# Distribution of heavy metals (Cu and Fe) in sea water of Gresik coastal area

Ayu Nindyapuspa<sup>1,\*</sup>, Achmad Chusnun Ni'am<sup>2</sup>

<sup>1,2</sup> Department of Environmental Engineering, Faculty of Civil and Planning, Institut Teknologi Adhi Tama, Surabaya - Indonesia

**Abstract.** The improvement of industrial activities at Gresik Regency will increase the heavy metals concentration on the seawater at Gresik Regency. Therefore, the research of Fe and Cr distribution on the seawater at Gresik Regency has been conducted. Methods that were used is sampling by Nansen water sampler at three sampling points (housing in northern coastal Gresik Regency, Maspion V Industrial Estate, and Petrokimia Port). Samples were analyzed by Atomic Absorption Spectrophotometry (AAS) to determine the concentration of heavy metals. The results showed that the highest Fe and Cr concentration are located at Maspion V Industrial Estate (0.452 mg/L and 0.081 mg/L respectively). Meanwhile, Fe and Cr concentrations at the housing in northern coastal are (0.408 mg/L and 0.081 mg/L respectively). The concentration of Fe and Cr at Petrokimia Port are 0.174 mg/L and 0.021 mg/L respectively.

#### 1 Background

Coastal area is the fishery field that is very important. Therefore, it need a special focus because amount of hazardous waste such as heavy metals will end up at the sea. Heavy metals can be derived from industrial, transportation, mining, and farming. Most of the Gresik Regency is the coastal area with length coastline 69 km, start from Kebomas, Gresik, Manyar, Bungah, Sidayu, Ujungpangkah, and Panceng sub-regency. Moreover, Gresik Regency has a coastline 71 km at Sangkapura sub-regency and Bawean Island. The most economic activity that was conducted in Gresik is industrial sector, with percentage 46,53%. There are 494 middle and large industries in Gresik Regency. As an industrial city, the improvement of industrial activity will increase the generated pollutant. The pollutant is disposed to the sea caused by industrial activity, agricultural activity, and household activity. One of the pollutants that are disposed of by industries is hazardous waste. The coastal area more susceptible with hazardous waste disposal. The toxicity of heavy metals spread widely contaminating the environment at the coastal area in Indonesia. Heavy metals contamination is located at the northern beach on Java Island and eastern beach on Sumatra Island. Seawater contamination caused a problem globally, especially for the marine ecosystem. [1-2]. Heavy metal is the natural element of the marine ecosystem. Heavy metals such as Fe and Cr are pollutants in the marine environment. Heavy metals that are penetrated by the body water such as lake, river, and groundwater can cause healthy damaged [3]. To protect the seawater quality and human health at the Gresik coastal area, heavy metals measurement is needed. The purpose of this research is to determine the distribution of heavy metals pollutant, especially Fe and Cr. Data of Fe and Cr distribution can be used as a database for advanced environment monitoring.

## 2 Literature Study

Heavy metals that penetrate into the aquatic environment will be sediment, diluted and dispersed, then absorbed by aquatic organism [4]. Based on the toxicology, heavy metal was divided into two types. The first type is essential heavy metal whereas at the certain concentration are needed by organisms, but at the large concentration, it will be toxic, such as Fe concentration at the seawater. The excess of Fe can result vomiting, intestinal damage, premature aging, and death [5]. The second type is non-essential heavy metal, whereas the benefit for human health still not found and toxic such as Pb [6]. Cr is toxic heavy metal. The toxicity depend on the valence of its ion. The toxicity of  $Cr^{6+}$  is hundred times higher than the toxicity of  $Cr^{6+}$  [7]. The  $Cr^{6+}$  is corrosive and carcinogenic.

### 3 Methods

Sampling was conducted at two areas with a dense industrial activity, seawater at the industrial area on Manyar sub-regency and seawater at around PT Petrokimia Gresik Port. There are three stations for sampling location. Sampling was conducted in the morning at 07.00 AM - 10.00 AM. The wind blew to the north west. The method that was used for this research is purposive sampling. Seawater was taken by Nansen water sampler. Fe and Cr were measured by Atomic Absorption Spectrophotometer (AAS) in the laboratory.

Corresponding author: ayunindyapuspa@itats.ac.id

The results of Fe and Cr analysis will be compared with Ministry of Environment Regulation Number 51 The year 2004 about Seawater Quality Standard. Climatological data (rainfall, wind direction, wind velocity) while sampling was conducted were taken from Meteorology station Perak I Surabaya. The amount of industries in Gresik was taken by Industrial Agency of Gresik Regency.

### 4 Results and discussion

Sampling of seawater were conducted at the coastal area at Gresik Regency. There was coastal area at Gresik subregency and Manyar sub-regency. These sub-regencies were chosen because there are many industries such as PT Petrokimia Gresik and PT Maspion. Based on the Gresik Regional Development Planning Agency 2016, there are 45 industries at Gresik sub-regency and 22 industries at Manyar sub-regency. The seawater sampling location shown in Figure 1.



Fig. 1. Seawater Sampling Location

The station 1 is located at PT. Petrokimia Port, station 2 is located at marine area near Maspion V Industrial Area, and Station 3 is located at downstream at Manyar sub-regency. The coordinates of sampling location were described in Table 1.

 Table 1. Coordinates of Sampling Location

Location	Coordinates		
Station 1	7° 8'36.40"S and 112°39'25.80"E		
Station 2	7° 7'17.50"S and 112°38'50.10"E		
Station 3	7° 6'8.40"S and 112°37'58.80"E		

Samples were analyzed at laboratory using AAS. Data were compared with Ministry of Environment Regulation Number 51 The year 2004 about Seawater Quality Standard. The seawater quality standard of Fe were unregulated. The results of Fe and Cr analysis shown in Table 2.

Table 2. Result of Fe and Cr Analysis

Location	Fe (mg/L)	Cr (mg/L)	Cr Quality Standard (mg/L)*
Station 1	0.408	0.078	0.002
Station 2	0.452	0.081	0.002
Station 3	0.174	0.021	0.002

\* Based on the Ministry of Environment Regulation Number 51 The year 2004 about Seawater Quality Standard for Marine Tourism



Fig. 2. Graphic of Fe and Cr Distribution in Sea Water of Gresik Regency

The results showed that the highest Fe and Cr concentration is located at Station 2 (Figure 2). The lowest Fe and Cr concentration are located at Station 3. Based on the Ministry of Environment Regulation Number 51 the year 2004 about Seawater Quality Standard, the Cr concentration at 3 stations did not meet the standard. Meanwhile, the quality standard of Fe concentration is unregulated. Because Fe unregulated, comparing with the previous research is needed. Data were compared with the previous research, but similar with the sampling location. Data were compared with [6] and [9]. These two researches were taken at Paranggi Village's Seaport [6] and Taipa's Ferry Harbor [9]. These location are similar with Gresik Regency. The Fe concentration near with Paranggi Village's Seaport was 0.307 mg/L. Meanwhile, the Fe concentration near with Taipa's Ferry Harbor was 0.546 mg/L. Dissolved iron can exist in seawater in two oxidation states, Fe(II) and Fe(III), free or complexes with inorganic and organic ligands [10].

The Cr species most frequently found in marine media are: (i) chromate  $(Cr^{VI}04^{2-})$ ; (ii)  $Cr^{III}$  hydroxo complexes,  $Cr(OH)_3$ ,  $Cr(OH)_2^+$  and  $Cr(OH)_2^+$ . Chromium(VI) is considered to be highly toxic mainly on account of its ability to interact favourably with biological substances. According to thermodynamic calculations, only the hexavalent form of Cr should be present oxygenated sea-waters at pH 8 [11].

Coastal ecosystems are affected by industrial and anthropogenic activities such as wastes from iron and steel factories, shipyards, shipbuilding/breaking. Heavy metals concentration depends on seawater condition. When human activities are getting higher at the land or the beach, the concentration of heavy metals will be enlarged. The amount of Fe concentration caused by daily activity at household, such as domestic waste disposal containing Fe and effect of pipe corrosion so that Fe concentration is getting higher [8]. The increasing of Fe concentration caused by mineral rock erosion because of sea waves. Ship and pile port corrosion may contribute to sea water pollution by Fe [6]. In this case, industrial activity at Maspion V Industrial Area may contribute Fe and Cr to the marine pollution.

#### **5** Conclusion

The Fe and Cr pollutant at Station 2 are the highest of all with concentration 0.452 mg/L and 0.081 mg/L respectively. The Fe and Cr pollutants at Station 3 is the lowest of all with concentration 0.174 mg/L and 0.021 mg/L. The concentrations of Cr and Fe in the sea water at Gresik coastal area was exceeded quality standard based on the Ministry of Environment Regulation Number 51 The year 2004 about Seawater at Gresik Coastal Area is polluted by Cr. Cr pollution caused by industrial, port, and household activities.

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