Analysis of Fe in Coral Reefs for Monitoring Environmental Areas of Prigi Coast Waters Using the Tessier-Microwave Method

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Abstract. This study revealed the analysis of Fe content in the coral reef of Prigi Coast to monitor its waters as an environmental biomonitoring agent. Fe can accumulate into the coral structure through food, the mucous tissue, the mesenterium filament, and calcium element substitution that built-in the each of Fe coral fractions. Fe can be leached in the coral reef fractions using the Tessier-microwave method. Tessier microwave method divided of Fe in the ion exchange (fraction 1), carbonate bound (fraction 2), reduction (fraction 3), oxidation (fraction 4) and residual (fraction 5), respectively. The Tessier-microwave method results detected of Fe in the fraction 3 only, indicated that all of the Fe in the coral reefs was bound to the reduction fraction. The Fe content in the fraction 3 at 6 selected locations of Prigi Coast was 127.10 ppm, 39.12 ppm, 56.64 ppm, 78.10 ppm, 11.46 ppm, and 47.62 ppm, respectively. According to several calculations of CF, PLI and Igeo indexes, it indicated the contaminated of Fe in the coral reefs, especially at reduction fraction.

1. Introduction
Coral bleaching caused by heavy metals is a major threat to coral reefs. Heavy metal concentrations at a certain level will cause bleaching in corals[1]. Heavy metals accumulated in the coral aragonites structure are associated with ion-exchange reactions, where carbonate ions in aragonites are replaced by heavy metal ions[2], as in the following equation:

\[ \text{CaCO}_3(S) + aX(aq) \rightleftharpoons \text{CaX(s)} + \text{CO}_3^{a-}(aq) \]

Heavy metals accumulate into the coral reef through four mechanisms. First, through food, coral reefs eat zooplankton, where zooplankton is affected, and heavy metals accumulate in it. Second, through the mesenterial filaments that capture foods, not only zooplankton but also particulates which are subsequently and periodically digested by coral reefs[3]. Third, through mesentrium filaments that take heavy metals bound from the sediments directly. Fourth, with the substitution of the calcium element by certain metals, organic material fragments containing heavy metals that enter the pores of the coral structure[4]. The coral reef and sediment structure can assimilate the metal over a period of hundreds of years so that it can be used for monitoring purposes[5–8].

Considering of monitor natural and anthropogenic sources of Fe, meteorites and terrestrial highly contain Fe as a heavy metal, which is 90.85%[9]. The Fe concentration in basaltic rocks was 86.5 ppm, in granite rocks with high calcium of 29.6 and in granite rocks with low calcium of 14.2 ppm[9]. This shows that Fe exists in nature in large quantities. Fe contained in coral reefs can either come from natural
sources or anthropogenic factors [10]. Examples of anthropogenic factors that increase the Fe content in coral reefs include port and tourism activities, industrial development around the sea and mining areas. There is so many marine natural products are applied by researcher to reduce heavy metals and pollution including Fe and material organic in the human body[5,10,11].

Some researcher used the BCR and Tessier-microwave methods to analyze the heavy metals bound in each fraction [6,12–14]. The Tessier-microwave method is divided into 5 fractions with shorter stages, namely the ion exchange fraction, the carbonate bound fraction, the fraction reduction, the oxidation fraction and the residual fraction. Research using this method was conducted to determine the location of Fe bound in coral reefs and its status for environmental monitoring detailed.

2. Method
The coral reef analyzed is the Acropora reef in the Prigi Coast waters. Each coral reef sample was taken from 6 different locations (Figure 1). We used those locations as a preliminary mapping of Fe to explore more detailed Fe minerals.

The Tessier-microwave procedures have been adapted and modified by Wijaya et al. (2019)[12]. The coral reef sample was dried in an oven at 60°C until a constant weight achieved. Then it was smoothed out and is weighed as much as 1 gram and treated with the Tessier-microwave method. In the first fraction, 1 gram of dry coral was added to 4 mL MgCl₂ and was heated in the microwave at 50% power irradiation (399 W) for 3 minutes. The mixed coral and chemicals were then centrifuged and filtrated as the solution in the fraction 1. In fraction 2, CH₃COONa has added about 4 mL and heated in the microwave at 50% power irradiation (399 W) for 3 minutes. After microwaved, the centrifuged and filtrated samples were taken as a solution in fraction 2. Then, 10 mL NH₂OH.HCl was added and heated in the microwave at 50% power irradiation (399 W) for 3 minutes and repeated them at two times. The sample was then centrifuged to obtain filtrate for the solution in the fraction 3. There is no residue in the fraction 3, Fe in the fraction 4 and fraction 5 were almost completely not detected. The solutions in the fraction 1-3 were analyzed of Fe using the AAS instrument.

![Figure 1. Six sampling locations in Prigi Coast Waters area.](image-url)
3. Results and Discussion

The Tessier-microwave method was applied to analyze the Fe from the fraction 1 to fraction 5 by using specific solvents. It started from fraction 1 to fraction 3, all of their residues were completely dissolved by attacking solvents. But, Fe in fraction 4 and 5 could not continue analyzed. The applied of Tessier-microwave method in the coral reef is different from their applied in sediment. Fraction 4 and 5 contained humic acid and silica-alumina. It suggested the investigated coral reef did not content of humic acid and silica-alumina.

The reaction of each fraction shows different chemical strengths in the level fraction. In the ion-exchange fraction is known as a mobile fraction and has the lowest strength and easily dissolved in the waters (fraction 1). The carbonate bound fraction has a greater strength in binding Fe than ion-exchange fraction (fraction 2). The third fraction or reduction fraction has a greater strength in binding the metal where a stronger acid was added.

Figure 2 shows the Fe concentrations in fraction 1, 2, and 3. The contents of Fe dominantly were recorded at fraction 3. The ranged concentrations of Fe in the fraction 3 was recorded from 22.46 to 127.1 ppm. All of Fe concentrations in Fraction 1 and 2 were low.

![Figure 2. Fe concentrations in coral reefs at each location.](image)

This indicates that a few Fe content in coral reefs was bound to the ion exchange fraction through ion exchange reactions with Mg$^{2+}$. In the fraction 2, it indicates there was also a few Fe binding by CH$_3$COO$^-$ in the coral reef. In fraction 3 (reduction fraction), the various concentrations of Fe were dominantly obtained from all sampling locations. The Fe detection signifies that all reaction that occurs in fraction 3 undergoing the reduction of Fe$^{3+}$ to Fe$^{2+}$ due to the attacking of NH$_2$OH.HCl in coral reef samples. The fraction 3 as the final fraction in coral reefs indicates that there is neither Fe bound to organic material (humic acid) as fraction 4 nor bound to silica-alumina or fraction 5. There is no Fe bound to fraction 4 and 5 because the coral reef has been totally leached of Fe in fraction 3. It suggests there is no Fe effect contributed from natural sources associated with coral reefs. The geochemical fraction of silica and alumina was found in the natural sources. The chemical reactions of Fe in the reducible fraction in the coral reefs may be described as follows:

1. Coral-MnO$_2$-Fe$_{(s)}$ + 2 NH$_2$OH.HCl$_{(aq)}$ → Mn$^{2+}$(aq) + Cl$_2$(g) + Pb$^{2+}$(aq) + H$_2$O(l) + 2NH$_3$(g)

2. Coral-Fe$_2$O$_3$-Fe$_{(s)}$ + 2NH$_2$OH.HCl$_{(aq)}$ → 2Fe$^{2+}$(aq) + Cl$_2$(g) + Pb$^{2+}$(aq) + H$_2$O(l) + 2NH$_3$(g)

3. Coral-Fe(OH)$_3$-crystal-Fe$_{(s)}$ + 2NH$_2$OH.HCl$_{(aq)}$ → 2Fe$^{2+}$(aq) + Cl$_2$(g) + Pb$^{2+}$(aq) + H$_2$O(l) + 2NH$_3$(g)
Diversing and fluctuating Fe concentrations in coral reefs can be caused by a variety of factors, including varied sampling locations. The coral reefs where near the coast are more exposed to anthropogenic activities compared to those that are far from the coast or human activities. Furthermore, this can be due to the various periods of Fe accumulation in coral reefs. Consequently, if the coral reefs used for the analysis are in a highly contaminated area, the reefs will grow earlier and receive Fe exposure than coral reefs. The subsequently high Fe content in the coral reef was recorded at 1, 4, 3, 6, 2 and 5 locations respectively.

Table 1. The CF\(^a\), PLI\(^b\), and Igeo\(^c\) indexes of Fe.

| Location | CF | PLI | Igeo |
|----------|----|-----|------|
| 1        | 8.95 | 127.10 | 2.58 |
| 2        | 2.75 | 39.12  | 0.88 |
| 3        | 3.84 | 54.64  | 1.36 |
| 4        | 5.50 | 78.10  | 1.87 |
| 5        | 1.58 | 22.46  | 0.07 |
| 6        | 3.35 | 47.62  | 1.16 |

\(^a\)Non pollutant (CF<1), pollutant (CF>1)  
\(^b\)uncontaminated (0<PLI≤1), uncontaminated to moderately contaminated (1<PLI≤2), moderately contaminated (2<PLI≤3), moderately to highly contaminated (3<PLI≤4), highly contaminated (4<PLI≤5), or very highly contaminated (PLI>5).  
\(^c\)uncontaminated (Igeo≤0), uncontaminated to moderately contaminated (0<Igeo≤1), moderately contaminated (1<Igeo≤2), moderately to heavily contaminated (2<Igeo≤3), heavily contaminated (3<Igeo≤4), heavily to extremely contaminated (4<Igeo≤5), or extremely contaminated (Igeo>5)

CF calculation for Fe refers to the Earth’s Crust database[9]. CF calculation results of Fe in the coral reef obtained from all sampling locations have a value greater than 1 which indicates that the entire sampling location is in “contaminated Fe” status. In addition, the CF value at each location was proportional to the PLI and Igeo values. Pollution area was indicated by CF status > 1 and PLI was categorized with highly contaminated area status. While the status at Igeo varies, locations 2 and 5 are categorized into the uncontaminated status until moderate contamination, locations 3, 4 and 6 are in moderate contamination area and location 1 is in moderate status until contaminated categorized.

The new findings of these researches indicate that the contaminated of Fe in the coral reefs in Prigi Coast is caused by human activities or anthropogenic factors that occur around its waters. The future research is needed to use Pb Isotope linked by Fe to search the originated anthropogenic input. In addition, the Prigi coast waters where close to the residence area, a national port and is highly visited by tourists were suspected as a source of anthropogenic activities to distribute of Fe in the Prigi coast water.

4. Conclusion

The Fe was bound from fraction 1 to fraction 3 in the Prigi coral reef leached by the Tessier-microwave method. Only Fe in the fraction 3 was dominantly detected by AAS suggesting Fe was associated in the reduction fraction in the coral reef. The indexes PLI and CF calculation at the fraction 3 showed that the Prigi Coast waters were in contaminated status. Almost in the sampled location, the contaminated coral reefs by Fe indicated from anthropogenic inputs. The future research is needed to search for detailed anthropogenic input to seek the contaminated Fe using Pb isotopes associated with Fe in the coral reefs.
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