Distribution of Pb and Fe heavy metal contamination in sea water and sediment in Bangkalan Madura Sea Waters

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Abstract. The high level of industrial and port activity in Surabaya and Gresik causes the potential for heavy metal waste pollution in Bangkalan sea waters. Heavy metal pollution will accumulate in several organs causing mild to severe illnesses. Sea water in Bangkalan waters is also used as raw water for shrimp cultivation and salt production, so it needs to meet water quality standards. The research was conducted in 4 locations determined using the random purposive sampling method. Each location requires one seawater and sediment sample each. Each sample will be tested using a Flame Atomic Absorption Spectrophotometry (AAS) instrument to determine the concentration of Pb and Fe. From the results of laboratory tests it is known that St.1 (Modung Coast), contains the highest Pb and Fe contamination values in sea water and marine sediment, where the Pb value = 0.04 ppm and Fe = 0.1 ppm, for marine sediment the Pb value = 4.25 ppm and Fe = 0.38 ppm. Then proceed to determine the contamination distribution coefficient (Kd). The highest value is at St.4 (Tajungan-Kamal) where Kd Pb = 149.78, and Kd Fe = 7.94. The next step is modeling visualization to determine the distribution of pollution using a color gradient scale.

1 Introduction

Bangkalan is a district located at the western tip of Madura Island, East Java, with an area of around 1.260.15 km² with a coastline length of 124.10 km. From 18 Districts in Bangkalan Regency, with 10 sub-districts, has a coastline which is a busy strait for shipping traffic and it is suspected that there is a lot of pollution. [1].

Sea water in the Madura Strait is also known as raw water for shrimp cultivation ponds. The potential for heavy metal content in sea water in the Madura Strait which is above quality standards poses a serious threat to the continuity of shrimp farming businesses. In general, heavy metals accumulate in shrimp from the feed they are given, groundwater pollution, mining and industrial waste [2].

Apart from that, sea water is also the raw material for water for salt production businesses, especially along the coast of Madura. Heavy metal contamination also has the potential to reduce the quality of sea salt production. The quality of water raw materials must be free from heavy metal contaminants, because salt is one of the complementary needs in food as a kitchen spice, and is a source of electrolytes for the human body [3-4]. In addition, the Madura Strait, which is located in Bangkalan district, has also been designated as a tourist area that needs to meet sea water quality standards in accordance with applicable laws and regulations. This is important considering that compared to other districts in Madura, Bangkalan has the most tourist attractions. [5-6].

Bangkalan is directly bordered by the sea directly with the city of Surabaya & Gresik Regency on the Madura Strait [7]. Surabaya and Gresik themselves are known as areas that are growing rapidly with various

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industrial areas, especially Surabaya which incidentally is the location of the largest port in eastern Indonesia, namely the Port of Tanjung Perak. The high level of industrial activity in Surabaya and Gresik as well as the busy port activity has resulted in the potential for heavy metal waste contamination in Bangkalan sea waters. 

The Gresik Special Economic Zone (KEK) which is shown in Fig.1, where the main activities include; Metal Industry (Copper & Steel Smelters), Electronics Industry, Chemical Industry, Energy Industry, and Logistics [8].

Heavy metals are metals that have a specific gravity of 5.0 or more [9]. Heavy metals can be found in water, air and soil as a result of human activities, for example transportation, industrial activities, soil erosion, agriculture, urbanization, sewage discharge, etc [10-11]. In the particulate phase, metals decompose easily transported from land to estuaries via river flows and from the coast to the open sea [12].

The biggest source of heavy metals entering the sea is industrial waste. Waste from the chemical industry, food, metal industry, photography, metal plating, printing, textile factories and the tanning industry will transmit heavy metal contamination through rivers or discharge directly into the sea. Apart from that, metal pollution in the sea can also come from an atmosphere polluted by vehicle fumes, burning rubbish, and smoke from cement, zinc and other metal factories [13]. This is in line with the results of research by [14] which stated that heavy metal contamination in Korean coastal sediments was influenced by anthropogenic sources related to human activities in coastal areas.

Quality Standards for heavy metal content in sea water for use in Ports, Marine Tourism and Marine Biota are listed in attachments to VI and VIII of Peraturan Pemerintah no. 22 of 2021 (Table 1) where the quantities have been determined for the parameters Ar, Cd, Cu, Pb, Zn, Ni, and Fe [15].

**Table 1. National water quality standards for heavy metals.**

<table>
<thead>
<tr>
<th>Metal Type</th>
<th>Unit</th>
<th>Seaports</th>
<th>Marine Tourism</th>
<th>Marine Biota</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic (Ar)</td>
<td>mg/L</td>
<td>-</td>
<td>0.025</td>
<td>0.012</td>
</tr>
<tr>
<td>Cadmium (Cd)</td>
<td>mg/L</td>
<td>0.01</td>
<td>0.002</td>
<td>0.001</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>mg/L</td>
<td>0.05</td>
<td>0.05</td>
<td>0.008</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>mg/L</td>
<td>0.05</td>
<td>0.005</td>
<td>0.008</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>mg/L</td>
<td>0.1</td>
<td>0.095</td>
<td>0.05</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>mg/L</td>
<td>-</td>
<td>0.075</td>
<td>0.05</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>mg/L</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Heavy metals are usually found in very small amounts in water naturally at less than 1 µg. The level of metal concentration in water is divided according to the level of pollution, such as heavy pollution, moderate pollution, and non-pollution. Water that is heavily polluted usually has a high content of heavy metals in the water and the organisms that live in it. At moderate pollution levels, the content of heavy metals in water and organisms is very low and even undetectable [16].

Metal toxicity depends on several factors including dose, exposure route, and chemical species, as well as the age, gender, genetics, and nutritional status of the exposed individual [17].

The heavy metals studied here are iron (Fe) and lead (Pb). Iron (Fe) is an important component of proteins containing iron-sulfur clusters that play an important role in key cellular processes such as oxygen transport, mitochondrial respiration, or DNA synthesis. Severe iron deficiency will cause growth arrest and cell death. Meanwhile, in the case of a hereditary disease called hemochromatosis, the accumulation of excess iron will cause oxidative stress and subsequent tissue damage, resulting in potentially fatal liver and heart failure [18].

Lead (Pb) is a very toxic metal. So it is classified as a non-essential heavy metal [19]. Lead causes environmental pollution and health problems in many parts of the world. Lead is a bright silvery metal, becoming slightly bluish in dry conditions. The color fades when exposed to air. Lead forms a complex mixture of compounds, depending on certain conditions [20].

Therefore, it is important to carry out research aimed at identifying the potential for heavy metal pollution in the Bangkalan Madura sea waters. Identification of potential pollution will be carried out at four sampling points in the Bangkalan Madura sea waters. At each location, sea water and marine sediment will be taken as samples. The samples will be taken to the laboratory to be analyzed for heavy metal levels. From the data obtained on heavy metal levels in sea water and marine sediments, a visualization of their distribution will then be created. We hope that the results of this visualization can be useful for the general public, fishermen, shrimp farmers, salt producing entrepreneurs, and the government as policy makers.

### 1.1 Experimental design

In this research, quantitative methods were used. Quantitative methods are collecting and analyzing numerical data to answer scientific research questions. Quantitative methods are used to summarize, determine averages, find patterns, make predictions, and test cause and effect relationships [21].

### 1.2 Sampling locations

This research was carried out in the coastal waters of the Bangkalan Madura sea with 4 sampling points labeled St.1, St.2, St.3, and St.4, the details of which can be seen in Fig 2 and Table 2. Determining the number and placement of location points was carried out using the Random Purposive Sampling method. The meaning of purposive sampling is the random selection of sampling units within the population segment that has the most information about a desired characteristic [22]. Then the location is selected by considering the position and distance of the sampling location to possible sources of pollution from the
industrial area of Gresik Regency and Surabaya City. Seawater and sediment samples were taken at each location.

Fig 2. Sampling location point on the sea coast of Bangkalan, Madura.

Table 2. Sampling location point coordinates.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sampling Point</th>
<th>Locations Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>St. 1</td>
<td>7°12'26.89&quot;S, 113°00'17.50&quot;E</td>
</tr>
<tr>
<td>2.</td>
<td>St. 2</td>
<td>6°53'06.43&quot;S, 112°58'58.45&quot;E</td>
</tr>
<tr>
<td>3.</td>
<td>St. 3</td>
<td>6°53'06.43&quot;S, 112°58'58.45&quot;E</td>
</tr>
<tr>
<td>4.</td>
<td>St. 4</td>
<td>7°09'19.37&quot;S, 112°41'44.44&quot;E</td>
</tr>
</tbody>
</table>

1.3 Research design

The content of heavy metal parameters tested at each location point is Lead (Pb) for non-essential heavy metals, and Iron (Fe) for essential heavy metals. Pb and Fe values were tested in seawater and marine sediment samples.

Each seawater sample requires approximately 500 ml. The sample is placed in a tightly closed bottle or jar. The seawater data sampling method follows the SNI 6964.8: 2015 guidelines concerning seawater quality, section 8: seawater test sampling method. Sampling sea water data using tools with the following requirements. The equipment used in taking seawater test samples is required; (a) Made from materials that do not affect the properties of the test sample, (b) Easy to clean from contaminants, (c) Safe and practical, (d) The test samples taken can be easily transferred into the test sample container [23].

Sediment sampling is carried out with tools such as shovels or grabbers in coastal waters which are still influenced by tides. Each sediment sample requires approximately 500 grams and is superficial sediment (at a depth of 5 cm). The sediment samples were then dried by manual drying. Once completely dry, the sample is placed in a tightly closed plastic or jar [24-25].

The number of seawater and sediment test samples at each location is one sample. This research took samples at four location points, so each of them obtained four Pb values in seawater and sediment, as well as four Fe values in seawater and sediment. Test samples are then labeled with the number, location and time of sampling to avoid the risk of being mixed up. After being closed tightly, the containers are then put into a special storage box so that the samples do not break or spill during the journey to the laboratory location [26].

The seawater and sediment test samples obtained were then taken to the laboratory for a series of tests. First, at the preparation stage, the samples are transferred to a microwave digestion container for decomposition, then analyzed using the furnace method on a flame Atomic Absorption Spectrophotometry (AAS) tool to determine the levels of heavy metals contained in each test sample. [27]

The next step, after the values for the heavy metal content Pb and Fe of all test samples have been obtained, is to analyze the distribution of heavy metal contamination using modeling software [28-30]. This results in a visualization of the distribution of heavy metal contamination in Bangkalan sea waters.

2 Results and discussion

This research activity has produced data in the form of values for the heavy metal content Pb and Fe found in sea water and marine sediments in the waters of Bangkalan, Madura. This data (Table 3) is the result of measuring test samples in the form of sea water and sediment originating from 4 location points which were tested in the laboratory using the flame Atomic Absorption Spectrophotometry (AAS) instrument.

Table 3. Concentration of heavy metal contamination in sea water & marine sediment in Bangkalan Sea Waters.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sampling Point</th>
<th>Lead (Pb)</th>
<th>Iron (Fe)</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Sea Water</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>St.1</td>
<td>0.042</td>
<td>0.097</td>
<td>ppm</td>
<td></td>
</tr>
<tr>
<td>St.2</td>
<td>0.031</td>
<td>0.048</td>
<td>ppm</td>
<td></td>
</tr>
<tr>
<td>St.3</td>
<td>0.022</td>
<td>0.031</td>
<td>ppm</td>
<td></td>
</tr>
<tr>
<td>St.4</td>
<td>0.009</td>
<td>0.016</td>
<td>ppm</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>Marine Sediment</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>St.1</td>
<td>4.254</td>
<td>3.382</td>
<td>ppm</td>
<td></td>
</tr>
<tr>
<td>St.2</td>
<td>3.419</td>
<td>0.386</td>
<td>ppm</td>
<td></td>
</tr>
<tr>
<td>St.3</td>
<td>1.926</td>
<td>0.184</td>
<td>ppm</td>
<td></td>
</tr>
<tr>
<td>St.4</td>
<td>1.348</td>
<td>0.127</td>
<td>ppm</td>
<td></td>
</tr>
</tbody>
</table>

Based on the data that has been obtained, it is then plotted on the following line graph. Fig. 3 is a graph of Pb and Fe concentrations in Bangkalan sea water, and Fig. 4 is a graph of Pb and Fe concentrations in Bangkalan sea sediments.

It can be concluded that in sea water when compared to Pb and Fe, the heavy metal that has the highest value is iron (Fe). The highest Fe value is found at St.1 and the lowest Fe is at St.4. Meanwhile, in marine sediments, when comparing Pb and Fe, the heavy metal that has the highest value is Lead (Pb). The highest Pb value is at St.1 and the lowest is at St.4. So at St.1, the sampling point at Modung beach has the highest levels of Pb and Fe contamination in both sea water and marine sediment.
The distribution of heavy metals in marine waters and sediments is based on the distribution coefficient (or partition coefficient). The distribution coefficient ($K_d$) is the ratio of pollutant concentrations between sediment and water, calculated using the following equation 1, where $K_d$ (L/kg) is the distribution coefficient, $Metal_{s}$ is the concentration of pollutants in sediment (mg/kg), and $Metal_{w}$ is the concentration of pollutants in water (mg/L). This coefficient is useful for knowing the potential migration of pollutants in the liquid phase where the pollutant is in contact with sediment or suspended material. This coefficient also serves as a tool to quantitatively describe the partition of an element or compound between sediment and the water column [31-34].

$$K_d = \frac{[Metal_s]}{[Metal_w]} \frac{L}{kg}$$  \hspace{1cm} (1)

Determination of location-specific $K_d$ values is influenced by natural concentrations in seawater and sediment. Efforts are required to obtain $K_d$ values with conditions as close as possible to site-specific conditions, taking into account the chemicals and chemical species present at the site [32]. In Table 4 below are the $K_d$ values and Log($K_d$) values for Pb and Fe which are determined from equation 1, as well as the distribution of the $K_d$ values in Fig. 5. The highest $K_d$ value was at sampling location St.4 for both Pb and Fe, while the lowest $K_d$ value was at St.3 for lead (Pb) and St.1 for iron (Fe).

The next step after the $K_d$ value is obtained is to calculate Log($K_d$). Log($K_d$) which can indicate the nature of the pollutant chemical element or compound. Based on Nabelkova & Kominkova, a Log($K_d$) > 5 indicates that the nature of the chemical element or compound tends to be bound or fixed in the solid phase; if the value is in the range 3 < Log($K_d$) < 4 then the chemical element or compound is more easily released from the solid phase; and Log($K_d$) < 3 indicates the chemical tends to be in the liquid phase [35].

### Table 4. $K_d$ and Log($K_d$) values for Pb and Fe at each sampling location.

<table>
<thead>
<tr>
<th>Sampling Point</th>
<th>$K_d$ Lead (Pb)</th>
<th>Log($K_d$) Pb</th>
<th>$K_d$ Iron (Fe)</th>
<th>Log($K_d$) Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>St.1</td>
<td>101.29</td>
<td>2.01</td>
<td>3.94</td>
<td>0.60</td>
</tr>
<tr>
<td>St.2</td>
<td>110.29</td>
<td>2.04</td>
<td>5.96</td>
<td>0.78</td>
</tr>
<tr>
<td>St.3</td>
<td>87.55</td>
<td>1.94</td>
<td>5.94</td>
<td>0.77</td>
</tr>
<tr>
<td>St.4</td>
<td>149.78</td>
<td>2.18</td>
<td>7.94</td>
<td>0.90</td>
</tr>
</tbody>
</table>

The distribution of heavy metal contamination Pb and Fe was then visualized based on the data obtained. Visualization is carried out with the help of modeling software with the assumption that environmental conditions and ocean currents are stagnant. Below in Fig. 6, Fig. 7, Fig. 8, and Fig. 9 are the results of visualization of the distribution of Pb and Fe contamination in sea water and marine sediments in Bangkalan, Madura.
Visualization modeling of the distribution of Pb and Fe contamination was made based on pollutant levels in seawater and marine sediment. Visualization uses modeling software with the assumption that sea waters are stagnant. Visualization using color gradations. Red to orange-yellow colors indicate high pollutant concentrations, leading to green gradations which indicate lower concentrations, and ending in blue to purple gradations which indicate the lowest concentrations. The visualization results show that the red gradient color dominates St.1 as a whole because the Pb and Fe concentrations are the highest.

3 Conclusion

Based on the data obtained as well as the graphs and distribution visualizations created, it was concluded that the St.1 sampling point located on the Modung coast received the highest concentration of heavy metal contamination Pb and Fe compared to other sampling location points. In contrast, the St.4 sampling point located in the Tajungan Kamal waters received the lowest concentrations of Pb and Fe contamination.

Pb and Fe concentration values in seawater at all sampling locations still meet national water quality standards for port areas, but do not meet water quality standards for marine biota. Meanwhile, most of the Pb and Fe concentration values in marine sediments at all locations do not meet national water quality standards for seaports and biota.

It is necessary to find out the factors that cause the sampling location at point St.1 to have the highest concentration of heavy metal pollution, and the factors that cause the location at point St.4 to have the lowest concentration of pollution. Further and in-depth study is needed. Researchers must conduct a survey of environmental conditions around the sampling point to determine the exact location of the source of pollution, and whether the pollution is influenced by industrial areas in Surabaya City and Gresik Regency.

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References


