Analysis of research methodology on the content of heavy metals in sediments on the Indonesian coastal

Sayed Abdul Azis¹, Muhammad Irham²³*, Sugianto², Ichsan Setiawan³, Amri Adnan¹

¹Master Program in Integrated Coastal Resources Management, Graduate School, Universitas Syiah Kuala, Banda Aceh 23111, Indonesia.
²Research Center for Marine and Fisheries, Universitas Syiah Kuala, Banda Aceh 23111, Indonesia.
³Faculty of Marine and Fisheries, Universitas Syiah Kuala, Banda Aceh 23111, Indonesia.

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Heavy metal pollution is one of the problems that often occurs in Indonesian coastal waters. Comparative methods of looking at heavy metal content in coastal sediments include a way to show similarities and differences between one or more articles by using certain criteria. Different comparison methods to see the heavy metal content in sediments include the AAS (Atomic Absorption Spectrophotometry) method, AAN (Neutron Activation Analysis), Regression, and USEPA methods. Based on the comparison of 2 methods, namely: AAS and AAN methods, the most efficient in analyzing heavy metals in sediments in coastal areas is the Atomic Absorption Spectrophotometry (AAS) method compared to the Neutron Activation Analysis (AAS) method.

Introduction

Coastal waters are waters that are very susceptible to various kinds of pressure, one of which is heavy metals. There are several factors that can affect coastal environmental conditions including: population growth, human activities, sedimentation, industrial waste, mining, liquid waste and pollution (Nontji, 2002; Bayram et al., 2013; Strokal and Kroeze, 2013; Lestari and Fitri Budiyanto, 2013). Amin et al. (2011) stated that one of the pollutants that has the potential to reduce and damage the carrying capacity of the coastal environment is heavy metal. Heavy metal pollution is one of the problems that often occurs in coastal waters (Lestari, 2004). Indonesian Coastal Areas are very vulnerable to pollution, especially related to heavy metals in sediments (Effendi et al., 2017; Mahidin et al., 2021). Draszawka and Bolzan (2014) stated that to see the best method for handling heavy metals, it is necessary to study the comparison of heavy metal test methods in sediments in coastal areas of Indonesia. The results of the heavy metals study in sediments can directly affect the aquatic ecosystem. It will cause contamination of aquatic biota such as fish, shrimp and shellfish, where these biota live on the bottom of the waters. In addition, the presence of heavy metals in the waters can damage the food chain system and affect the life of organisms on the coast. Based on the case study of Rochyatun et al. (2006) the content of heavy metals in sediments is higher than in water, this indicates an accumulation of heavy metals in the sediments (Irham et al., 2019).

Comparison in studying the content of heavy metals in coastal sediments includes a way to show the effectiveness and efficiency tests provided by each method. This is the result of a review between one article and several other articles by studying the basics of certain methods used (Jupp et al., 2017; Salas et al., 2017; Irham et al., 2017). The results of
the comparative analysis will show whether there is a significant difference between one method and another. There are many methods for determining heavy metal content in sediments, including AAS (Atomic Absorption Spectrophotometry), AAN (Neutron Activation Analysis), Regression, USEPA, Gravimetry, and Spectrograph methods (Balachandran et al., 2005; SEPA, 2000).

One of the appropriate methods to determine the status of heavy metal pollution of a coastal area is by looking at the accuracy of one method with another (Marchand et al., 2006; Saher and Siddiqui, 2016). There are many studies on pollution and heavy metal contamination in sediments in a waters using several methods (Bastami et al., 2014; Ho et al., 2010; Nethaji et al., 2017; Peña-Icart et al., 2017; Sundararajan et al., 2017).

The reason for using the comparison of the AAS and AAN methods is because the AAS method is commonly used by researchers, while the AAN method is not often used. The AAS method has the advantages of an easy-to-use instrument, good performance, and relatively little interference. Meanwhile, the AAN method has advantages such as: it can determine multi-element samples in various matrices, and is relatively low in contamination (Kucera et al., 2004; Isnaeni, 2021).

In this paper, the author will review 2 comparative methods of heavy metals in sediments in the Indonesian Coastal region. The comparison methods that will be reviewed are the Atomic Absorption Spectrophotometry (AAS) method and the Neutron Activation Analysis (AAN) method. The AAS method has advantages such as 10-15 seconds of analysis speed, 0.1 - 2.0% precision, and easy method development. While the AAN method has advantages, as high sensitivity, relatively low contamination, and multi-element technique (Kucera et al., 2004; Isnaeni, 2021). Therefore, this review paper aims to find out the comparison between AAS and AAN is effective in analyzing heavy metal content in sediments in coastal areas of Indonesia.

Materials and Methods

This study is a literature study of two chemical analysis methods, namely the Atomic Absorption Spectrophotometry (AAS) method and the Neutron Activation Analysis (AAN) method. The researchers compared the results of heavy metal sediment analysis based on the two methods.

1. Atomic Absorption Spectrophotometer method

Analysis of heavy metal content in sediments can be carried out using the Atomic Absorption Spectrophotometry (AAS) method. The tool used is Atomic Absorption Spectrophotometry (AAS). Figure 1 shows the AAS instrument.

![Figure 1. AAS Instrument](image)

Based on Skoog et al. (2000) the AAS method analyzes elements quantitatively whose measurements are based on the absorption of light with a certain wavelength by metal atoms in a free state.

The choice of atomic absorption spectrometry method has some advantages because it has high sensitivity, is easy, cheap, simple, fast, and requires little sample (Supriyanto et al., 2007). In addition, it can be used to determine the levels of elements whose concentrations are very small without having to be separated first. Disadvantages of this method include: it can only be used for solutions with low concentrations, requires a relatively large amount of solution (10-15 ml), and is very dependent on the power source. Several studies of heavy metals in sediments using the AAS method have been carried out by (Setiawan and Subiandono, 2015; Warni et al., 2017; Rizkiana et al., 2017; Alisa et al., 2020).

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Warni et al., 2017; Rizkiana et al., 2017; Alisa et al., 2020).

2. AAN (Netron Activation Analysis) method

Determination of heavy metals in sediments using the neutron activation analysis method was carried out by utilizing the Multipurpose Reactor Installation facility, G.A Siwabessy, BATAN, Serpong. Figure 2. Shows the AAS instrument.

Several studies of heavy metals in sediments using the AAN method have been carried out by (Susiati et al., 2014; Suparminingsih et al., 2016). The AAN method for heavy metals in sediments in coastal areas can be used for qualitative and quantitative analysis. Qualitative analysis is to find out what elements are contained in the sample, while quantitative analysis is to determine the level or concentration of these elements in the sample. This quantitative analysis was carried out after the qualitative analysis was carried out (Mulyaningsih, 2002).

The Neutron Activation Analysis (AAN) method has several advantages over other methods, namely it can determine the type of element and its content (Wijayanti, 2010), does not damage the sample (Purwandhani, 2007), has a higher sensitivity to nanograms (10-12 g) (Mireles et al., 2011), can distinguish each isotope from the same sample, and can be used to determine the content of metallic elements in liquids, solids and gases (Purwandhani, 2007), and use relatively few samples (50-100). 100 mg (Wijayanti, 2010). The weakness of the AAN method requires facilities and equipment such as a fission reactor or particle accelerator, the laboratory used to carry out this analysis must have special equipment for handling radioactive substances and for the analysis of long-lived radionuclides it takes a relatively long analysis time.

Data analysis

The data obtained were described quantitatively. The main variable concerning the topic of this research is based on a comparison of two methods in analyzing the content of heavy metals in sediments in the Indonesian Coast, namely the AAS method and the AAN method. The comparison methods were used to see which of the two methods is more efficient and effective to determine the metal content in the sediment.

Results

The results we obtained, we display in the comparative method of this study.

1. Study results of the AAS method (Table 1)

<table>
<thead>
<tr>
<th>No</th>
<th>Researcher</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Natsir et al. (2019)</td>
<td>Pb and Cd content in sediment is higher than in water.</td>
</tr>
<tr>
<td>2</td>
<td>Alisa et al. (2020)</td>
<td>The Pb content in the sediment ranged from 14.1176 – 24.1952 mg/l so that it had exceeded the safe limit and the Cd content ranged from 1.968 – 2.760 mg/l, exceeding the maximum quality standard set by ANZECC/ARMCANZ.</td>
</tr>
<tr>
<td>3</td>
<td>Setiawan and Subiandono (2015)</td>
<td>The highest heavy metal content in the sediment for heavy metals Pb, Cd and Cu came from the mouth of the Tallo River with concentrations of 66.6 ppm, 5.16 ppm and 31.1 ppm.</td>
</tr>
<tr>
<td>4</td>
<td>Nuraini et al. (2017)</td>
<td>Chromium (Cr) content in water in Trimulyo waters is &lt;0.003 mg/L, Chromium (Cr) content in sediments ranges from 20.49 – 45.78 mg/kg.</td>
</tr>
</tbody>
</table>
2. Study results of the AAN method (Table 2)

<table>
<thead>
<tr>
<th>No</th>
<th>Researcher</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Susiati et al. (2014)</td>
<td>Heavy metal concentrations of Co, Cr, Cs, As, Sc, and Fe in the sediments of the Muria Peninsula waters ranged on average between 15.5 – 17.4 ppm for Co; 44.2 – 56.2 ppm for Cr metal; 5.1 – 5.8 ppm for Cs metal; 9.6 – 12.9 ppm for metal As; 15.7 – 18.4 ppm for Sc metal; and 44.7 – 47.5 ppm for Fe metal.</td>
</tr>
<tr>
<td>2</td>
<td>Suparminingsih et al. (2016)</td>
<td>Sediments in Kaligarang contain Co-59, Zn-64, Fe-58, Cr-50 and Mg-26 while plants contain Co-59, Zn-64, Fe-58 and Cr-50.</td>
</tr>
<tr>
<td>3</td>
<td>Taftazani (2007)</td>
<td>The analysis obtained are samples of water, sediment and biota containing Hg and Cr metals.</td>
</tr>
<tr>
<td>4</td>
<td>Taftazani et al. (2018)</td>
<td>The level of heavy metals in sediments has no quality standard from the Minister of Health or the Minister of Environment.</td>
</tr>
</tbody>
</table>

Discussion

The continuously increasing activity in the coastal areas of Indonesia makes researchers want to compare various methods in the analysis of heavy metals in coastal sediments. Research on the content of heavy metals in sediments has been carried out by Natsir et al. (2019) in Tulehu Coast, Central Maluku Regency, Maluku Province using the Atomic Absorption Spectrophotometry (AAS) tool. The results of this method indicate that the Pb and Cd content in the sediment is higher than in the water.

Other studies have been reviewed by Alisa et al. (2020) on the Coast of Untung Jawa Island, Jakarta using the AAS method. The results of the method indicated that the Pb in the sediment ranged from 14.1176 – 24.1952 mg/l so that it had exceeded the safe limit and the Cd content ranged from 1.968 – 2.760 mg/l, exceeding the maximum quality standard set by ANZECC/ARMCANZ. Another case study was conducted by Setiawan and Subiandono (2015) using the AAS method to see the heavy metal content in sediments in the Coastal Zone of South Sulawesi Province. The results of this method obtained that the highest heavy metal content in the sediment for heavy metals Pb, Cd and Cu came from the mouth of the Tallo River with concentrations of 66.6 ppm, 5.16 ppm and 31.1 ppm. water, sediment and biota contain Hg and Cr metals. Nuraini et al. (2017) also conducted a case study of heavy metal content in water and sediment in Trimulyo Waters, Semarang. The results of the study showed that the content of Chromium (Cr) in the water in Trimulyo waters was <0.003 mg/L, the content of Chromium (Cr) in the sediments ranged from 20.49 – 45.78 mg/kg.

The results of the analysis show that the four studies (Table 1) conducted by Nuraini et al. (2017), Natsir et al. (2019), Alisa et al. (2020), and Setiawan and Subiandono (2015) using the AAS method, which is to analyze elements quantitatively whose measurements are based on the absorption of light with a certain wavelength by metal atoms in a free state (Skog et al., 2004). According to Kusnadi (2016), the AAS method determines metal and metalloid elements from the radiation absorption process by free atoms. The principle of AAS in the four studies conducted by these researchers is the absorption of light energy with certain wavelengths by free atoms resulting from the atomization process (Hidayat et al., 2008). Studies have been conducted by Susiati et al. (2014) in the Muria Peninsula Coast by using the AAN (Netron Activation Analysis) method. The results showed that the concentration of heavy metals Co, Cr, Cs, As, Sc, and Fe in the sediments of the Muria Peninsula waters averaged between 15.5 – 17.4 ppm for Co; 44.2 – 56.2 ppm for Cr metal; 5.1 – 5.8 ppm for Cs metal; 9.6 – 12.9 ppm for metal As; 15.7 – 18.4 ppm for Sc metal; and 44.7 – 47.5 ppm for Fe metal.

The results of the study using this method showed that the sediment in Kaligarang contained Co-59, Zn-64, Fe-58, Cr-50 and Mg-26 while plants contained Co-59, Zn-64, Fe-58 and Cr-50. The levels of Zn and Cr in the Kaligarang sediment have not exceeded the threshold, while the threshold for Co, Fe, Mg and plants has not been determined. Furthermore, there is a study from (Taftazani, 2007) using the AAN method. The results of the analysis obtained were samples of water, sediment and biota containing Hg and Cr.
metals. The same method is still carried out by Taftazani et al. (2018) by looking at the distribution of sediment in the waters of Surabaya III. It was found that the levels of heavy metals in the sediment have no quality standards from the Minister of Health or the Minister of Environment.

The results of the analysis show that the four AAN methods (Table 2) were reviewed by Taftazani (2007), Susiati et al. (2014), Suparminingsih et al. (2016), and Taftazani et al. (2018) were analyzed qualitatively and quantitatively. Qualitative analysis by looking at the elements contained in the sample of the type of nuclear reaction that occurs, this can be done because each isotope emits typical gamma radiation (Rosyid et al., 2013). Determination of the type of element is carried out by determining the peak of the gamma energy spectrum of the sample. The amount of gamma energy is matched with the Neutron Activation Tables (Erdmann, 1976), in order to obtain the types of elements contained in a sample (Yulianti et al., 2009).

Quantitative analysis by looking at the amount of elemental content in a sample. Samples irradiated using neutrons will cause the reaction of the nucleus of the element atoms contained in the sample with neutrons, so that the atoms of these elements will be radioactive. Because the nucleus is radioactive, it will decay to get to a stable state. Activity is defined as the number of decays per second (Dwijananti, 2012).

Among the various descriptions above, the Atomic Absorption Spectrophotometry (AAS) method is efficient in analyzing heavy metals in sediments in coastal areas compared to the Neutron Activation Analysis (AAS) method. Generally, the neutron activation analysis method by looking at sediments on the coast on some heavy metal samples still partially uses the AAS method. The comparison of AAS and AAN methods aims to evaluate the performance of each method in analyzing sediment samples for heavy metal content in the coast. In addition, the comparison of these two methods aims to complement each other, as cross-checking the results of the analysis, to overcome the limitations in the analysis and to determine the suitability of the two methods in analyzing the elements in sediment samples.

Metallic elements and metalloids based on the absorption (absorption) of radiant energy by free atoms. AAS was chosen because compared to AAN or other spectrophotometry, the AAS method is more specific because one cathode lamp can only detect one element according to what is contained in the lamp. AAS has a low detection limit and analysis is fast. In addition, researchers often use the Atomic Absorption Spectrophotometry (AAS) method compared to the AAN (Netron Activation Analysis) method in assessing the heavy metal content in coastal sediments due to the fast processing time, sensitivity and very specificity for the element to be analyzed (Supriyanto et al., 2007).

The AAN method is a nuclear analysis technique that has been widely applied in various fields including the coastal environment. This technique has advantages such as multi-element, high selectivity and sensitivity, good accuracy and precision, relatively free from matrix disturbances associated with nuclear reactions and decay processes. Not affected by the physical and chemical structure of the material/sample during and after irradiation, very low contribution of blanks. However, AAN, in this case the instrumental also has several drawbacks, so that researchers rarely use this method, including: requiring reactor facilities, longer analysis time than AAS due to the cooling process, and difficulty in measuring several important elements related to the small cross-section of activation (Djingova, 2000).

**a. Principles of AAS and AAN**

The principle of analysis with AAS is based on the energy absorption process by atoms that are in the ground state, while AAN is an elemental analysis method based on induced radioactivity if a sample is irradiated using neutrons.

**b. Advantages and disadvantages of AAS**

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific and faster analysis time</td>
<td>Lack of perfect sample preparation</td>
</tr>
<tr>
<td>Low detection limit</td>
<td>Matrix error</td>
</tr>
<tr>
<td>Measurements can be carried out directly on the sample solution</td>
<td>The sample flow on the burner is not the same speed</td>
</tr>
<tr>
<td>Can be applied to many types of elements in many types of examples</td>
<td>Chemical disturbances in the form of incomplete dissociation, and ionization</td>
</tr>
<tr>
<td>Instrument prices and maintenance costs are relatively cheaper</td>
<td>1-10 elements per analysis</td>
</tr>
</tbody>
</table>
### c. Advantages and Disadvantages of AAN

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>High sensitivity</td>
<td>Requires facilities and equipment such as a fission reactor or particle accelerator</td>
</tr>
<tr>
<td>Does not damage the sample</td>
<td>The laboratory used for perform this analysis must have special equipment for substance handling radioactive</td>
</tr>
<tr>
<td>Relatively low contamination and no matrix interference</td>
<td>Relatively long analysis time</td>
</tr>
<tr>
<td>Multi element technique</td>
<td>Instruments and maintenance costs are relatively more expensive</td>
</tr>
</tbody>
</table>

(Source: Kucera et al., 2004)

### Conclusion

The Indonesian coast is one of the waters that is very vulnerable to various kinds of pressure, one of which is heavy metal pollution in sediments. Comparison of methods is a way to evaluate the suitability between two analytical methods. Comparative methods of looking at heavy metal content in coastal sediments to show the similarities and differences between one or more articles by using certain criteria. Various methods commonly used to assess the coastal environment based on the content of heavy metals in sediments include: AAS (Atomic Absorption Spectrophotometry), AAN (Netron Activation Analysis), Gravimetry, and Spectrography. Among the various descriptions above, the Atomic Absorption Spectrophotometry (AAS) method is more effective in analyzing heavy metals in sediments in coastal areas compared to the Neutron Activation Analysis (AAN) method. The AAS method is better because it is a user friendly instrument; quick analysis; good in performance; very complete instrument; relatively few disturbances; and low coast instrument including its maintenance costs.

### References


