

Trace metal in sediment from a deep-sea floor of Makassar Strait

F Budianto¹ and Lestari¹

¹Research Center for Oceanography, Indonesian Institute of Sciences, Ancol, Jakarta 14430
E-mail: fitri.budiyanto@gmail.com

Abstract. Makassar Strait is located in the entrance of Indonesian Through Flow (ITF). However, the geochemistry of metals in sediment within Makassar Strait remains unexplored. The aim of this study was to measure the concentration of metals in sediment and to assess the sediment quality based on those metals concentrations. The sediment was collected from 632-4730 m in depth using giant piston corer on R/V Baruna Jaya VIII in December 2014. In each observation point, three layers of sediment were sub-sampled from the core i.e. surface layer (0-5 cm), middle layer (45-55 cm) and bottom layer. The metals were analyzed using acid digestion procedure followed by Atomic Absorption Spectrophotometer. The result indicated that the metal has spatially insignificant differences in sediment and the increase of metal concentration by depth was noticed. The Enrichment factor presented as no enrichment to minor enrichment of metal in sediment.

1. Introduction

Makassar Strait is located in a strategic position occupied right in one of the entrance of the Indonesia Through Flow (ITF) [1, 2]. The ITF itself is part of the Great Ocean Conveyor Belt which is a hydrodynamic system circulating the global seawater mass from the Pacific Ocean thru the Indian Ocean to the Atlantic Ocean [3]. The system is transporting all ocean potential around the world passing through the ITF [4]. The chemical like trace metal is part of the natural sources transported by the seawater mass [5]. Interestingly, the trace metals are considered as both natural and anthropogenic generated substances [6-8] providing the wide consideration the sources.

The metals transported by sea current will be deposited on the sea bottom as sediment. However, the metal will be either released from the sediment or sunk and covered by other layers of sediment. Thus, the sediment acts as a metal source and archive marking the complex geochemistry of this substance [9, 10]. Moreover, in the deep sea like Makassar Strait, the geochemistry process of the metal in sediment is becoming more interesting with the presence of the depth variable. Comparing with the shallow waters, the study of factors influencing the fate of metal like benthic activities, the sea current, pH, oxidation-reduction and other physiochemical process are limited [11].

The hydrodynamic system like the current circulation of Makassar Strait was intensively studied [12-14]. Current circulation plays a role in transporting and distributing metal before the deposition and re-deposition process [12]. The biogeochemistry of microbial methane, ethane, ethylene, and propylene from gas hydrate nodules of Makassar Strait was also investigated [15]. However, the study on the geochemistry of trace metals in the sediment of the strait was finite. Thus, the aim of this study is to measure the concentration of trace metals Cd, Cu, Fe, Ni, Pb and Zn in sediment and to assess the sediment quality based on those metals concentration.



2. Material and Methods

The sediments were collected using a giant piston corer between 00 53'-30 14' N and 118 09'-1200 6' E in December 2014 from the deck of R/V Baruna Jaya VIII during the E-win VII cruise. The depth of observation points (stations) spread from 632 m to 4730 m below the sea surface as presented in Figure 1.

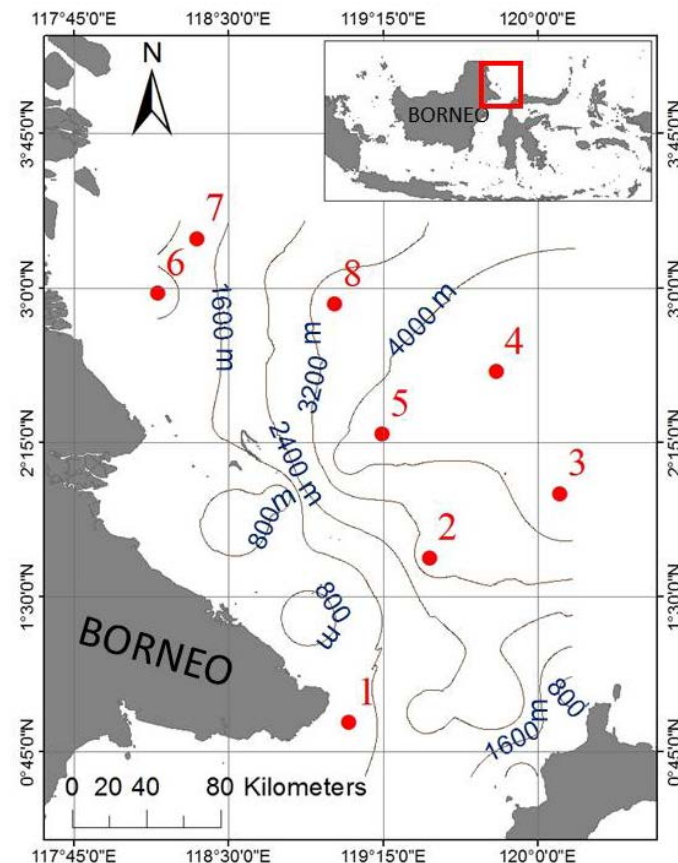


Figure 1. The sampling points of collected sediment in the Makassar Strait.

The sediment core successfully lifted from the sea floor varied from 50 cm-283cm. Within this variation of the sediment core, the sample which was divided only into 3 layers i.e. the surface layer (0-5 cm), the middle layer (45-55 cm) and the bottom layer was selected in the bottom of the core which means the bottom was in variation between 50 cm to 283 cm. The sub-sampling of sediment into different layers was based on the differences of period during sediment deposition. This study used non-exact date for the sediment age; the top layer represented recent deposition process, bottom layer resembles the initial deposition in that particular location and middle layer represents period between the top and bottom layer. The collected sediment was then stored in pre-cleaned PE box under low temperature (4°C) during the field observation. This preservation of sediment for metals analysis procedure followed the suggestion of [16].

The analytic grade of Nitric acid 65% (Cat No. 1.00456.2500), hydrochloric acid 37% (Cat No. 1.00317.2500) and hydrogen peroxide 30% (Cat No. 1.08597.1000) used in the analysis was purchased from Merck®. All glassware was pre-cleaned by submerging the glassware into nitric acid in a period of 24 hours before used.

The sediment used in the analysis was based on dry basis and the analysis was carried out based on acid digestion procedure as suggested by [16]. The whole analysis was carried out in the Research

Center for Oceanography-Indonesian Institute of Sciences. The acid digestion procedure was selected due to the solid data (both accuracy and precision) produced by this method. The accuracy was obtained using the comparison of the measured value with the certified value of Certified Reference Material (CRM). The CRM used in the analysis was CRM PACS-2® produced by National Research Council Canada. The accuracy (presented as % error) of Cd, Cu, Ni, Pb, Zn, and Fe was 9%; 4%; 6%; 5% 3% and 1% respectively with the precision values (presented as % RSD-Relative Standard Deviation) were 0.02-4.6%.

The following was the procedure used in the metal analysis in sediment. A gram of sediment was dissolved using nitric acid, hydrogen peroxide, and hydrogen chloride under the reflux system at 95 ± 2 °C for 8 hours. The filtrate generated at the end of the dissolving step was injected into Flame Atomic Absorption Spectrophotometer Varian SpectrAA 20 plus® to measure the concentration of Cd, Cu, Fe, Ni, Pb, and Zn. ANOVA analysis was carried out to the data set to find out the statistical different among stations. To assess the sediment quality, the Enrichment Factor (EF) index was computed. The index [17] was formulated as an Equation (1).

$$EF = \left[\frac{C_i}{C_r} \right]_{sample} \times \left[\frac{C_i}{C_r} \right]_{background}^{-1} \quad (1)$$

C_i sample and C_r sample resemble the concentration of metals in the sample and the concentration of reference metals in the sample, respectively. Thus, C_i background and C_r background represent the concentration of metals in the background and the concentration of reference metals in the background, respectively. EF value is interpreted following the description of [17] as in Table 1:

Table 1. The interpretation of EF score.

Score	Interpretation
EF <1	no enrichment
$1 \leq EF < 3$	minor enrichment
$3 \leq EF < 5$	moderately enrichment
$5 \leq EF < 10$	moderately severe enrichment
$10 \leq EF < 25$	severe enrichment
$25 \leq EF \leq 50$	very severe enrichment
EF > 50	extremely severe enrichment

3. Result and Discussion

The concentration of trace metals in sediment was presented in Figure 2 as the profile concentration of each metal by the stratigraphy. The trace metal in Makassar Strait was ordered as Cd, Pb, Cu, Ni, Zn and Fe with the value ranged from 0.2-0.9, 1.9-12.5, 7.7-65.2, 28.8-144.8, 62-101, and 23658-47038 mg/kg dry, respectively. Those concentrations were in order from minor to major metals in the average crust concentration of metal by [18] in such an order: Cd (0.1 mg/kg), Pb (14.8 mg/kg), Cu (25.0 mg/kg), Ni (56.0 mg/kg) and Zn (98.0 mg/kg). There were two other studies on metals on the earth crust i.e. study by [19] and study by [20]. However, those two studies indicated distinguished order and value of the metal in sediment. The study of [19] on metals in average crust depicted the order of metals as follow: Cd (0.2 mg/kg), Pb (12.5 mg/kg), Cu (55 mg/kg), Zn (70 mg/kg), Ni (75

mg/kg) and Fe (56300 mg/kg). On the other hand, the study on metals on upper crust by [20] determined the order of metals as follow: Cd (0.1 mg/kg), Cu (14.3 mg/kg), Pb (17.0 mg/kg), Ni (18.6 mg/kg) and Zn (53.0 mg/kg).

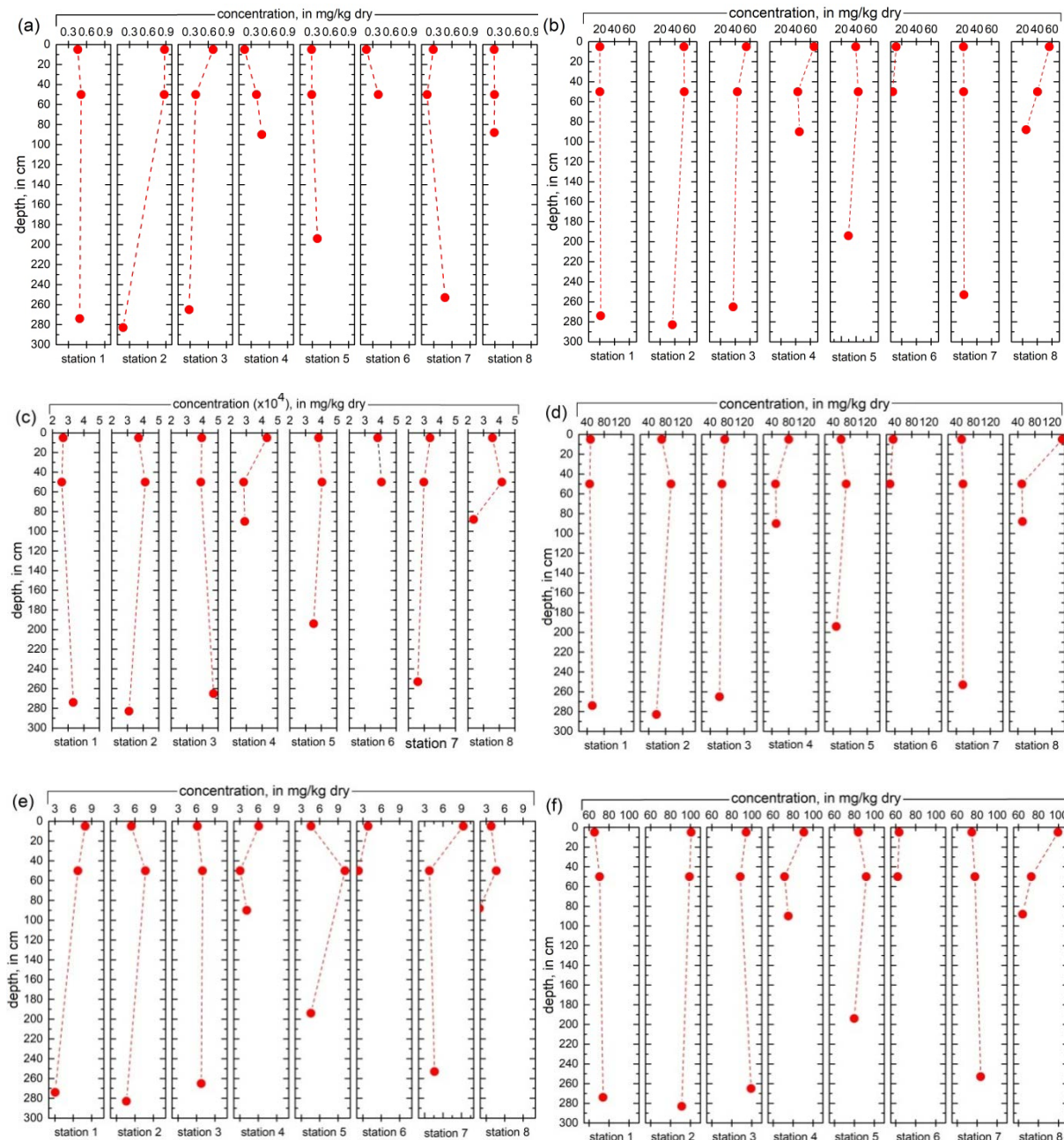


Figure 2. The profile of concentration by stratigraphy of trace metals in sediment: (a) Cd; (b) Cu; (c) Fe; (d) Ni; (e) Pb and (f) Zn.

ANOVA analysis revealed that metals concentration was insignificantly different among observation points except for Cu, Ni, and Zn in station 1, 6 and 7. Interestingly, the spatial distribution of metal identified the identical pattern. Dominantly, in the top layer, station 1, 6 and 7 hosted the relatively lower concentration of metal. In the opposite, station 2, 3 and 4 were nominated to exhibit a higher concentration of metal. That pattern was also applied for middle and bottom layer though the ascribed metal would be different. At least, 2 factors were able to explain those spatial distributions

i.e. the current circulation and the sediment grain size. Even, station 1, 6 and 7 were located closed to Kalimantan Island, the current was circulated southward [21] transporting the particulate matter or sea water as a source of metal in the same direction of the current. In the opposite, the current in station 2, 3 and 4 circulated as a local vortex-like [21]; stimulating the deposition of sediment in the location. The sediment texture was supported this argument for metal tend to accumulate in fine sediment [22]. The sediment texture was spread from sand to silty clay. Silty clay was observed in station 2, 3 and 4 and the coarser texture was identified in sediment closed to Kalimantan Island like station 6 [23].

The vertical distribution of metals revealed that dominantly metals tend to increase by the depth, from the top layer to bottom layer. Thus, the metal was considered to decline by time though that decrease was not significant, less than two-fold from the concentration in the bottom layer, yet. The bottom layer was considered as the reference for each sediment stratigraphy as the bottom layer play an initial deposition step of the sediment. This decline in metal concentration was most probably affected by the reduction of metal release to the environment due to the improvement of waste treatment technology as other reports around the world. The sediment quality based on trace metals around either eastern part or western part of India's coastal line was improved [24]. The Northern Baltic Sea was also showing the decline of metal concentration after two decades [25].

Table 2. The computed EF score for trace metal concentration in each observation point.

station no	Depth in cm	EF score				
		Cu	Pb	Cd	Ni	Zn
1	5	0.8	1.3	4.8	1.3	2.0
	50	0.8	1.2	5.5	1.3	2.2
	274	0.7	0.4	4.1	1.2	1.8
2	5	1.4	0.7	6.7	1.4	2.2
	50	1.3	0.8	6.0	1.7	1.9
	283	1.2	0.7	1.8	1.4	2.4
3	5	1.4	0.7	4.8	1.4	1.9
	50	1.1	0.8	2.8	1.3	1.8
	265	0.8	0.7	1.7	1.0	1.7
4	5	1.5	0.6	1.3	1.4	1.7
	50	1.6	0.5	3.9	1.3	2.0
	90	1.6	0.6	4.6	1.3	2.1
5	5	1.1	0.5	2.1	1.1	1.8
	50	1.1	1.1	2.0	1.3	1.8
	194	0.9	0.6	3.1	1.0	1.8
6	5	0.3	0.5	1.4	0.7	1.3
	50	0.2	0.3	2.7	0.5	1.2
	5	0.7	1.2	2.4	1.2	1.8
7	50	0.8	0.6	1.8	1.4	2.1
	253	0.9	0.8	5.3	1.6	2.6
	5	1.6	0.5	2.3	3.0	2.2
8	50	1.0	0.5	2.0	0.9	1.4
	88	1.1	0.4	3.5	1.6	2.2

Understanding the sediment quality, the index called Enrichment Factor (EF) was computed. EF was calculated by dividing the metals with either Al or Fe as reference metals as normalization [25]. Those metals are abundant in marine sediment and not affected by human activity [26] and in this study, Fe was selected as normalizing metals due to the absence of the Al analysis. The metals in the average crust by [18] as ascribed above were selected as background concentration.

Table 2 presented the EF score. The computed EF indicated that the sediment was in the no enrichment to minor enrichment conditions. These conditions reflected the minor or undisturbed sediment in the Makassar Strait. Surprisingly, the Cd only approached the level of the moderately enriched state. This state was stimulated by the nature of the Cd itself present in a normally low concentration in the sediment, so the small input of Cd to the system triggered significant alteration.

4. Conclusions

The trace metal concentration in sediment closed to Kalimantan Island was relatively low compared with other locations. However, considering the vertical distribution of metal, the concentrations, dominantly, increased by depth. Moreover, station number 1, 6 and 7 located closed to Kalimantan Island indicated lower metals concentration than other observation points due to the current circulation and coarser sediment texture. On the other hand, station 2, 3 and 4 exhibited relatively higher concentration of metal. Thus, the metals presented no enrichment to minor enrichment of metal in sediment except for Cd. The Cd concentration leveled up to the moderately enriched state of metal in sediment. However, the possibility to increase the data is still wide open to obtain a better understanding on trace metals concentration by the sediment stratigraphy.

Acknowledgments

This research was funded by Research Center for Oceanography, Indonesian Institute of Sciences thru EWIN (Ekspedisi Widya Nusantara) VII grand.

References

- [1] Susanto R D, Ffield A, Gordon A L and Adi T R 2012 *J. Geophys. Res.* **117** 1-16.
- [2] Gordon A L, Giulivi C F, and Ilahude A G 2003 *Deep-Sea Res. II* **50** 2205-28.
- [3] Yaohua Z, Zexun W, Guohong F, Yonggang W and Yuping G 2014 *Acta Oceanol. Sin.* **33** 11-23.
- [4] Gordon A L, Susanto R D, Ffield A, Huber B A, Pranowo W and Wirasantosa S 2008 *Geophys. Res. Lett.* **35** 1-5.
- [5] Fang H, Huang L, Wang J, He G, Reible D 2016 *J. Hazard. Mater.* **302** 447-457.
- [6] Harikrishnan N, Ravisankar R, Chandrasekaran A, Gandhi M S, Kanagasabapathy K V, Prasad M V R and Satapathy K K 2017 *Mar. Poll. Bull.* **121** 418-24.
- [7] Liu L, Wang L, Yang Z, Hu Y and Ma M 2017 *Mar. Poll. Bull.* Article in press <http://dx.doi.org/10.1016/j.marpolbul.2017.07.021>
- [8] Prasetya G S, De Lange W P and Healy T R 2001 *Nat. Hazards* **24** 295-307.
- [9] Liu X, Zhang L and Zhang L 2017 *Mar. Poll. Bull.* **121** 216-21.
- [10] Zhang P, Hu R, Zhu L, Wang P, Yin D and Zhang L 2017 *Mar. Poll. Bull.* **119** 429-38.
- [11] Sensarma S, Chakraborty P, Banerjee R and Mukhopahyay 2016 *Chemie der Erde* **76** 39-48.
- [12] Schröder J F, Holbourn A, Kuhnt W and Küssner K 2016 *Quaternary Sci. Rev.* **154** 143-56.
- [13] Pujiana K, Gordon A L, Metzger E J, Ffield A L 2012 *Dynam. Atmos. Oceans* **53-54** 17-35.
- [14] Wajsowicz R C, Gordon A L, Ffield A and Susanto R D 2003 *Deep-Sea Res. II* **50** 2163-81.
- [15] Sassen R and Curiale J A 2006 *Org. Geochem.* **37** 977-80.
- [16] Loring D H and Rantala R T T 1992 *Earth-Sci Rev.* **32** 235-83.
- [17] Varol M 2011 *J. Hazard. Mater.* **195** 355-64.
- [18] Wedepohl K H 1995 *Geochim. Cosmochim. Acta* **59** 1217-32.
- [19] Taylor S R 1964 *Geochim. Cosmochim. Acta* **28** 1273-85.
- [20] Turekian K K and Wedepohl K H 1961 *Bull. Geol. Soc. Am.* **72** 175-92.
- [21] Purwandana A, Atmadipura A, Suranarti D, Iskandar M R, Avianto P, Irianto D and Muhadjirin 2014 *Integrative study on oceanography characteristic, Geology and Marine Biodiversity of deep-sea in Makassar Strait* ed A Rachman (Jakarta: Research Center for Oceanography-LIPI) pp 12-27.
- [22] Brady J P, a Ayoko G, Martens W N and Goonetilleke A 2014 *Mar. Pol. Bul.*, **81**: 248–255

- [23] Munasri, Suyarso, Hendrizan M, Witasari Y, Natsir S M and Wibowo S P A 2014 *Integrative study on oceanography characteristic, Geology and Marine Biodiversity of deep-sea in Makassar Strait* ed A Rachman (Jakarta: Research Center for Oceanography-LIPI) pp 90-101.
- [24] Chakraborty P, Ramteke D, Chakraborty S and Nath B N 2014 *Mar. Poll. Bull.* **78** 15-25.
- [25] Vallius H 2014 *Mar. Poll. Bull.* **79** 359-64.
- [26] Gopal V, Krishnakumar S, Peter T S, Nethaji S, Kumar K S, Jayaprakash M and Magesh N S 2017 *Mar. Poll. Bull.* **114** 1063-71.