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BCR Sequential Leaching for Geochemical Fractions and Assessment of Fe, Ni, and Mn in the Coastal Sediments Sendang Biru Port, East Java, Indonesia

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BCR Sequential Leaching for Geochemical Fractions and Assessment of Fe, Ni, and Mn in the Coastal Sediments Sendang Biru Port, East Java, Indonesia

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Abstract. The changes in the aquatic environment by either natural or anthropogenic sources may affect the presence of heavy metals in the sediment of Sendang Biru Port. Heavy metals such as Fe, Ni, and Mn possibly give a negative impact on ecological and biological systems in the sea water. To monitor the status of sediment of the Port Sendang Biru, we investigated the geochemical fraction of Fe, Ni, and Mn in sediment using the BCR (European Community Bureau of Reference) sequential leaching method. The precision test of BCR method showed that Fe, Ni, and Mn has 4.82; 3.73; and 3.16 Relative Standard Deviation (RSD), respectively. The accuracy test of BCR method showed that percentage recovery for Fe, Ni, and Mn were 85.5%; 96.2%; and 63.0%, respectively. The fractionation of Fe, Ni, and Mn in the sediment of Sendang Biru Port showed that Fe was dominant in residual fraction (90.7%), whereas Ni and Mn were dominant in non-residual fraction (78.8% Ni and 77.2% Mn). The dominance of Fe in the residual fraction indicated that Fe was from natural sediment minerals bound to silicate and aluminate, whereas the dominance of Ni and Mn in non-residual fractions was possibly derived from anthropogenic effects. Assessment from index calculation of sediment had the category contaminated at moderate levels by Ni and contaminated at low levels by Fe and Mn.

Keywords: Sediment, metal fractionation, BCR, sequential leaching

1. Introduction

Sendang Biru Port is one of the major ports in East Java. This Port has about 3000 fishermen in Sendang Biru with fish catch reached 11500 tons per year. Some human's activities (anthropogenic) that occurred surrounding Sendang Biru Port are possibly contributed by fishing boat activities, waste disposal from the fish market and domestic waste disposal causing the heavy metal contamination in sediment.

Sediment is the final site of an accumulated heavy metal compound in the aquatic environments [1]. Heavy metals (Fe, Ni, and Mn) in dominant sediment may have a toxic effect on the human being.

Some researchers used the method of partial leaching to assess Fe, Ni, and Mn in sediment and coral [1–4]. This method is only for the first assessment of that metals and cannot explain their concentrations in their sediment fraction. The fraction of metal binding in sediment is very important to understand metals mobility which can affect ecological and biological systems in the aquatic environment surrounding the Port. To understand the geochemical fractions, we used sequential leaching for Fe, Ni, and Mn in sediment to know each of fraction mobility which can influence environmental systems.

One of sequential leaching methods that is commonly used is the BCR (European Community Bureau of Reference) method. The BCR method fractionates metals into four fractions comprising exchangeable and easily soluble fraction (F1), easily reducible fraction (F2), oxidizable fraction (F3) and residual fraction (F4). F1, F2, and F3 easily indicate heavy metal mobility in the sediment or non-residual fractions, whereas F4 represents a difficult fraction mobilized [5]. Here, we report and assess using BCR method to leach Fe, Ni, and Mn in port sediment fractions.

2. Experimental Methods

2.1. Sample Collection and Pretreatment for Analysis

Figure 1 shows the collected samples of sediment in the center of Sendang Biru Port. The samples were collected on November 12, 2016 using a stainless-steel grab, put in the plastic bag, and then transferred to the Analytical Chemistry Laboratory.

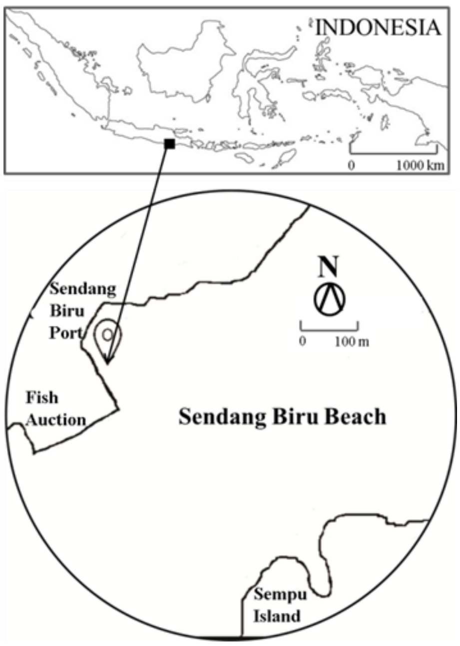

Figure 1. Sampling location of sediment Sendang Biru Port.

The sediment samples are fine grains and composed of mud and silt. The samples were separated from rock, bone, corals, and wood. The sediment samples were homogenized and then dried in an oven at 60 °C [3]. The qualitative metal composition of representative sediment samples was determined using X-ray Fluorescence. The samples were powdered by hand using an agate mortar and pestle. The instrument used was a PANalytical, Minipal 4. The chemical substances in sediment are listed in Table 1.

Table 1. Chemical substances in sediment

Metal	Concentration (%)
Al	6+/-0.6
Si	5.8+/-0.3
K	0.3+/-0.2
S	0.2+/-0.6
Ca	57.9+/-0.003
Ti	1.1+/-0.6
V	0.05+/-0.009
Cr	0.079+/-0.004
Mn	0.17+/-0.004
Fe	18.8+/-0.2
Ni	0.21+/-0.004
Cu	0.15+/-0.005
Zn	0.02+/-0.005
Br	0.21+/-0.01
Sr	4.60+/-0.12
Zr	0.2+/-0.2
Mo	3.28+/-0.94
In	0.8+/-1.0
Ba	0.1+/-0.03
Yb	0.08+/-0.007
Re	0.38+/-0.04

2.2. The Sequential Leaching Experiment

The sample sediments from Sendang Biru Port and reference sediment of Geochemical Survey of Japan (JSD-1) were analyzed for Fe, Ni, and Mn contents in fraction sediment using BCR method. The determination of metal concentration in the reference sediment was used to control the quality of data through precision and accuracy tests, while the determination of metal concentration in Sendang Biru Port's sediment was aimed to find out the concentration of its geochemical fraction and status of Fe, Ni, and Mn.

Analysis of Fe, Ni, and Mn in the sediment consisted of four stages: (1) exchangeable and easily soluble fractions. 0.5 grams of sediment samples were leached with 20 mL of acetic acid solution (0.11 M) for 16 hours; (2) the easily reducible fraction. The residue of the exchangeable and easily soluble fraction was leached with 20 mL of hydroxylamine hydrochloride solution (0.1 M; pH 2) for 16 hours; (3) the oxidizable fraction. The residue from the easily reducible fraction was leached using 5 mL of hot hydrogen peroxide (30%) to nearly dry twice, then leaching followed by 25 mL of ammonium acetate solution (1.0 M; pH 2) for 16 hours; (4) the residual fraction. The residue from the oxidized fraction was leached with 5 mL of concentrated nitric acid for 24 hours, then put in a sonic bath for 30 min and heated to 110 °C. After drying, the residue was added with 20 drops of concentrated nitric acid and 10 drops of fluoride acid, then heated until dry. Finally, the residue was dissolved and diluted with 2 mL of 1% HNO_3 five times [3,6]. The leached sample was then analyzed using an AAS (PerkinElmer A Analyst 700) to determine the concentration of Fe, Ni, and Mn of each fraction in sediment.

3. Results and Discussion

3.1. The BCR Method for Leaching Fe, Ni, and Mn in Sediment

The effectiveness of BCR method in leaching Fe, Ni, and Mn in sediment was tested. This test aimed to ensure that the method is able to produce the correct data which are in accordance with its designation. Testing parameters of the effectiveness of this method are the precision and accuracy.

The results of precision test of BCR method for leaching Fe, Ni, and Mn using RSD are listed in Table 2. The leached Fe, Ni, and Mn has relative standard deviation (RSD) of 4.82, 3.73, and 3.16, respectively. The test of BCR method indicated high precision for leaching Fe, Ni, and Mn which has RSD less than 5%. Therefore, it can be stated that the BCR is a precision method for leaching Fe, Ni, and Mn in Sendang Biru Port sediment.

The accuracy test of BCR method for leaching Fe, Ni, and Mn showed the percentage recovery for Fe (85.5%), Ni (96.2%), and Mn (63.0%) (Table 2). The range of percentage recovery for standard accuracy was 85-110%. This suggests that the applied BCR method is accurate for leaching Fe and Ni, but is less accurate for leaching manganese in sediments.

The low accuracy of Mn obtained using BCR method indicated that Mn was not able to be perfectly leached by this method. According to [7], the low Mn accuracy is due to the inability of the solvent used in the second fraction (F2) of the BCR method for leaching MnO. The low Mn accuracy can also be affected by disturbance of sedimentary matrices such as Cu, Ni, Ca, and Fe [8].

Table 2. The precision and accuracy tests of the BCR method

Metal	RSD	Percentage Recovery (%)
Fe	4.82	85.4
Ni	3.73	96.2
Mn	3.16	62.3

The precision and accuracy tests of BCR method (Table 2) showed that the BCR method is capable of leaching Fe and Ni precisely and accurately, but it is not effective for leaching Mn accurately. This suggests that the BCR method is feasible to be used for leaching Fe and Ni, but less feasible to be used for leaching Mn in Sendang Biru Port sediment.

3.2. Fractionations of Fe, Ni, and Mn Concentrations in Sediment

Metal fractionation in sediments reflects the mechanism of metal binding in sediments. The difference of metal binding in these sediments shows the difference of metal source. Generally, anthropogenic metals are presented in non-residual fractions, whereas metals derived from natural sedimentary materials are in residual fractions [9]. BCR method breaks metals binding in the sediment into four fractions, namely (1) exchangeable and easily soluble fraction (F1), (2) easily reducible fraction (F2), (3) oxidizable fraction (F3), and (4) residual fraction (F4). F1, F2, and F3 are referred to a non-residual fraction.

Three dominant metals are suspected to be anthropogenic contaminants surrounding the port (Table 1). The results of Fe, Ni, and Mn fractionation are illustrated in Figure 2. Based on the Figure, it is known that Fe is dominant in the residual fraction while Ni and Mn are dominant in the non-residual fraction.

As shown in Figure 2 and Table 3, the contents of Fe in ion exchangeable and soluble, easily reducible, and oxidizable fractions are 26.2(104) mg/Kg (1.51%), 25.0(104) mg/Kg (1.44%), and 110(104) mg/Kg (6.33%), respectively. The total contents of Fe in this three fractions indicated the Fe binding in the non-residual fraction in sediment. These fractions may be contributed from anthropogenic source surrounding Sendang Biru Port.

Table 3. Metal contents of Fe, Ni, and Mn in sediment fraction

Metal	Metal Contents (mg/kg)		
	Fe (104)	Ni	Mn
F1	26.2	23.6	69.8
F2	25.0	22.4	58.1
F3	110	22.9	58.6
F4	1572	18.5	55.3

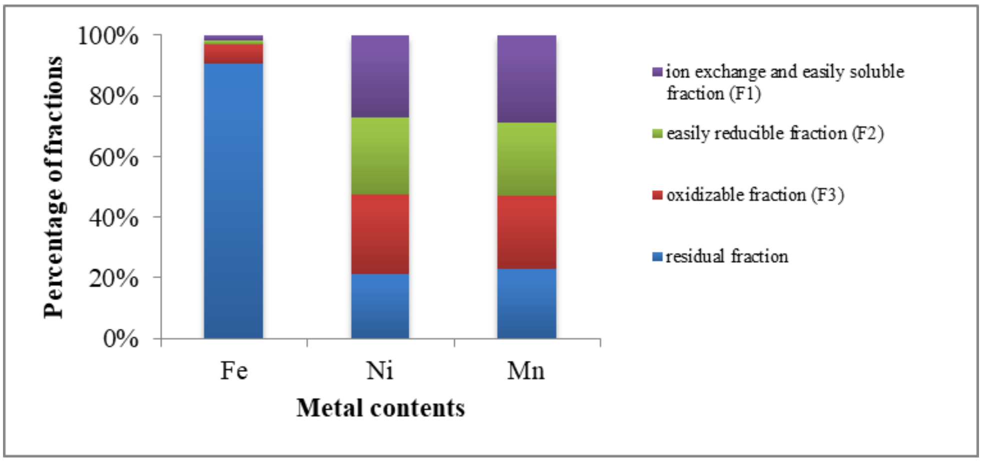

Figure 2. Geochemical fractions of Fe, Ni, and Mn in sediment

The concentration of Fe in residual fraction was 1572(104) mg/Kg (90.7%) (Table 3; Figure 2). The dominance of Fe in residual fractions suggests that Fe in the sediment of Sendang Biru Port is strongly binding with silicate and alumina in natural mineral sediments [10]. The high concentration of Fe in the residual fraction indicated that the sediment was relatively uncontaminated by Fe and it was not harmful to the ecological and biological systems in the waters. The possible chemical reaction in this fraction can be written as follow [3]:

$$\text{Sediment–}SiO_2\text{–}Al_2O_3\text{–Fe(III)}(s) + HNO_3(aq) + HF(aq) \rightarrow Fe(NO_3)_3(aq) + Al(NO_3)_3(aq) + SiF_4(g) + H_2O(l) + H_2(g)$$

$$\text{Sediment–}SiO_2\text{–}Al_2O_3\text{–Fe(II)}(s) + HNO_3(aq) + HF(aq) \rightarrow Fe(NO_3)_2(aq) + Al(NO_3)_3(aq) + SiF_4(g) + H_2O(l) + H_2(g)$$

Fractionation of Ni and Mn in the sediment of Sendang Biru Port shows that both metals are dominant in non-residual fractions (Figure 2). The concentrations of metals in non-residual fraction were 18.53 mg/kg (78.8%) and 186 mg/kg (77.2%), while in residual fraction were 18.5 mg/kg (21.2%) and 55.3 mg/kg (22.9%) (Table 3, Figure 2). These results indicated that Ni and Mn had a little bit similar percentages. The high concentrations of Ni and Mn in non-residual fractions suggested that Ni and Mn were contributed from anthropogenic process surrounding Sendang Biru Port. Ni and Mn in non-residual fractions may be released from sediment when there is a change in the aquatic environment so that it affects the ecological and biological systems in Sendang Biru Port.

The higher concentrations of Ni and Mn in exchangeable and easily soluble fraction were 23.6 and 69.8 mg/kg, respectively (Table 3). The high concentration of Ni and Mn at the most unstable fraction is due to the input of the resident's waste surrounding Sendang Biru Port. Metals in this fraction can impact on ecological and biological systems. These metals are very weakly associated with negative organic or inorganic binding site in the sediment. The presence of a decrease in pH in the aquatic environment can cause Ni and Mn in this fraction dissolved into the surface water so that it can cause the negative impact on the environment.

The high concentrations of Ni and Mn were also found in the oxidizable fraction (22.9 and 58.6 mg/kg) (Table 3). Ni and Mn in this fraction form a stable complex with humic acid (HA) derived from organic matter. The high concentrations of Ni and Mn in this fraction may be contributed from anthropogenic inputs around Sendang Biru Port such as the disposal of fish market waste or domestic waste. This study supports previous similar studies reported by Passos et al. 2010 [9] for suggesting input of human’s activity surrounding the site. Ni and Mn can be released into waters when the process degradation of organic matter occurs.

The concentrations of Ni and Mn were found in the easily reducible fraction (22.4 and 58.1 mg/kg) (Table 3). The presence of Ni in this fraction is bound to Fe-Mn oxide, whereas Mn in this fraction is derived from Mn bound to Fe and Mn oxides in its oxidant form [11]. Ni and Mn at a reduced fraction may be due to the activity of fishing vessels and discharges from industry [3]. Ni and Mn contained in this fraction can be released into the waters when the aquatic environment becomes anoxic [12].

The possible chemical reaction of Ni and Mn in non-residual fraction can be written as follows, (which Me = Ni or Mn) [3]:

1. Ion exchangeable and soluble fraction
   $\text{Sediment–Me}^{2+}(s) + CH_3COOH(aq) \rightleftarrows \text{Sediment–}(H)_2(s) + (CH_3COO)_2Me(aq)$
   $\text{Sediment–}MeCO_3(s) + CH_3COOH(aq) \rightleftarrows \text{Sediment}(s) + (CH_3COO)_2Me(aq) + H_2CO_3(aq)$

2. Easily reducible fraction
   $\text{Sediment–}MnO_2\text{–}Me(s) + NH_2OH.HCl(aq) \rightarrow \text{Sediment}(s) + MnCl_2(aq) + MeCl_2(aq) + NH_3(g) + H_2O(l) + O_2(g)$

3. Oxidizable fraction
   $\text{Sediment–HA–Me}(s) + H_2O_2(aq) + CH_3COONH_4(aq) \rightarrow \text{Sediment–HA}(s) + (CH_3COO)_3Fe(aq) + NH_3(g) + H_2O(l) + O_2(g)$

The lowest concentration of Ni and Mn were in residual fraction 18.5 mg/kg and 55.3 mg/kg, respectively (Table 3). This is probably related to the abundance of Ni and Mn in the earth's crust, including sediment in Sendang Biru Port. Metals in the residual fraction are strongly bound to natural minerals and resistant components of the solid matrix in sediment so that they are difficult to mobilize into pore-waters through dissociation. The possible chemical reaction in this fraction can be written as follow, (where Me = Ni or Mn) [3]:

$$\text{Sediment–}SiO_2\text{–}Al_2O_3\text{–}Me(s) + HNO_3(aq) + HF(aq) \rightarrow Me(NO_3)_2(aq) + Al(NO_3)_3(aq) + SiF_4(g) + H_2O(l) + H_2(g)$$

3.3. Assessment of Fe, Ni, and Mn in Sediment

Assessment of sediment status of Sendang Biru Port is used to know the level of contamination of Fe, Ni, and Mn in the sediment associated with water pollution. The determination of this status is based on the calculation of the contamination factor (CF), Geo-accumulation Index (Igeo), and Pollution Load Index (PLI) [2,13]. The calculations of CF, Igeo, and PLI values are respectively based on the mathematical equations expressed by some researchers. CF and Igeo are used to determine the level of contamination of each heavy metal (Fe, Ni, or Mn) in sediment, whereas PLI is used to determine the level of total heavy metal contamination (Fe, Ni, and Mn) in sediment [13–15].

Table 4. Assessment of Fe and Mn in Sediment

Sampling site	**CF**		I_{geo}	
	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

As listed in Table 4, CF calculations showed that the sediment of Sendang Biru Port has been contaminated by Fe, Ni, and Mn with a moderate category for Ni and low category for Fe and Mn. In case of Igeo calculation, the sediment was contaminated in the low to moderate category by Ni, whereas

Fe and Mn were contaminated in low category low (Table 4). Based on the calculation, the PLI value was 0.95 (Table 4). These results indicated that the sediment of Sendang Biru Port was low contaminated by Fe, Ni, and Mn. The low contaminated sediment can improve the quality of seawater and its productivity such as increasing fish, lobster, and shrimp (Chitosan) [16].

4. Conclusion

The BCR method was effective for leaching Fe and Ni but was less effective for leaching Mn in sediments. The BCR method was capable of leaching Fe and Ni precisely and accurately but was not effective for leaching Mn accurately. Fe dominant was in residual fraction, while Ni and Mn were dominant in a non-residual fraction. The dominance of Fe in the residual fraction indicated Fe was strongly binding with silicates and alumina in the natural minerals of the sediment. Ni and Mn were dominant in the non-residual fraction indicating that they were contributed from anthropogenic around the Sendang Biru Port. Assessment from the index calculation of sediment had a moderate category contaminated by Ni and a low category contaminated by Fe and Mn.

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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 I_{geo} 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).

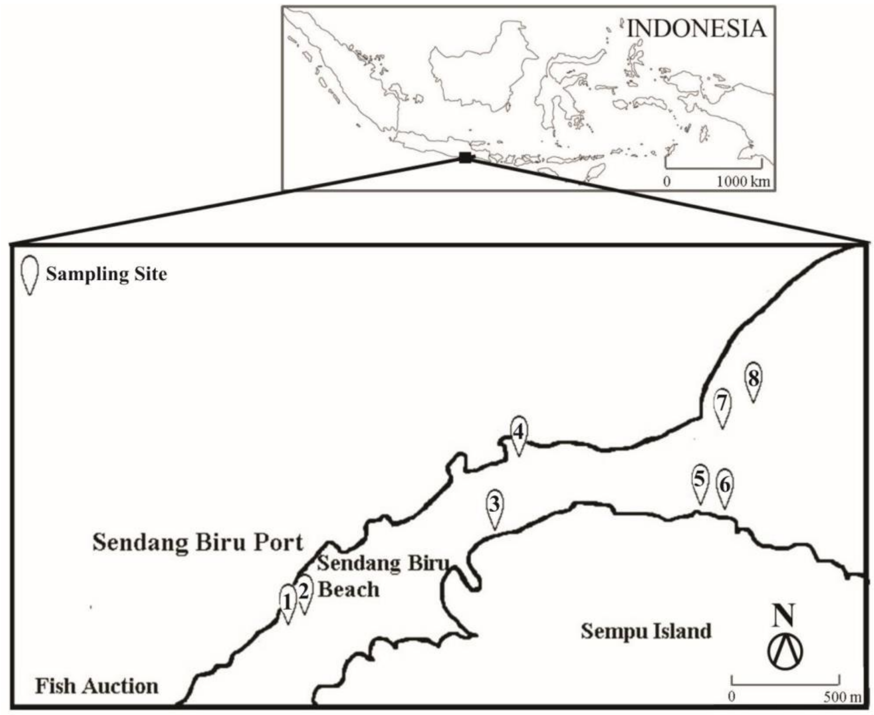

Figure 1. Sampling Site

Table 1. The procedure of sequential leaching of BCR and Tessier methods

Fe-BCR	**Metal Mobility**	**Mn-Tessier**	**Metal mobility**
20 mL of CH_3COOH 0.11 M solution, room temperature, shake in 16 hours	Acid Soluble (F1)	4mL of $MgCl_2$ 1 M solution, pH = 7, room temperature, shake in 1 hour	Exchangeable (F1)
20 mL of $NH_2OH.HCl$ 0.5 M solution, pH 2, room temperature, shake in 16 hours	Reducible (F2)	4 mL of CH_3COONa 1 M, pH = 5 with CH_3COOH, room temperature, shake in 5 hours	Associated to carbonate (F2)
5 mL of H_2O_2 8.8 M solution, pH 2, room temperature, shake in 1 hour, repeat in 85 °C, shake in 1 hour 5 mL of H_2O_2 8.8 M solution, pH 2, 85 °C, shake in 1 hour 25 mL of CH_3COONH_4 1M, pH 2, room temperature, shake in 16 hours	Oxidizable (F3)	10 mL of $NH_2OH.HCl$ 0.04 M solution in 25% CH_3COOH solution, 96 °C, shake in 6 hours	Reducible (F3)
1 mL of 65% HNO_3 solution and 3 mL of 36% HCl solution, room temperature, shake in 2 hours, add 3 drops of HF solution	Residual (F4)	1.5 mL of HNO_3 0.02 M solution and 2.5 mL of 30% H_2O_2 solution, pH = 2, 85 °C, shake in 2 hours, add 1.5 mL of 30% H_2O_2 solution, 85 °C, shake in 3 hours 2.5 mL of CH_3COONH_4 3.2 M solution in 20% HNO_3 solution, room temperature, and shake in a half hour	Oxidizable (F4)
		1 mL of 65% HNO_3 solution and 3 mL of 36% HCl solution, room temperature, shake in 2 hours and add 3 drops of HF solution	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. The 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_3COOH*(aq)* ⇄ Sediment–$(H)_3$*(s)* + $(CH_3COO)_3Fe$*(aq)*

Sediment–$Fe_2(CO_3)_3$*(s)* + CH_3COOH*(aq)* ⇄ Sediment*(s)* + $(CH_3COO)_3Fe$*(aq)* + H_2CO_3*(aq)*

Sediment–Fe^{2+}*(s)* + CH_3COOH*(aq)* ⇄ Sediment–$(H)_2$*(s)* + $(CH_3COO)_2Fe$*(aq)*

Sediment–$Fe_2(CO_3)_2$*(s)* + CH_3COOH*(aq)* ⇄ Sediment*(s)* + $(CH_3COO)_2Fe$*(aq)* + H_2CO_3*(aq)*

F2: Sediment–MnO_2–Fe*(s)* + $NH_2OH.HCl$*(aq)* → Sediment*(s)* + $MnCl_2$*(aq)* + $FeCl_3$*(aq)* + NH_3*(g)* + H_2O*(l)* + O_2*(g)*

Sediment–MnO_2–Fe*(s)* + $NH_2OH.HCl$*(aq)* → Sediment*(s)* + $MnCl_2$*(aq)* + $FeCl_2$*(aq)* + NH_3*(g)* + H_2O*(l)*+ O_2*(g)*

F3: Sediment–HA–Fe*(s)* + H_2O_2*(aq)* + CH_3COONH_4*(aq)*→ Sediment–HA*(s)* +$(CH_3COO)_3Fe$*(aq)* + NH_3*(g)* + H_2O*(l)*+ O_2*(g)*

Sediment–HA–Fe*(s)* + H_2O_2*(aq)* + CH_3COONH_4*(aq)*→ Sediment–HA*(s)* +$(CH_3COO)_2Fe$*(aq)* + NH_3*(g)* + H_2O*(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_2O_3–Fe*(s)* + HNO_3*(aq)* + HF*(aq)* →$Fe(NO_3)_3$*(aq)* + $Al(NO_3)_3$*(aq)* + SiF_4*(g)* + H_2O*(l)* + H_2*(g)*

Sediment–SiO_2–Al_2O_3–Fe*(s)* + HNO_3*(aq)* + HF*(aq)* →$Fe(NO_3)_2$*(aq)* + $Al(NO_3)_3$*(aq)* + SiF_4*(g)* + H_2O*(l)* + H_2*(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*) ⇄ Sediment-Mg^{2+}(*s*) + $2MnCl_2$(*aq*)

F2: Sediment-$2MnCO_3$(*s*) + $4CH_3COONa$(*aq*) ⇄ $2Na_2CO_3$(*aq*) + $2Mn(CH_3COO)_2$(*aq*)

F3: Sediment-Fe_2O_3-Mn(*s*) + $2NH_2OH.HCl$(*aq*) → $2Fe^{2+}$(*aq*) + Cl_2(*g*) + Mn^{2+}(*aq*) + $2H_2O$(*l*) + $2NH_3$(*g*)

Sediment-$Fe(OH)_3$-Mn(s) + $2NH_2OH.HCl$(*aq*) → 2 Fe^{2+}(*aq*) + Cl_2(*g*) + Mn^{2+}(*aq*) + H_2O(*l*) + 2 NH_3(*g*)

F4: Sediment–HA–Mn*(s)* + H_2O_2*(aq)* + CH_3COONH_4*(aq)*→ Sediment–HA*(s)* + NH_3(g) +H_2O(l) + O_2(g) + $(CH_3COO)_2Mn$*(aq)* +

F5: Sediment–SiO_2–Al_2O_3–Fe*(s)* + HNO_3*(aq)* + HF*(aq)* → $Fe(NO_3)_2$*(aq)* + $Al(NO_3)_3$*(aq)* + SiF_4*(g)* + H_2O*(l)* + H_2*(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].

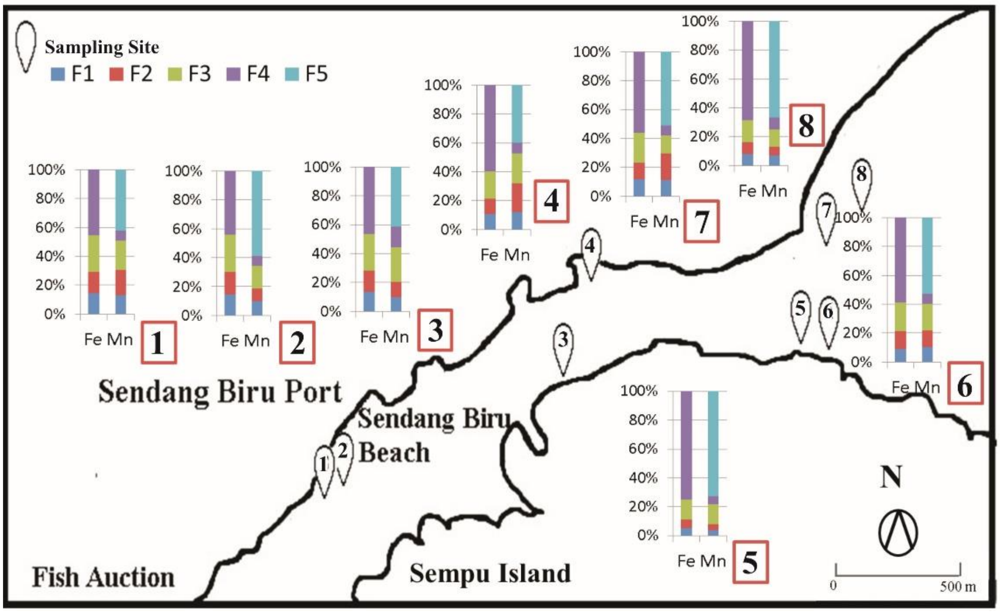

Figure 2. The portion of Fe and Mn Contents in Sediment's Fraction of Sendang Biru Beach

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 $C_{metal}/C_{background}$. 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, $1 \leq CF < 3$: moderate contamination factor; $3 \leq CF < 6$: considerable contamination factor; $CF \geq 6$: 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 $I_{geo}= \log_2 (C_n/1.5\ B_n)$, 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.

Table 3. Assessment of Fe and Mn in Sediment

Sampling site	CF		I_{geo}	
	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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