Assessment of sediment quality in the waters around of Ternate city, North of Maluku, Indonesia based on an index analysis approach

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Abstract

The purpose of this study was to determine the levels of heavy metals in sediments and to assesses the sediment quality based on an index analysis approach. Sediment samples were collected from five different stations located along the coast around Ternate City waters. Heavy metal content was measured using Atomic Absorption Spectrophotometer (AAS). The results showed that mercury levels ranged from: 0.592-3.571 mg/kg, Lead: 10.4-12.4 mg/kg, Cadmium: 0.095-0.298 mg/kg and Copper: 0.713-40.494. The average levels of Pb, Cd and Cu are still lower than the sediment quality threshold values, exception Hg. The results of the index analysis showed that the average value of enrichment factors of Hg, Pb, Cd, Cu are 786.162, 104.511, 118.195 and 30.810 (no enrichment to very high enrichment), contamination factors are 4.363, 0.568, 0.653 and 0.208 (no contamination to slight), geo-accumulation index are 1.291, -1.404, -1.288 and -4.586 (unpolluted to moderate polluted) respectively. Based on the pollution load index value (PLI <1), sediments in these waters are categorized as not yet polluted by Hg, Pb, Cd and Cu.

Keywords: quality sediment assessment, index analysis approach, Ternate

1. Introduction

Ternate is the one of the biggest city in the North Maluku, Indonesia. As a result of rapid expansion of industrial activity and population increase in Ternate city and in the surrounding area, the coastal waters around of Ternate city is heavily impacted by human activities where the waters act as a disposal area for sewage, industrial and agricultural wastewaters originating from the city of Ternate and its surroundings. These wastes are mostly unprocessed and directly discharged to and mixed with the receiving waters via riverine pathways into the waters. Subsequently, toxic materials have been accumulating in Ternate waters sediments.

One of that contaminant is heavy metal. Heavy metals are considered as an important contaminant of the environment if they are present in concentrations that are more than their natural concentration [1]. Heavy metals are a natural component of rocks. As a result of rocks weathering they are transferred to soil and bottom sediments, where they are supplemented with metals originating from anthropogenic activity such as urbanization, industrialization, transportation, and energy production [2,3]. Heavy metals due to their toxicity, persistence and potential to bio-accumulate present a serious problem of environmental pollution [4,5]. Heavy metals in marine sediments mainly come from nature (input from rivers) and anthropogenic sources (coastal human settlements) and if they enter to sea waters, their distribution is strongly influenced by physical-chemical factors and are considered as contaminants if the levels exceed the safe threshold values for environmental protection [6].

The purpose of this study was to assess the quality of sediments in the waters around Ternate City using the index analysis approach and explore the degree of contamination and pollution impacts by using the pollution indicator such as enrichment factor (EF), contamination factor (CF), pollution load index (PLI), geo-accumulation index (I-geo).
2. Materials and Methods

2.1. Sampling area

The sediment samples were collected from five sampling stations along the coastal of Ternate City waters during May 2013. Five samples were collected (Fig. 1). Station 1 is in front of the Bastion Port, Station 2 is in the Fishing Port, Station 3 is in the Ahmad Yani Port, Station 4 is in front of the Vegetable Market (traditional market), and Station 5 is the back of Shopping Center (Hypermart).

![Figure 1. Research Location in Ternate](image)

2.2. Sample collection

Grab sediment sampler was used to collect surface coastal sediment at 10 cm depth. The sediment samples were then kept in a cleaned polyvinyl plastic container to avoid any contamination and transported to the laboratory for further treatment and analysis.

2.3. Sample treatment

All samples were air dried for fourteen days and were then oven dried at 100°C for 24 hours before being grounded into fine particles using pestle and mortar and were sieved for 2 mm mesh. For Pb, Cd, Cu and Zn analysis, sediment samples were put into a Teflon dish and dried in an oven at 105°C for 24 hours. After drying, shake several times with distilled water. Sediment samples were dried again at 100°C for 24 hours, then being grounded into fine particles using pestle and mortar. A mixture of 5 ml of 65% HNO3, 15 ml of 37% HCl and 2 ml of 35% H2O2 were used to digest 0.5 g of the fine samples. For Hg, sediment samples are destructed with HNO3/H2SO4, then reduced by SnCl2. Hg, Pb, Cd and Cu content was determined by using a Flame Atomic Absorption Spectrophotometer (Varian SpectraAA 20 Plus) following the US EPA 3050b method (USEPA, 1996).

A reference material PACS-2 was used to ensure the accuracy of the data. The typical recovery ranges between 95-100% and with the percent difference for the reference material is <5%. The concentration of heavy metal is expressed in mg of metals per kg of sediment (dry weight).
2.4. Data analysis

2.4.1. Contamination Factor (CF)

The contamination factor (CF) was used to determine the contamination status of the study area. The formula and terminology for describing contamination factor (CF) [7,8] are shown as follows.

\[
CF = \frac{C_{\text{metal}}}{C_{\text{background}}} \quad (1)
\]

Where \( C_{\text{Metal}} \) is the concentration of a given metal in the sediment and \( C_{\text{Background}} \) is a metal concentration of a control sample. The range are: low (CF<1), moderate (1≤CF<3), considerable (3≤CF<6) and very high (CF≥6).

2.4.2. Pollution Load Index (PLI)

The pollution load index (PLI) is a simple method to assess the level of pollution in sediments. The pollution load index for each site was evaluated using the procedure of [8]:

\[
PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots \times CF_n)^{1/n} \quad (2)
\]

Where: \( n \) = number of metals and \( CF = \) contamination factor. PLI=0 (background concentration), 0<PLI≤1 (unpolluted), 1<PLI≤2 (unpolluted to moderately), 2<PLI≤3 (moderately polluted), 3<PLI≤4 (moderately to highly polluted), 4<PLI≤5 (highly polluted) and PLI>5 (very highly polluted).

2.4.3. Enrichment Factor (EF)

According to Ergin et al., (1991) the metal enrichment factor (EF) defined in this study as the concentration ratio of metal to iron in the sample compared to the ratio in the natural background, average shale standards of metals described by [9] were taken as geochemical reference values in the present study. The enrichment factor was calculated using the following equation:

\[
EF = \frac{[\text{Me/Fe}]_{\text{sample}}}{[\text{Me/Fe}]_{\text{background}}} \quad (3)
\]

where \( (\text{Me/Fe})_{\text{sample}} \) is the metal to Fe ratio in the sample of interest; \( (\text{Me/Fe})_{\text{background}} \) background is the background value of the metal to Fe ratio. Iron was chosen as the element of normalization because natural sources (1.5%) vastly dominate its input. EF<2 indicated that the metal is entirely from crustal materials or natural process, EF: 2-5 (moderate enrichment), EF: 5-20 (significant enrichment), EF: 20-40 (very high enrichment) and EF>40 (extremely high enrichment).

2.4.4. Geoaccumulation Index (Igeo)

The geoaccumulation index is generally used to determine the anthropogenic contamination in sediments as introduced by [10-11]. The Igeo is expressed using the following Muller equation:

\[
I_{\text{geo}} = \log_2 \left( \frac{C_n}{1.5B_n} \right) \quad (4)
\]

Where: \( C_n = \) measured concentration of element \( n \) in the sediments. \( B_n = \) geochemical background for the element \( n \), 1.5 is incorporated in the relationship to account for possible variation in background data owing to lithogenic effects. Igeo<0, class 0 (uncontaminated), 0<Igeo<1, class 1 (unpolluted to moderately), 1<Igeo<2, class 2 (moderately polluted), 2<Igeo<3, class 3 (moderately to heavy polluted), 3<Igeo<4, class 4 (heavily polluted), 4<Igeo<5, class 5 (heavily to extreme polluted) and Igeo>5, class 6 (extremely polluted).
3. Results and Discussions

3.1. Distribution of Heavy metal in sediment

The concentration of Hg, Pb, Cd, Cu, and Fe were listed in Table 3. Among the five elements studied, the concentration of Fe, Pb, Cu and Hg were higher, whereas Cd was lower. The highest concentration of Fe was detected in Station 4 that is 420,000 mg/kg, Hg Station 5 that is 3,571 mg/kg, Pb in Station 5 that is 12,400 mg/kg, Cd in Station 5 that is 0.298 mg/kg and Cu in Station 5 that is 40,494 mg/kg.

| Heavy metal concentration (mg/kg dry weight) | Hg  | Pb   | Cd   | Cu   | Fe   |
|---------------------------------------------|-----|------|------|------|------|
| Sampling location                           |     |      |      |      |      |
| 1                                           | 0.592 | 10.400 | 0.197 | 1.456 | 211.5 |
| 2                                           | 0.599 | 10.600 | 0.095 | 2.102 | 219.6 |
| 3                                           | 1.997 | 11.200 | 0.193 | 0.713 | 194.2 |
| 4                                           | 2.728 | 12.200 | 0.198 | 2.201 | 420.0 |
| 5                                           | **3.571** | **12.400** | 0.298 | **40.494** | **333.3** |
| Min                                         | 0.592 | 10.400 | 0.095 | 0.713 | 194.2 |
| Max                                         | 3.571 | 12.400 | 0.298 | 40.494 | 420.0 |
| SD                                          | 1.312 | 0.909 | 0.071 | 17.396 | 97.533 |
| Average                                     | 1.897 | 11.360 | 0.196 | 9.393 | 275.72 |
| Background                                  | 0.4* | 20** | 0.3** | 45** | 47200# |

* Odat et al. (2010). **Harikumar et al. (2010). #Turekian & Wedepohl (1961).

The concentration of Hg range from 0.529-3.571 mg/kg with an average of 1.897 mg/kg, which higher than the background value 0.4 mg/kg [13]. The highest concentration of Hg found in Station 5 and the lowest in station 1. This showed that sediments in station 5 accumulate Hg more than other stations. The average concentration of Hg was higher compared to the criteria set by [14] for protection of marine organisms that is 0.15-1.0 mg/kg and [15] states that the allowable threshold value of Hg in sediments is 0.17 mg/kg. Based on the provisions of [14,15] this sediment is not good for marine organism.

The concentration of Pb range from 10.4-12.4 mg/kg with an average of 11.36 mg/kg, which didn’t exceed the background value 20 mg/kg [16]. The highest concentration of Pb found in Station 5 and the lowest in station 1. It indicates that Station 5 receives more input of waste containing Pb compared to other stations. [17] stated that the threshold value of Pb levels in sediments for marine organisms that is 35 mg/kg. Sediments with Pb levels less than 40 mg/kg are categorized as not polluted [18]. The Office of the Minister of Environment of Indonesia [19] stated the threshold value of Pb in sediments for a marine organism that is 36.8 mg/kg. Based on the provisions of CCME and OMERI, sediments in this water is still good for marine organisms.

The concentration of Cd range from 0.095-0.298 mg/kg with an average of 0.196 mg/kg which didn’t exceed the background value 0.3 mg/kg [9]. The highest concentration of Cd found in station 5 and the lowest in Station 2. It indicates that Station 5 receives more input of waste containing Cd than other stations. This average Cd concentration was low. The Canadian Council of Ministers for the Environment [17] sets the Threshold Value of Cd in sediments for biota protection is 0.6 mg/kg. [19] sets the threshold value of Cd in sediments for marine organism that is 6.2 mg/kg. Cd concentrations in unpolluted sediments is 0.11 mg/kg [20]. Based on the provisions of CCME and OMERI, the sediments in this water is still good for marine organisms.

The concentration of Cu range from 0.713-40.494 mg/kg with an average of 9.393 mg/kg, which didn’t exceed the background value 45 mg/kg [12]. The highest concentration of Cu found in Station 5 and the lowest in Station 3. It indicates that station 5 receives more input of waste containing Cu. This average concentration of Cu is low. [17] states that the threshold value of Cu in sediments for marine organism protection is 35.7 mg/kg. Sediment Quality
Guidelines [18] determine uncontaminated sediments of Cu <25 mg/kg. [19] determined threshold value of Cu in sediments for a marine organism is 108 mg/kg. Thus, when referring to the CCME and OMERI above, the sediments in this waters is still good for the marine organism.

Based on the average values, the metals follow the decreasing concentration in the order of Pb>Cu>Hg>Cd. The data shows that Pb and Cu are the dominant metals found in the surface sediment from the study area. Hg and Cd were measured at lower levels compared to Pb and Cu. Fe had the highest values in all the stations investigated, this may be because of its natural sources (1.5%) vastly dominate its input [21] and Cd had the lowest.

3.2. Estimating Metals Pollution Impact

3.2.1. Enrichment Factor, Contamination Factor and Geo-Accumulation Index

The enrichment factor (EF), contamination factors (CF) and the geo-accumulation index (I-geo) of Hg was presented in Table 4. The average EF value of Hg is 786.162, this value is very high, EF value> 40 indicates the level of enrichment is extremely high enrichment.

Table 2. Enrichment Factors (EF), Contamination (CF) and Geoaccumulation Index (Igeo) Hg

| St | EF    | CF   | I_geo |
|----|-------|------|-------|
| 1  | 333.214 | 1.480 | -0.020 |
| 2  | 324.714 | 1.497 | -0.003 |
| 3  | 1224.190 | 4.992 | 1.734 |
| 4  | 773.238 | 6.820 | 2.184 |
| 5  | 1275.456 | 8.927 | 2.573 |
| Min | 324.714 | 1.480 | -0.003 |
| Max | 1275.456 | 8.927 | 2.573 |
| Average | 786.162 | 4.743 | 1.291 |

The average value of the contamination factor (CF) of Hg is 4.743, this value is greater than 3 and smaller than 6, which means that the level of contamination is considerable. The average geoaccumulation index (Igeo) of Hg is 1.291, this value is greater than 1 and smaller than 2, which means that sediment is categorized as moderately polluted, class 2.

Table 5 showed the value of enrichment factor (EF), contamination factor (CF) and Geoaccumulation Index (Igeo) of Pb. The average EF of Pb is 104.511, this value is larger than 40, which means that the level of enrichment is extremely high enrichment.

Table 3. Enrichment Factors (EF), Contamination Factors (CF) and Geoaccumulation Index (Igeo) Pb

| St | EF    | CF   | I_geo |
|----|-------|------|-------|
| 1  | 116.054 | 0.52 | -1.531 |
| 2  | 114.027 | 0.53 | -1.502 |
| 3  | 136.116 | 0.56 | -1.412 |
| 4  | 68.556  | 0.61 | -1.300 |
| 5  | 87.806  | 0.62 | -1.275 |
| Min | 68.556  | 0.52 | -1.531 |
| Max | 136.116 | 0.62 | -1.275 |
| Average | 104.511 | 0.568 | -1.404 |
| SD  | 26.431 | 0.045 | 0.115 |

The average of Pb contamination factor (CF) is 0.568, this value is smaller than 1, which means that the sediment has low level of contamination. The average of Pb I-geo value is -1.404, this value is smaller than 0, which means that the sediment is unpolluted, class 0.

The following table shows the value of enrichment factor (EF) of Cd is 118.195, this value is greater than 40, which means that the level of enrichment is extreme high enrichment. The average value of Cd contamination factor (CF) is 0.653, this value is smaller than 1 which
means that the level of contamination is in low category and the mean geoaccumulation index value is -1.288, this value is smaller than 0, which means is unpolluted, class 0.

Table 4. Contamination Factors (CF) and Geoaccumulation Index (Igeo) Cd

| St  | EF      | CF   | I_geo |
|-----|---------|------|-------|
| 1   | 147.841 | 0.656 | -1.194 |
| 2   | 68.660  | 0.316 | -2.244 |
| 3   | 157.746 | 0.643 | -1.224 |
| 4   | 74.825  | 0.660 | -1.184 |
| 5   | 141.904 | 0.993 | -0.595 |
| Min | 68.660  | 0.316 | -2.244 |
| Max | 147.841 | 0.993 | -0.595 |
| Average | 118.195 | 0.653 | -1.288 |
| SD  | 42.836  | 0.239 | 0.595  |

Tabel 7 was presented enrichment factors, contamination factors and geoaccumulation index of Cu. The average value of enrichment factor of Cu is 30.810, this value is in the criteria of 20-40, which means the level of very high enrichment. The average value of Cu contamination factor is 0.208, this value is less than 1, which means that sediment is low contamination. The average of I-geo value is -4.586, this value is smaller than 0, which means that sediment is unpolluted.

Table 5. Enrichment Factors (EF), Contamination Factors (CF) and Geoaccumulation Index (Igeo) Cu

| St  | EF      | CF   | I_geo |
|-----|---------|------|-------|
| 1   | 7.221   | 0.032 | -5.573 |
| 2   | 10.040  | 0.046 | -5.011 |
| 3   | 3.851   | 0.015 | -6.643 |
| 4   | 5.497   | 0.048 | -4.965 |
| 5   | 127.445 | 0.899 | -0.739 |
| Min | 3.851   | 0.015 | -6.643 |
| Max | 127.445 | 0.899 | -0.739 |
| Average | 30.810 | 0.208 | -4.586 |
| SD  | 54.068  | 0.386 | 2.254  |

3.2.2. Index of Pollution Load (PLI)

In Table 10 showed the PLI values at each station. PLI value ranges from 0.0161-3.952 with an average of 0.831, this value is smaller than 1 (PLI <1), which means that overall sediment in the waters around of Ternate city is unpolluted by heavy metals Hg, Pb, Cd and Cu. The levels of Hg, Pb, Cd and Cu in sediments are relatively varied at each station. This variation can be caused by differences in each station position.

Table 6. PLI Value of Heavy Metals

| St  | CF Hg | CF Pb | CF Cd | CF Cu | PLI (Pollution Load Index) |
|-----|-------|-------|-------|-------|---------------------------|
| 1   | 1.480 | 0.520 | 0.656 | 0.032 | 0.0161                    |
| 2   | 1.497 | 0.530 | 0.316 | 0.046 | 0.0294                    |
| 3   | 4.992 | 0.560 | 0.643 | 0.015 | 0.0269                    |
| 4   | 6.820 | 0.610 | 0.660 | 0.048 | 0.1317                    |
| 5   | 8.927 | 0.620 | 0.993 | 0.899 | 3.9529                    |
| Min | 1.480 | 0.520 | 0.316 | 0.015 | 0.0161                    |
| Max | 7.142 | 0.620 | 0.993 | 0.899 | 3.9529                    |
| SD  | 2.769 | 0.045 | 0.239 | 0.386 | 1.7456                    |
| Average | 4.743 | 0.568 | 0.653 | 0.208 | 0.8314<1                 |
4. Conclusion
The total levels of heavy metals detected in surface sediments around of Ternate City waters corresponded to the order: Pb>Cu>Hg>Cd. The levels of heavy metals in sediments in the waters around Ternate City are still in accordance with sediment quality standards with the exception of Hg. When referring to PLI values, sediments in these waters are generally unpolluted (PLI <1).

References

[1] Bing H, Zhou, J, Wu Y, Wang X, Sun H, Li R (2016) Current state, sources, and potential risk of heavy metals in sediments of Three Gorges Reservoir, China. Environ. Pollut. 214, 485–496. [CrossRef] [PubMed]

[2] Omwene PI, Öncel, MS, Çelen M, Kobya M (2018) Heavy metal pollution and spatial distribution in surface sediments of Mustafakemalpasa stream located in the world’s largest borate basin (Turkey). Chemosphere, 208, 782–792. [CrossRef] [PubMed]

[3] Xia F, Qu L, Wang T, Luo, L, Chen H, Dahlgren RA, Zhang, M, Mei K, Huang, H. (2018) Distribution and source analysis of heavy metal pollutants in sediments of a rapid developing urban river system. Chemosphere,207, 218–228

[4] Islam S, Ahmed, K., Habibullah-Al-Mamun, M, Masunaga, S (2015) Potential ecological risk of hazardous elements in different land-use urban soils of Bangladesh. Sci. Total Environ. 512–513, 94–102

[5] Vodyanitskii YN (2016) Standards for the contents of heavy metals in soils of some states. J. Ann. Agrarian Sci. 2016,14, 257–263

[6] Shaari H, Siti Nurul Hidayu, Mohamad Azmi, Khawar Sultan, Joseph Bidai and Yuzwan Mohamad (2005) Spatial Distribution of Selected Heavy Metals in Surface Sediments of the EEZ of the East Coast of Peninsular Malaysia. Hindawi Publishing Corporation. International Journal of Oceanography Volume 2015. Article ID 618074. 10 pages http://dx.doi.org/10.1155/2015/618074

[7] Hakanson. L. (1980) “An ecological risk index for aquatic pollution control. A sedimentological approach”. Water Research. 14(8). 975-1001.

[8] Tomlinson LD, J G Wilson, C R Harris and DW Jeffrey (1980) Problems in the assessment of the avy-metal levels in estuaries and the formation of a pollution index [J] Environmental Evaluation 33, 566-575

[9] Turekean K K and KH Wadepohl. (1961). Distribution of elements in some amjor units of the earth’s crush. Geological Society of America. Bulletin 72, 175-192

[10] Müller, G. (1979). Heavy Metals in the Sediment of the Rhine-Changes Seity. Umschau in Wissenschaft und Technik, 79, 778-783

[11] Müller, G. (1981) The Heavy Metal Pollution of the Sediments of Neckars and its Tributary A Stocktaking. Chemiker Zeitung, 105, 157-164

[12] Mohiuddin KHM, Zakir K, Otomo S, Sharmin & N Shikazono 2010 Geochemical distribution of trace metal pollutants in water and sediments of downstream of an urban river. International Journal Environmental Science Technology. 7 (1): 17-28

[13] Odat S & Ahmed M. Alshammara 2011 Seasonal Variations of Soil Heavy Metal Contaminants along Urban Roads: A case Study from City of Hail. Saudi Arabia. Jordan Journal of Civil Engineering. Vol 5. No. 4: 581-591.

[14] ANZECC/ARMCANZ (2000) Australian and New Zealand Guidelines for Fresh and Marine Water Quality, Vol I (Chapter 1-7). The Guidelines Australian and New
Zealand Environment and Conservation Council and Agriculture and Resources Management Council of Australia and New Zealand, 314p

[15] Burton AG (2002) *Sediment quality criteria in use around the world*. Limnology 3: 65-75

[16] Ra. Kongtæe, Eun-Soo-Kim, Kyung-Tae-Kim, Joung-Keun-Kim, Jung-Moo Lee & Jin-Young Choi (2013) *Assessment of heavy metal contamination and its ecological risk in the surface sediments along the coast of Korea*. Journal of Coastal Research. Special Issue No. 65: 105-110

[17] Canadian Council of Ministers for the Environment (CCME). (2002). *Canadian Sediment Quality Guidelines for the Protection of Aquatic Life Summary Table*. Winnipeg, MB. 7 p.

[18] Harikumar S P, UP Nasir & M P, Mujeebu Rahman (2010) *Distribusi of heavy metals in the core sediments of a tropical wetland system*. International Journal Environmental Science Technology. 6 (2): 225-232

[19] OMERI (The Office Ministry of Environment of Republic of Indonesia) (Kantor Menteri Negara Lingkungan Hidup. (2010) *State Environment Minister's Decision Draft*. http://www.klh.go.id. Kamis. 16 Februari 2012.

[20] Siddique MA, Mohammad & Mahbuba Aktar (2012) *Heavy Metals in Salt Marsh Sediments of Porteresia Bed along the Karnafully River Coast*. Chittagong. Soil & Water Res. 7. 2012 (3): 117–123

[21] Onjefu S A, Kgabi N A, and Taole S H 2016 *Heavy metal seasonal distribution in shore sediment samples along the coastaline of Erongo Region, Western Namibia*. European Journal of Scientific Research, 139, 49-63