Heavy metal distribution in sediments around the offshore tin mining area of Central Bangka Regency, Indonesia

Irvani1,*, S Adibrata2, M Yusuf3, M Hudatwi4 and A Pamungkas4

1Department of Mining Engineering, Universitas Bangka Belitung, Indonesia
2Department of Aquatic Resources Management, Universitas Bangka Belitung, Indonesia
3Department of Marine Science, Universitas Diponegoro, Indonesia
4Department of Marine Science, Universitas Bangka Belitung, Indonesia

*E-mail: bujangbabel@yahoo.co.id

Abstract. Vary heavy metals scattered in suspension loads and re-sedimentation from the tailing of the offshore-alluvial tin mining at Tanah Merah and its surroundings, Central Bangka Regency. Research is needed to determine the type, composition, spatial distribution of heavy metals, and potential pollution. The active surface-sediments were taken from shallow marine systematically around the offshore tin mining area in the east season. Geochemical analysis of sediment using x-ray fluorescence, coupled with minerals and sieve analysis, and support by spatial analysis. These sediments have dominant the sand-size (range very-fine sand to coarse sand) and silt, contained predominantly large quantities of quartz minerals and shell fragments of marine animals. The metals are in the following decreasing order: Cr>Zn>Pb>Ni>Cu>As>Co>Cd. The spatial distribution of heavy metals generally has a relatively south, east, and north position, with concentrations occurring along the coastline and showing the degradation composition towards the open sea. The marine sediments are uncontaminated to moderately contaminated by Cd and Pb, indicate both natural and anthropogenic enrichment, low the pollution load index (PLI), and have various potential ecological risks index (RI) (low to very high RI).

1. Introduction
Offshore tin mining is quite a lot in Tanah Merah and its surrounding area, the mining activity, generally using mini-suction pontoons. The location is close to Pangkalping City, the Capital of the Kepulauan Bangka Belitung Province. As a principle, tin mining is an inseparable part of tin production. Dismantling of marine sediments results in tailings from mining sites following sea currents. Big waves carry a lot of material, with bathymetry affecting wave height [1].

The physical and chemical characteristics of tailings are dependent on the parent rock [2]. Tailings can release toxic elements and hazardous materials, resulting in contamination to the environment [3]. The heavy metal content in the former mine sediment is Fe, Al, Mg, Zn, Cu, and Mn [4]. The heavy-metal, in surface sediments on Bangka-Island, have been studied by some researchers. For example, the average concentrations of Pb, Cu dan Zn in Klabat Bay double compared to the other place. The heavy metal accumulation of Pb and Cu in shellfishes [5], comparing the Pb content in the sediment at the Batu Belubang area is smaller than the Pb content in sediment at the Kelabat Bay. Pb accumulation in sediments is higher than in seawater. The marine sediments in the Batu Belubang area close to Tanah Merah are still in good condition [6]. Based on these conditions, research needs to clearly understand
the texture, type of mineral compositions, spatial distribution, and ecological risk of heavy metals from sediments in Tanah Merah and its surrounding area.

2. Method
Tanah Merah Coastal administratively belongs to the District of Pangkalan Baru, Central Bangka Regency. Figure 1 illustrates the sampling map area located on the eastern side of Bangka Island. A total of seven sample points were collected using an Ekman grab device, one being the location of offshore tin mining conducted by residents. Generally, the pattern of sampling technic follows the longitudinal direction of the coastline, which has shallow depth. At the time sampling, the condition of the season is in the east season.

Petrological analysis-way is megascopic and petrography using a stereomicroscope to identify minerals within sediments. Geochemical analysis of the heavy metal elements in sediment samples using x-ray fluorescence [7, 8, 9]. Sieve analysis quantifies grain size distribution in every sample. Enrichment factors (EF) analysis [10], Geo-accumulation index (I-geo) [11], the potential ecological risk index (RI) developed by Hakanson [12], and pollution load index PLI [13]. Spatial analysis using IdW [14] for understanding the surface spatial distribution of metals.

3. Result and Discussion
3.1. Sediment composition and texture
Based on microscopic analysis, the mineral composition in active sediment samples contained predominantly large quantities of quartz minerals and shell fragments of marine animals. The other minerals are clay minerals, cassiterite, ilmenite, monazite, tourmaline, and iron. The shape of sediment grains is in the range of rounded-angular, and generally, they have rounded form.
Grain size in the formed gravel to clay, and generally sized sand (range of very fine to coarse sand). Figure 2 illustrates the texture of grain size distribution for all active sediment samples. The code samples of L-2, L-3, L-5, L-6, and L-S have sand sizes dominantly, while samples L-1 and L-4 had quite a lot of silt-sized. The sediment sorting texture is classified as medium-poor and tends to be poor. The Averaging percent weight and range of pebble is rarely about 0.39%, absent in Sample L-5. The other granule size is 3.39%, then sands size dominantly until average 68.57% as coarse-medium-fine sand, the silt size is 24.33%, dominant in Sample L-1 and L-4, and relatively low content of clay size 3.33% (Figure 2-A).
3.2. Heavy metal concentrations

The results, geochemical analysis show, the sediments contain heavy metals of chromium (Cr), zinc (Zn), and lead (Pb) in large quantities in ppm (Table 1). Figure 2-B illustrates the relative linearity of heavy metal distribution for each sample, the high content of Cr, Zn, and Pb metals in all the active sediment around Tanah Merah. Other metals Ni, Cu, As, Co, and Cd have a low concentration.

Based on Spearman correlation, the heavy metals As, Cu, Ni, and Zn have a strong positive correlation with sandy sediment, while Co, Pb, and Cr have a weak positive correlation (Table 2). Silty sediments have a strong correlation to Cd metals, weak correlation to Pb, and have negatively correlated with Co, As, Cu, Ni, Zn, and Cr. The clay texture has a weak correlation with Cd metal and a negative correlation to the other metals.

Table 1. Statistics of heavy metal contents in surface marine sediments from Tanah Merah background values in ppm.

|        | Cd  | Co  | As  | Cu  | Ni  | Pb  | Zn  | Cr  | Fe  | Sand% | Silt% | Clay% |
|--------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-------|-------|-------|
| Min    | 0.01| 2.46| 0.01| 1.94| 5.53| 2.64| 17.98| 38.45| 17,214.08| 0.16  | 0.28  | 0.13  |
| Max    | 5.15| 4.83| 10.12| 9.65| 12.00| 47.18| 38.10| 55.23| 34,744.48| 60.05 | 64.29 | 8.37  |
| Median | 2.21| 3.91| 6.98| 8.10| 29.36| 31.44| 48.93| 24291.96| 76.35 | 18.83 | 1.60  |
| Mean   | 1.90| 3.76| 5.83| 8.75| 24.77| 27.65| 47.08| 24,887.03| 22.86 | 24.33 | 3.33  |
| SD     | 1.82| 0.86| 4.46| 2.39| 2.57| 15.30| 7.92 | 5,280.30| 28.09 | 26.00 | 3.57  |

Note: CV* crustal value of sediment as background levels [15]

Table 2. Spearman correlation matrix for heavy metals concentrations in sediments.

|       | Cd  | Co  | As  | Cu  | Ni  | Pb  | Zn  | Cr  | Fe  | Sand | Silt | Clay |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|------|------|------|
| Cd    | 1   |    |     |     |     |     |     |     |     |      |      |      |
| Co    | -0.434 | 1 |     |     |     |     |     |     |     |      |      |      |
| As    | 0.245 | 0.026 | 1   |     |     |     |     |     |     |      |      |      |
| Cu    | -0.105 | -0.121 | 0.328 | 1   |     |     |     |     |     |      |      |      |
| Ni    | -0.498 | -0.091 | 0.523 | 0.595 | 1   |     |     |     |     |      |      |      |
| Pb    | 0.012 | -0.157 | 0.478 | 0.170 | 0.557 | 1   |     |     |     |      |      |      |
| Zn    | -0.435 | -0.117 | 0.467 | 0.561 | 0.932 | 0.770 | 1   |     |     |      |      |      |
| Cr    | -0.241 | 0.207 | 0.508 | 0.275 | 0.654 | 0.914 | 0.815 | 1   |     |      |      |      |
| Fe    | 0.234 | 0.283 | 0.286 | 0.310 | 0.071 | 0.629 | 0.313 | 0.694 | 1   |      |      |      |
| Sand  | -0.466 | 0.281 | 0.611 | 0.568 | 0.743 | 0.026 | 0.531 | 0.270 | -0.136 | 1 |      |      |
| Silt  | 0.499 | -0.121 | -0.515 | -0.506 | -0.759 | 0.043 | -0.509 | -0.152 | 0.341 | -0.969 | 1    |      |
| Clay  | 0.085 | -0.753 | -0.419 | 0.126 | -0.103 | -0.232 | -0.058 | -0.497 | -0.473 | -0.264 | 0.114 | 1    |
Another author, Wahyuni et al. [6] in Batu Belubang, found the metal content of Pb in marine sediments between 0.0918-0.1897 ppm and Zn metal ranged from 0.0565-0.1806 ppm. Another researcher, Arifin [5] in The Teluk Klabat, obtained content Pb 1.04-22.01 ppm, Cd unidentified-0.47 ppm, Cu 0.18-6.43 ppm Zn 2.27–34.40 ppm. Both of them using Atomic Absorption Spectrophotometry (AAS) analysis to identify heavy metals in sediments.

3.3. Spatial distribution pattern of heavy metals
The spatial distribution of heavy metals Cr, Zn, Pb, and Cd in sediments generally have a relatively high concentration in the south, east, and Zn metal in the north position. The metals composition Cr and Zn in all samples lower than average their composition in sediments of crust. The heavy metals have relatively high magnitude as long the coastline, showing the degradation composition towards the open sea at the eastern. The heavy-metal deposition is higher near the beach area and shallowing seawater bathymetry around L-1, L-3, L-S, and L-5 Stations (Figure 3), where L-S is an active tin mining location.

![Figure 3. Spatial distribution of heavy metals: Cr, Zn, Pb and Cd.](image)

3.4. Source identification and contamination of heavy metals
The mean I-geo values for heavy metal elements as follow : Cd 1.68, Co -2.96, As -2.22, Cu -3.65, Ni -3.60, Pb -0.69, Zn -2.42 and Cr -1.53. It can be arranged in decreasing order Cd>Pb>Cr>As>Zn>Co>Ni>Cu (Tabel 3). The I-geo range values fall in two classes (Class 0 and Class 1). Class 0 (I-geo ≤ 0), practically uncontaminated; Class 1 (I-geo 0–1) is uncontaminated to moderately contaminated. I-geo values more than one class for two elements, Cd (range -5.49 to 3.52) and Pb (range -3.51 to 0.65). Based on the above information, the marine sediments in Tanah Merah are mostly uncontaminated. Pb is uncontaminated to moderately contaminated, and Cd metal is uncontaminated to strongly contaminated.
The Enrichment Factor (EF) of heavy metals in Tanah Merah indicated element-Cd has the largest EF value, followed by Pb metal (Table 3). The range of EF of Cd varied from 0.06 to 29.88, Co 0.25 to 0.49, As 0.002 to 1.51, Cu 0.12 to 0.42, Ni 0.16 to 0.35, Pb 0.26 to 3.40, Zn 0.33 to 0.78 and Cr 0.83 to 1.17. The mean EF values arranged in the following increasing order: Cu-Ni<Co<Zn<As<Cr<Pb<Cd. The EF range values of elements Cd and Pb indicated both natural and anthropogenic enrichment, but the other elements (six metals) show metals are entirely from natural processes.

| Table 3. Minimum (Min.), Maximum (Max.) and Mean of Igeo, EF, CF and anthropogenic enrichment of heavy metals. |
|---|---|---|---|---|---|---|---|
| Igeo | Cd | Co | As | Cu | Ni | Pb | Zn | Cr |
| Min | -5.49 | -3.53 | -10.93 | -5.12 | -4.21 | -3.51 | -2.99 | -1.81 |
| Max | 3.52 | -2.56 | -0.95 | -2.81 | -3.09 | 0.65 | -1.90 | -1.29 |
| Mean | 1.68 | -2.96 | -2.22 | -3.65 | -3.60 | -0.69 | -2.42 | -1.53 |
| EF | Min | 0.06 | 0.25 | 0.002 | 0.12 | 0.16 | 0.26 | 0.33 | 0.83 |
| Max | 29.88 | 0.49 | 1.51 | 0.42 | 0.35 | 3.40 | 0.78 | 1.17 |
| Mean | 12.18 | 0.38 | 0.83 | 0.25 | 0.25 | 2.28 | 0.56 | 1.01 |
| CF | Min | 0.03 | 0.13 | 0.001 | 0.04 | 0.08 | 0.13 | 0.19 | 0.43 |
| Max | 17.17 | 0.25 | 0.78 | 0.21 | 0.18 | 2.36 | 0.40 | 0.61 |
| Mean | 6.35 | 0.20 | 0.45 | 0.13 | 0.13 | 1.24 | 0.29 | 0.52 |
| Er | Min | 1.00 | 0.65 | 0.01 | 0.22 | 0.41 | 0.66 | 0.19 | 0.85 |
| Max | 515.00 | 1.27 | 7.78 | 1.07 | 0.88 | 11.80 | 0.40 | 1.23 |
| Mean | 190.57 | 0.99 | 4.49 | 0.65 | 0.64 | 6.19 | 0.29 | 1.05 |

3.5. The ecological risk
The mean and range of contaminant factor (CF) value for Cd 6.35 (0.03-17.17) have a low (CF<1) to very high (CF≥6) contamination level, followed by Pb that has low (CF<1) to moderate level (1<CF<3) (Table 3). A low-CF (CF<1) for metals Co, As, Cu, Ni, Zn, and Cr. The Tr value using for determining ecological risk (Er). The Tr value of metal: Cd 30.00, Co 5.00, As 10.00, Cu 5.00, Ni 5.00, Pb 5.00, Zn 1.00, and Cr 2.00. The mean potential of ecological risk factor (Er) Cd is 190.57 (range 1.00 to 515.00), which falls into high ecological risk categories (160≤Tr<320). Generally, samples have low Er categories (Er<40), thus indicating that the sediment samples had a low-level ecological risk potential around the surface or active sediment in Tanah Merah.

| Table 4. Cd, mCd, PLI and RI values of heavy metals in sediments from Tanah Merah. |
|---|---|---|---|---|
| Sample | Cd | mCd | PLI | RI |
| L-1 | 12.45 | 1.56 | 0.50 | 269.95 |
| L-2 | 6.27 | 0.78 | 0.46 | 102.67 |
| L-3 | 3.81 | 0.48 | 0.27 | 20.66 |
| L-4 | 10.15 | 1.27 | 0.17 | 264.55 |
| L-5 | 11.29 | 1.41 | 0.56 | 240.95 |
| L-6 | 1.39 | 0.17 | 0.08 | 5.45 |
| L-S | 19.81 | 2.48 | 0.47 | 529.89 |

Based on the station, the Degree of Contamination (Cd) is generally moderate (n<Cd<2n) for samples L-1, L-4, and L-5 (Table 4). The Samples: L-2, L-3, and L-6 have low Cd values (Cd<n), but Sample L-S has a considerable degree of contamination. Another way, using Modified Contamination Degree (mCd) value, most of the sample has very low mCd (mCd<1.5), the other two sample L-1 and L-S in order has low (1.5≤mCd<2) to moderate mCd (2≤mCd<4). The pollution load index (PLI) overall sample of the surface or active sediments marine in Tanah Merah had PLI<1, indicated no pollution. The total potential ecological risk (RI) values at overall samples have to vary, from low ecological risk (RI<95) for Sample L-6 (RI 5.45) and L-3 (RI 20.66), moderate (95<RI<190) of Sample L-2 (RI 102.67), and considerably high ecological risk (190<RI<380) of Sample: L-5 (RI 240.95), L-4 (RI 529.89).
264.55) and L-1 (RI 269.95). Sample L-S has a very high potential ecological risk index RI 529.89 (RI>380).

4. Conclusion
The results show that the sediments have the dominant sand size, with large quartz minerals and shell fragments. Generally, they have rounded gravel to clay in generally sand-silt size with tends to be poor sorption. The heavy metal-containing metal in the following decreasing order: Cr>Zn>Pb>Ni>Cu>As>Co>Cd. The spatial distribution of heavy metals in sediments generally has a relatively south, east, and north direction. The metals concentrations have relatively high magnitude as long the coastline, with degradation towards the open sea at the eastern. The marine sediments in Tanah Merah are uncontaminated to moderately contaminated with Cd and Pb, indicate both natural and anthropogenic enrichment. The sediments sample had no pollution based on the PLI index but had to vary ecological risks (RI), low-moderate-very high.

5. References
[1] Purwanto C and Raharjo P 2015 Jurnal Geologi Kelautan 12 1 49-59
[2] Fall M, Celestin J C, Pokharel M and Toure M 2010 J. Engineering Geology 114 397-413
[3] Grangeia C, Avila P, Matias M and da Silva F 2012 J. Engineering Geology 123 359-372
[4] Espana J S, Pamo E L, Santofimia E, Advire O, Reyes J and Baretta D 2005 J. Applied Geochemistry 20 1320-1356
[5] Arifin Z 2011 Jurnal Ilmu dan Teknologi Kelautan Tropis 3 1 104-114
[6] Wahyuni H, Sasonoko, S B and Sasonkdo D P 2013 Prosiding Seminar Nasional Pengelolaan Sumberdaya Alam dan Lingkungan 489-494
[7] Staillard M O, Apitz S E and Dooley C A 1995 Marine Pollution Bulletin 31 4-12 297-305
[8] Towett E K, Shepherd K D and Cadisch G 2013 J. Sci Total Environ 463 374–388
[9] Olando G, Okaka L A, Okinda P O and Abuom, P 2020 J. SN Applied Sciences 2 279
[10] Ergin M, Saydam C, Basturk O and Erdem E, Yoruk R 1991 Chem Geol 91 269–285
[11] Muller G 1969 Geo J 2:108–118
[12] Hakanson L 1980 An ecological risk index for aquatic pollution control. A sedimentological approach. Water Res 14 8 975–1001
[13] Tomlinson D, Wilson J, Harris C and Jeffrey D 1980 Helgoländer meeresuntersuchungen 33 1 566
[14] Perumal K, Antony J and Muthuramalingam S 2021 South India Environmental Science Europe 33 63
[15] Turekian K K, Wedepohl K H 1961 Geol. Soc. Am. Bull. 72 175–192

Acknowledgments
We gratefully acknowledge the funding from Universitas Bangka Belitung through the RKAKL FT for the publication of this paper.