Distribution and Assessment of Fe and Mn in the Coastal Sediments of Sendang Biru, East Java, Indonesia

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Abstract. The high presence of heavy metals in sediment can affect the ecological and biological systems in East Java Indonesia. To monitor the environmental status of Fe and Mn, we investigated geochemical fraction and distribution of these metals at 8 sites in the sediment of Sendang Biru. BCR and Tessier sequential leaching methods were applied to leach Fe and Mn, respectively, due to high precision and accuracy of these methods. The pattern of geochemical fractions in sediment samples showed the maximum leached levels of Fe and Mn (>50%) in residual fractions in Sendang Biru Beach, indicating the natural effects surrounding sites. The portions of Fe and Mn in non-residual fractions located at Sendang Biru Port were higher compared with the site in the adjacent sea, indicating these metals were derived possibly from anthropogenic effects. The assessment from CF and Igeo calculations of Fe and Mn in sediment samples showed that the sediment near the Sendang Biru Port was moderately contaminated by Fe and Mn.

Keywords: Sediment, fraction, BCR, Tessier, leaching, Sendang Biru Beach

1. Introduction

The port in Sendang Biru Beach is one of the famous and big ports in East Java, Indonesia. The anthropogenic and natural activities can contribute heavy metal in seawater surrounding Sendang Biru Port. Sediment and coral can be used as media which reflect heavy metal contents including Fe and Mn in seawater [1]. To understand the Fe and Mn mobilities in each of fraction in sediment associated with the healthy environment, we used sequential leaching method to evaluate concentration and assessment of these elements. The dominant presence of Fe and Mn in Sendang Biru sediment suspected influences ecological and biological systems in the aquatic environment. To understand metals mobility which can influence environmental systems in Sendang Biru Beach, we used sequential leaching method for Fe and Mn contents in sediment. These metals have the main pathways residing in their fractions through chemical and physical processes [2–4]. The adsorption, complexation, and precipitation of Fe and Mn
in sediment are the main processes of these elements cooperated with iron and manganese hydroxides, particulate organic matter and clay minerals due to their strong affinities.

Commonly, sequential leaching of Fe and Mn from different sediment fractions were investigated using Tessier and BCR (Bureau Community of Reference) methods [5,6]. Some researchers recorded Fe in the fraction of sediment and applied Tessier method releasing with the range 80-100% recovery [7,8] and 0.74-4.40 %RSD [9,10]. BCR method of leached Mn releasing with the range 95-104 %recovery and 0.80-1.61 %RSD [5,6,11].

Now, the coastal area of Sendang Biru is prepared to improve towards international fishing and others marine products [12]. It is very important to monitor heavy metals such as Fe and Mn in seawater by sediment fraction. Here we applied these methods for determining Fe and Mn concentrations in the geochemical fractions of sediment of Sendang Biru Beach. The major objective of this study was to elevate the distribution and assessment of Fe and Mn in sediment surrounding Sendang Biru Beach.

2. Experimental Methods

The samples were collected on 12th of November 2016. The sediment samples were taken surrounding Sendang Biru Port with the geographical location between latitude -8°25'57.9" S and longitude 112°41'02.5" E (Figure 1). The sediments were taken from the surface of Sendang Biru Port with sediment grab. After the sediment grab was carefully opened, the sediment was transferred into the plastic bag. The samples were then leached using BCR method to leach Fe and Tessier method to leach Mn (Table 1).

![Figure 1. Sampling Site](image-url)
Table 1. The procedure of sequential leaching of BCR and Tessier methods

| Fe-BCR                          | Metal Mobility          | Mn-Tessier                        | Metal mobility          |
|---------------------------------|-------------------------|-----------------------------------|-------------------------|
| 20 mL of CH₃COOH 0.11 M solution, room temperature, shake in 16 hours | Acid Soluble (F1)        | 4 mL of MgCl₂ 1 M solution, pH = 7, room temperature, shake in 1 hour | Exchangeable (F1)       |
| 20 mL of NH₂OH.HCl 0.5 M solution, pH 2, room temperature, shake in 16 hours | Reducible (F2)           | 4 mL of CH₃COONa 1 M, pH = 5 with CH₃COOH, room temperature, shake in 5 hours | Associated to carbonate (F2) |
| 5 mL of H₂O₂ 8.8 M solution, pH 2, room temperature, shake in 1 hour, repeat in 85 °C, shake in 1 hour | Oxidizable (F3)          | 10 mL of NH₂OH.HCl 0.04 M solution in 25% CH₃COOH solution, 96 °C, shake in 6 hours | Reducible (F3) |
| 25 mL of CH₃COONH₄ 1M, pH 2, room temperature, shake in 16 hours | Residual (F4)            | 1.5 mL of HNO₃ 0.02 M solution and 2.5 mL of 30% H₂O₂ solution, pH = 2, 85 °C, shake in 2 hours, add 1.5 mL of 30% H₂O₂ solution, 85 °C, shake in 3 hours | Oxidizable (F4) |
| 1 mL of 65% HNO₃ solution and 3 mL of 36% HCl solution, room temperature, shake in 2 hours, add 3 drops of HF solution | Residual (F4)            | 2.5 mL of CH₃COONH₄ 3.2 M solution in 20% HNO₃ solution, room temperature, and shake in a half hour | Residual (F5) |
|                                |                         |                                   |                         |

3. Results and Discussion

3.1. Distribution of Fe and Mn contents in sediment

Fe and Mn concentrations, for the Sendang Biru samples, are reported in Table 2. The content of Fe was divided into four fractions (F1, F2, F3, and F4) followed by BCR method. The explanation of F1, F2, F3, and F4 is listed in Table 1. The range of Fe contents in F1, F2, F3, and F4 were 369-5621; 461-5853; 994-10019; and 5480-25965 mg/Kg and total fraction of Fe contents varied from 7304 to 42884 mg/Kg. The distribution of Fe contents in sediment has the same pattern values from F1 to F3.
lowest concentrations of Fe were detected at site 5 and the highest values at site 1. This result indicated Fe content was contributed by anthropogenic activities in Sendang Biru Port and then continued by the process of Fe dilution in the open sea.

The chemical reactions in the F1, F2, and F3 can be explained as follows [2]:

F1: Sediment–Fe\(^{3+}\)(s) + CH\(_3\)COOH(aq)  \Rightarrow \text{Sediment}–(H)\(_3\)(s) + (CH\(_3\)COO\(_3\))Fe(aq)  \\
Sediment–Fe\(_2\)(CO\(_3\))\(_3\)(s) + CH\(_3\)COOH(aq)  \Rightarrow \text{Sediment}–(s) + (CH\(_3\)COO\(_3\))Fe(aq) + H\(_2\)CO\(_3\)(aq)  \\
Sediment–Fe\(^{2+}\)(s) + CH\(_3\)COOH(aq)  \Rightarrow \text{Sediment}–(H)\(_3\)(s) + (CH\(_3\)COO\(_3\))Fe(aq)  \\
Sediment–Fe\(_2\)(CO\(_3\))\(_3\)(s) + CH\(_3\)COOH(aq)  \Rightarrow \text{Sediment}–(s) + (CH\(_3\)COO\(_3\))Fe(aq) + H\(_2\)CO\(_3\)(aq)

F2: Sediment–Mn\(_2\)O\(_2\)–Fe(s) + NH\(_2\)OH.HCl(aq)  \rightarrow \text{Sediment}–(s) + MnCl\(_2\)(aq) + FeCl\(_2\)(aq) + NH\(_3\)(g) + H\(_2\)O(l) + O\(_2\)(g)  \\
Sediment–Mn\(_2\)O\(_2\)–Fe(s) + NH\(_2\)OH.HCl(aq)  \rightarrow \text{Sediment}–(s) + MnCl\(_2\)(aq) + FeCl\(_2\)(aq) + NH\(_3\)(g) + H\(_2\)O(l) + O\(_2\)(g)

F3: Sediment–HA–Fe(s) + H\(_2\)O\(_2\)(aq) + CH\(_3\)COONH\(_4\)(aq) → Sediment–HA(s) + (CH\(_3\)COO\(_3\))Fe(aq) + NH\(_3\)(g) + H\(_2\)O(l) + O\(_2\)(g)  \\
Sediment–HA–Fe(s) + H\(_2\)O\(_2\)(aq) + CH\(_3\)COONH\(_4\)(aq) → Sediment–HA(s) + (CH\(_3\)COO\(_3\))Fe(aq) + NH\(_3\)(g) + H\(_2\)O(l) + O\(_2\)(g)

The concentration of Fe in F4 ranged from 5480-25965 mg/Kg (Table 2). The highest portion of Fe in F4 compared those in F1-F3 suggested the effect of lithogenic and terrestrial associated with natural source. Fe in F4 refers to the content of Fe in residual fraction. Possible of chemical reaction is followed [2]:

F4: Sediment–SiO\(_2\)–Al\(_2\)O\(_3\)–Fe(s) + HNO\(_3\)(aq) + HF(aq)  \rightarrow \text{Fe(NO}_3\text{)}_3(aq) + Al(NO\(_3\))_3(aq) + SiFe\(_2\)(g) + H\(_2\)O(l) + H\(_2\)O(g)  \\
Sediment–SiO\(_2\)–Al\(_2\)O\(_3\)–Fe(s) + HNO\(_3\)(aq) + HF(aq)  \rightarrow \text{Fe(NO}_3\text{)}_3(aq) + Al(NO\(_3\))_3(aq) + SiFe\(_2\)(g) + H\(_2\)O(l) + H\(_2\)O(g)

The contents of Mn in each fraction from site 1 to site 8 are listed in Table 2. The leached and determined of Mn concentrations followed the method by Tessier which divided as five fractions (F1, F2, F3, F4, and F5) (Table 1). The possibilities of chemical reaction are explained as followed [2]:

F1: Sediment–Mn\(^{2+}\)(s) + MgCl\(_2\)(aq) \Rightarrow \text{Sediment–Mg}^{2+}(s) + 2\text{MnCl}\(_2\)(aq)  \\
F2: Sediment–2MnCO\(_3\)(s) + 4\text{CH}_3\text{COONa}(aq)  \rightarrow 2\text{Na}_2\text{CO}_3(aq) + 2\text{Mn(CH}_3\text{COO)}_2(aq)  \\
F3: Sediment–Fe\(_2\)(OH\(_3\))–Mn(s) + 2NH\(_2\)OH.HCl(aq)  \rightarrow 2\text{Fe}^{2+}(aq) + \text{Cl}_2(g) + \text{Mn}^{2+}(aq) + 2\text{H}_2\text{O(l)} + 2\text{NH}_3(g)  \\
F4: Sediment–HA–Mn(s) + H\(_2\)O\(_2\)(aq) + CH\(_3\)COONH\(_4\)(aq) → Sediment–HA(s) + NH\(_3\)(g) + H\(_2\)O(l) + O\(_2\)(g) + (CH\(_3\)COO\(_3\))2Mn\(_2\)(aq)  \\
F5: Sediment–SiO\(_2\)–Al\(_2\)O\(_3\)–Fe(s) + HNO\(_3\)(aq) + HF(aq) → Fe(NO\(_3\))\(_3\)(aq) + Al(NO\(_3\))\(_3\)(aq) + SiFe\(_2\)(g) + H\(_2\)O(l) + H\(_2\)O(g)

The patterns of Mn contents in F1 and F2 were the same at site 1 and site 4 and the patterns in F3-F5 were different at site 2, 4, 5, 6, and 7 (Table 2; Figure 2). The portion of Mn contents in F1 and F2 tended to be stable due to the balance of cation and anion (carbonate) exchange from the open sea. The proportion of Mn contents ranged from 7.96-16.0 mg/Kg in F1 and 7.26-22.0 mg/Kg in F2 (Table 2).
Table 2. Distribution of Fe and Mn contents in sediment’s fraction of Sendang Biru Beach

| Sampling Site | Fe content (mg/Kg) | Mn content (mg/Kg) |
|---------------|-------------------|-------------------|
|               | F1    | F2    | F3    | F4    | Total | F1    | F2    | F3    | F4    | F5    | Total |
| 1             | 5621  | 5853  | 10019 | 17803 | 39297 | 16.0  | 22.0  | 25.2  | 8.80  | 52.4  | 124   |
| 2             | 5110  | 5406  | 9102  | 15581 | 35200 | 8.53  | 7.94  | 13.7  | 5.97  | 52.0  | 88.1  |
| 3             | 3806  | 4049  | 7108  | 12921 | 27884 | 12.5  | 13.5  | 31.0  | 18.6  | 53.0  | 129   |
| 4             | 4541  | 4592  | 8156  | 25595 | 42884 | 13.4  | 21.9  | 23.4  | 8.24  | 44.4  | 111   |
| 5             | 369   | 461   | 994   | 5480  | 7304  | 10.9  | 10.6  | 38.5  | 15.1  | 201   | 276   |
| 6             | 1149  | 1657  | 2613  | 7711  | 13129 | 11.1  | 12.6  | 20.1  | 7.96  | 57.6  | 109   |
| 7             | 2337  | 2382  | 4179  | 11338 | 20236 | 9.15  | 15.2  | 10.1  | 5.70  | 41.6  | 81.8  |
| 8             | 2969  | 3207  | 5628  | 25965 | 37769 | 7.96  | 7.26  | 14.0  | 9.79  | 77.6  | 117   |

The range of total Fe concentrations (7304-42884 mg/Kg) in the coastal area of Sendang Biru exceeded the chronic criterion for protection of aquatic organism for Fe (~1000 mg/kg) in natural marine sediment, USA [13]. Conversely, most sediment samples had a range of Mn concentrations (818-276 mg/Kg) that were below the 452 mg/Kg for standard marine sediment ocean [14].

Figure 2. The portion of Fe and Mn Contents in Sediment’s Fraction of Sendang Biru Beach

As shown in Figure 2, the pattern of geochemical fractions in sediment samples showed the maxima leached levels of Fe and Mn in the residual fraction from site 1 to site 8. The Fe and Mn contents in sediment possibly were contaminated by natural sources such as soil, agricultural, minerals surrounding Sendang Biru Beach bounded in silica and alumina. The portions of Fe and Mn in non-residual fractions were higher in Sendang Biru Port compared with the site in the adjacent sea indicating these metals possibly from anthropogenic effects.

3.2. Assessment of Fe and Mn in Sediment

To understand the level of contamination of Fe and Mn contents in sediment associated with water pollution, we performed an assessment using the calculation index of status pollution in sediments such as contamination factor (CF) and geoaccumulation index (Igeo) [3,15]. CF was calculated using $C_{\text{metal}}/C_{\text{background}}$. In this study, the content of Fe and Mn at site 7 (the lowest concentration) was considered as background.
The classification of CF is explained as follows: CF<1: low contamination factor, 1 ≤ CF < 3: moderate contamination factor; 3 ≤ CF < 6: considerable contamination factor; CF ≥ 6: very high contamination factor. As listed in Table 3, the value of CF from site 5 to site 7 in the calculation of Fe were recorded from 0.36 to 1.00. This indicates that Fe contents at site 5-7 reflected low risk, whereas the values of Fe contents in sediment from site 1 to site 1 were moderate risk. In the case of CF in Mn sediment, site 1 to site 8 was categorized as moderate contamination.

The second assessment of Fe and Mn contents using the geo-accumulation index (I$_{geo}$). I$_{geo}$ can be calculated using $I_{geo} = \log_2 \left( \frac{C_n}{1.5 \cdot B_n} \right)$, whereas $C_n$ is the concentration of Fe or Mn. The value of 1.5 is the factor of lithogenic effect and $B_n$ is the background as explained C background in CF index. I$_{geo}$ value is classified as follows: $I_{geo} \leq 0$, class 0, unpolluted; $0 < I_{geo} \leq 1$, class 1, from unpolluted to moderately polluted; and $1 < I_{geo} \leq 2$, class 2, moderately polluted. As listed in Table 3, the $I_{geo}$ of Fe and Mn contents ranged from -2.06 to 1.17 indicating the status of quality in sediment categorized from class 0 to class 2. These values reflect the status of sediment in the range from unpolluted to moderately pollution.

| Sampling site | CF Fe | Mn | Fe | Mn |
|---------------|-------|----|----|----|
| 1             | 1.94  | 1.52 | 0.18 | 0.02 |
| 2             | 1.74  | 1.08 | 0.16 | -0.32 |
| 3             | 1.38  | 1.57 | -0.13 | 0.07 |
| 4             | 2.12  | 1.36 | 0.28 | -0.10 |
| 5             | 0.36  | 3.37 | -2.06 | 1.17 |
| 6             | 0.65  | 1.13 | -1.21 | -0.17 |
| 7             | 1.00  | 1.00 | -1.69 | -0.18 |
| 8             | 1.87  | 1.42 | 0.51 | -0.06 |

4. Conclusion
In this Sendang Biru area, the majority of geochemical fractions of Fe and Mn contents in sediment were found within the high portions of Fe and Mn in residual fractions. This can be attributed substantially to the natural sources such as weathering or leaching of the rocks containing Fe and Mn minerals in the sediment. The distribution of Fe and Mn contents in non-fraction of sediment surrounding Sendang Biru Port showed highly compared with those in adjacent of the sea possibly associated with the dilution process of that metals through the sea current. The assessment of Fe and Mn contents in Sendang Biru sediment using CF and $I_{geo}$ revealed moderately health risk.

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