EF = \frac{(Me/Fe)_{Sample}}{(Me/Fe)_{Background}}$$

Where $(Me/Fe)_{Sample}$ is the metal-to-Fe ratio in the samples of interest and $(Me/Fe)_{Background}$ is the natural background value of metal-to-Fe ratio. As no previous studies were carried out in the ports of Inebolu and Bartin, the natural quantities of the elements in the earth's crust were used as past data (80000, 13, 0.3, 19, 90, 45, 47200, 850, 68, 16 ve 95 mg/kg was used for Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn, respectively).

The EF values obtained from the ports of Inebolu and Bartin for sediments are given in Table 7. According to the results, it is understood that Cd, Co, Cu and Ni derived from point and/or non-point sources due to the fact that the EF values of Cd, Co and Cu (3.18, 2.39 and 13.31, respectively) in Inebolu port and Cd, Cu and Ni (4.82, 1.83 and 12.07, respectively) in Bartin port were found more than 1.5. Similarly, As, Co, Cr and Mn derived from natural facts due to finding the EF values of As, Cr and Ni (1.10, 0.78 and 0.87, respectively) in Inebolu port and As, Co, Cr and Mn (0.86, 0.73, 0.61 and 0.55, respectively) in Bartin port were between 0.5 and 1.5. Accumulation of other metals were found insignificant. These results demonstrated that Cr, Cu and Ni pollution in the sediment samples in both ports was derived from loads, shipyard and submarine maintenance and repair facility, ships and river inputs.

**Geo-accumulation index (I-Geo)**

Another approach used in the assessment of heavy metal pollution in Inebolu and Bartin ports is the geological accumulation index. The aim of this approach is to compare the current amounts of metals...
In this way, the interested metal concentration in sediments is the background matrix correction factor to accommodate lithogenic effects. According to the results, it is observed that while Inebolu port can be labeled from unpolluted to moderately polluted in terms of Cd and Co (0.68, 0.27, respectively) and from moderately to strongly polluted in terms of Cu (2.74) pollution, whereas Bartin port labeled from unpolluted to moderately polluted in terms of Cd (0.93) and from moderately to strongly polluted in terms of Ni (2.26). It was determined that point and/or non-point sources led to these results.

### Conclusion

The study was conducted in Inebolu and Bartin ports located in Black Sea region of Turkey between August 2013 and July 2014. In both ports, Cr, Cu and Ni pollution in terms of sediment and As, Cd, Cu and Zn pollution in terms of *M. galloprovincialis* were determined. It was suggested that the main factors in achieving these results were: Loads in the ports, shipyard and submarine maintenance and repair facility, ships, and river inputs. Therefore, firstly, the handling of the loads should be so done more carefully. Secondly, submarine maintenance and repair facility and shipyard activities should be arranged to prevent the spread of pollution to the marine environment. Lastly, the pollution load from the river inputs to the ports should be reduced by constructing a wastewater treatment plant in both Inebolu and Bartin ports.

### Acknowledgement

We would like to thank Kastamonu University for the support of the study.

### References


<table>
<thead>
<tr>
<th>Table 7 — Enrichment factor values calculated for Inebolu and Bartin ports</th>
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<td>Cd</td>
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<td>Zn</td>
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<tr>
<th>Table 8 — Metal geoaccumulation index values in the sediments from Inebolu and Bartin ports</th>
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<td>Zn</td>
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<th>Table 9 — Müller’s classification scale for geoaccumulation index</th>
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<td><strong>Class</strong></td>
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<td>5</td>
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### Calculation

In the formula, $C_n$ is the observed concentration of the interested metal (n) and $B_n$ is the geochemical background concentration of the metal (n). Factor 1.5 is the background matrix correction factor to accommodate lithogenic effects.

The I-geo index results and their classification scale are presented in Tables 8 and 9, respectively. According to the results, it is observed that while Inebolu port can be labeled from unpolluted to moderately polluted in terms of Cd and Co (0.68, 0.27, respectively) and from moderately to strongly polluted in terms of Cu (2.74) pollution, whereas Bartin port labeled from unpolluted to moderately polluted in terms of Cd (0.93) and from moderately to strongly polluted in terms of Ni (2.26). It was determined that point and/or non-point sources led to these results.
3 Sivaperumal, P., Sankar, T. V., & Nair, P. V., Heavy Metal Concentrations in Fish, Shellfish and Fish Products from Internal Markets of India vis-a-vis International Standards. *Food chemistry*, 102(3)(2007) 612-620.


