Analysis of heavy metal content of Cd and Zn in ballast water tank of commercial vessels in Port of Tanjung Emas Semarang, Central Java Province

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Abstract. Commercial vessels that do not conduct ballast water exchange, in accordance with International Convention Ballast Water Management, will endager the environment of ports. This research is aimed to know the metal content in ballast water tank of commercial vessels that have not performed ballast water exchange, in accordance with regulations of International Maritime Organization (IMO). The present research is focused on the heavy metal content of ballast water of commercial vessels, both passenger or cargo vessells, berthing in Port of Tanjung Emas Semarang (PTES). Water sample in ballast tank is collected by method of AAS (Atomic Absorption Spectrophotometer). Results of the research show that the content of Cd is about 0.001-0.46 mg l^{-1}, and Zn is about 0.001-2.464 mg l^{-1}. Based on the Decree of Minister of Environment Number 51/2004, the heavy metal content of Cd and Zn has exceeded quality standards of sea water for port water, which is 0.1 mg l^{-1} both.

Key words : commercial vessels, ballast water tank, heavy metal content

1.Introduction

International Maritime Organization (IMO) is a United Nations organization that attempts to increase the safety of shipping and protection of marine environment. One of of comittees in the organization is the Commitee of Marine Environment Protection (MEPC) in 2004 that has legalized regulations of controlling management of vessel ballast water. The regulation of ballast water set by IMO which aims to minimalize the entrance of indigenous species and sediments to other water areas.

To minimalize the risk, based on D1 standards, each commercial vessel entering to port water areas is requested to do ballast water exchange in ballast water tank that is located 200 miles from the port, in depth of more than 200 meters, and by level of efficiency of at least 95%. There are three methods used in ballast water exchange. First, sequential method, a process of emptying and refilling ballast water to get at least 95% of volumetric exchange. Second, flow-through method, a process of pumped ballast water exchange so that the water comes through overflow pipes or other structures. Third, dilution method, a process of ballast water exchange that is filled through the upper parts of ballast water tank by simultaneous release from bottom of the tank [1].

The stability of the vessel depends on the cargo and stabilizer of the vessel. Recently, it uses sea water that is pumped in ballast water tank. When the cargo is empty,the vessel needs to pump sea water to ballast water tank to get positive GM and to avoid the instability of the vessel. When the vessel load cargo, sea water is pumped out of ballast water tank to stabilize the vessel and get positive GM. When

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the vessel does not pump out sea water, it can transfer sea water into the empty ballast water tank so that the vessel can be in *even keel* condition with the same mean draft and balanced listing. If ballasting is not conducted, the unstable equiribillium condition happens so that is easy to get influenced by other factor [2].

The research about the effectiveness of mid ocean ballast water exchange has been conducted on 34 container vessels (20 vessels are from Oakland, California) in Hong Kong Port. The research shows that in the beginning of September and in the middle of August, *Skeletonema costatum* dominates the ballast water tank (14,000 cells l^{-1}). There are dangerous *diatoms*, *Chaetoceros caoncavicornis* and *Alexandrium catenella*. Other researches are conducted to four vessels from Manzanillo, Mexico. The result of the research shows that effectiveness of mid ocean ballast exchange is about 48% in reducing the abundance of *diatom* and *dinoflagellata*. Old container vessels (≥ 15 years) are not effective to release *diatom* and *dinoflagellata* compared to the new vessels due to sediments on the bottom of ballast water tank [3].

Semarang estuary water is not deep. It is about 14 meters, dirty . It has high solid suspense. The bottom of the sea is muddy. The pollution comes from household waste originated from two main canals [4]. The heavy metal content of Pb on the sediments of Semarang Port pond is higher than the estuary water in the canals of Banjir Kanal Timur and Banjir Kanal Barat. The concentration of Zn in the sediments is about 84.14-131.74 mg kg^{-1}, with the average of 97.11 mg kg^{-1} [5].

Port of Tanjung Emas Semarang (PTES) is located in the north coast of Central Java Province, Indonesia ($6^0$53' S, $110^0$24' E). The port is situated in the narrow side of the coast, less than 10 km in width. It gets wider in the eastern side, maximum speed of general streams is 0,31 knot with the direction of 324^0 in the afternoons, when the water is going to lowest tidal , and in the late afternoon, for about 0,28 knot with the direction of 164^0. The stream of both the lowest and highest tidal are weak. There is hindered and weak stream in front of port entrance [6].

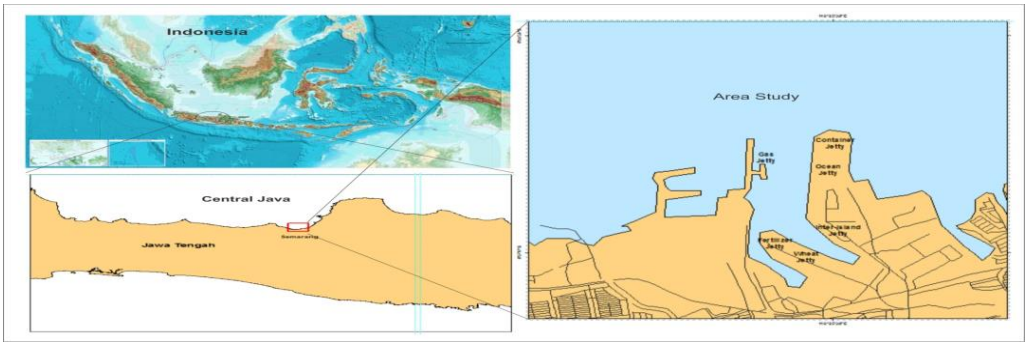


Figure 1. Research location

The study aims to determine implemention of Convention of Ballast Water Management 2004 through the measurement heavy metal content of Pb, physical parameters in ballast water, the origin of the commercial vessels, DWT, and vessels ballast tank capacity.

2.Material and Methods

The sample was gathered from vessels berthed in PTES, dated on December 18th 2014 to October 21st 2015. In the commercial vessels, sample collected twice on one ballast water tank with DWT more than 400 tons. Research in ballast water tank of commercial vessels is conducted by using purposive sampling that covers 6 wharfs, like Pusri fertiliser and oil, passenger, domestic, wheat, container and LPG wharfs.

The capacity of ballast water for each vessel berthed in port is calculated by using the formula of 36,5% of general cargo, 35% of solid cargo, 35% of liquid cargo, 30% of container, 33% of mixed cargo , and 33% mixed cargo, and 33% of Ro-Ro vessels from DWT [7].

The water sample in ballast tank is collected by using the method conducted by putting sounding meter in ballast water tank through sounding pipes. Portable pump and suction hoses are used to collect the water sample [8]. The portable pump is from Sanyo brand, model P-WH137C, 220 V~50 Hz of voltage source, 125 W of output power, 30 l min^{-1} of maximum water capacity. The suction hose has 0.019 m width of diameter and 10 m in length. The end of suction hose is completed by foot valve. The water sample of the ballast water in the surface of the tank can be collected by rising the end of suction hose, while the water sample from bottom of the tank can be collected by lowering the end of the suction hose.

Sample of the ballast water, that is on the surface of the tank, can also be collected by opening manhole in the ballast tank of commercial vessels. Sampel of water , that is at the bottom of the tank, is collected by using 10 liter bucket.

The water sample is filtered by using 40 (0.42 µm) whatman filter paper and washed by using HNO_3 concentrated to PH < 2. Then, it is placed in water sample of 5 l volume. The water sample is then brought to the laboratory. The water (100 ml) is mixed thoroughly and put in the beaker. Then, it is added by 5 ml of citric acid and heater, 50 ml of distilled water is added, and the mixture is put in 100 ml of graduated flask [9] [10]. The level of heavy metal Cd and Zn in the sample of ballast water of commercial vessel is determined by AAS (Atomic Absorption Spectrophotometer) type Shimadzu AA-6300 by using flame-mixed of air acetylene.

3.Results and Discussion

Deadweight of vessels are about 537 to 46,769 MT, while the capacity of ballast tank is about 196 to 16,269.2 tons. The sample of ballast water is mostly gathered from domestic ports in Palembang (JM, SB, MP, OK PI, IZ, Ce 8 and S vessels), and Jakarta (A, MB2, DF2 and GNA vessels). Sample of ballast water gathered from foreign ports is PA, SB and HL vessels (Figure 2)

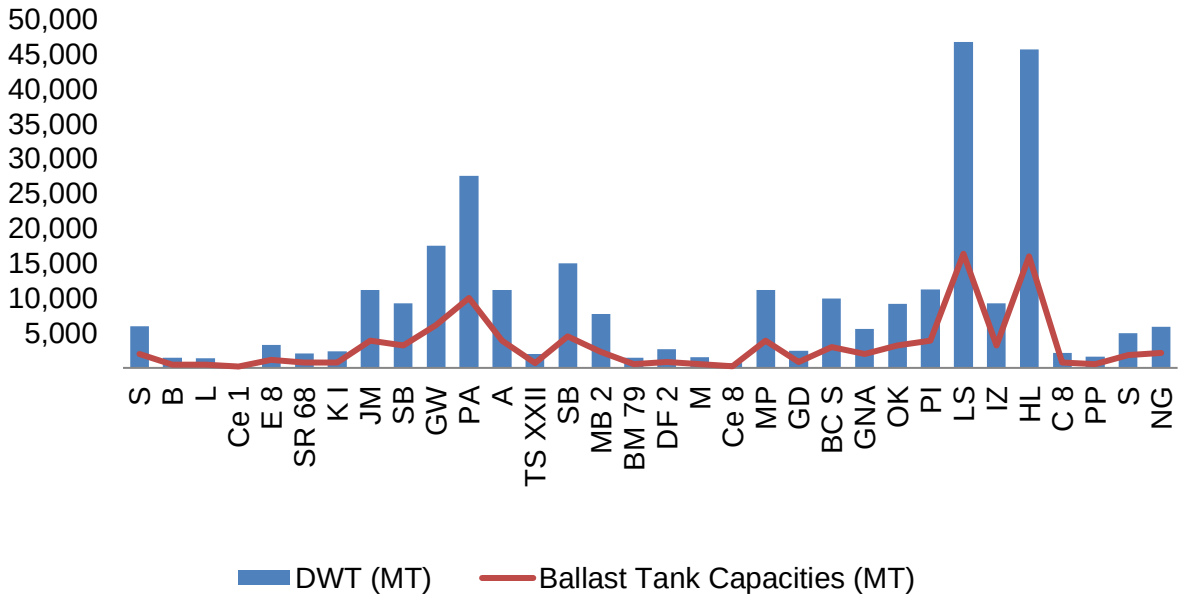


Figure 2. DWT and ballast tank capacities of vessels

The temperature of ballast water researched is about 28.4 to 32.4 ^{0}C. Ph is between 6.2 to 8.16. TSS and salinity ranges respectively are 1 to 686 mg l^{-1} and 1.6 to 36.3‰. DO is about 3.51 to 7.24 mg l^{-1}. The odor of all ballast water is nature, except for ballast water in S vessel, caused by oil content from the origin port, Jakarta (Table 1). Different salinity shows the different origin waters. The salinity of

4.8-12‰ is brackish waters, while the salinity of 30-40‰ is sea water. TSS above 400 mg l^{-1} shows that waters are dangerous for fishery [11].

Table 1. Results of ballast water of commercial vessels from in situ and ex situ

No.	Vessels/Parameter	Odors	TSS (mg l^{-1})	Temp. (^{0}C)	Ph	Salinity (ppm)	DO (mg l^{-1})
1.	S	Oily	686	30.6	6.92	36.3	NA
2.	B	Nature	28	31.2	7.71	34.7	NA
3.	L	Nature	30	29.6	7.39	34.1	6.24
4.	Ce 1	Nature	8	29.8	7.13	4.8	7.24
5.	E 8	Nature	7	29.1	6.3	28.7	6.72
6.	SR 68	Nature	7	29.1	6.72	20.4	6.52
7.	K1	Nature	6	28.4	8.16	1.6	6.52
8.	JM	Nature	7	30.8	6.71	31.1	5.27
9.	SB	Nature	6	30.6	6.92	31.2	5.07
10.	GW	Nature	6	30.3	7.01	30.8	5.37
11.	PA	Nature	3	32.4	7.97	27.5	4.83
12.	A	Nature	3	28.6	7.80	28.3	4.03
13.	TS XXII	Nature	7	30.3	7.24	12	4.23
14.	SB	Nature	3	28.4	7.59	27.1	5.24
15.	MB 2	Nature	1	28.9	6.63	11.3	6.14
16.	BM 79	Nature	2	29.6	6.68	31.3	5.85
17.	DF 2	Nature	2	29.4	7.65	30.8	6.22
18.	M	Nature	2	29.5	7.34	30.9	6.09
19.	Ce 8	Nature	2	29.5	7.44	22.2	5.49
20.	MP	Nature	2	29.8	7.26	11.6	5.09
21.	GD	Nature	1	31.5	7	31.5	5.01
22.	BC S	Nature	1	31.4	7.61	32	3.96
23.	GNA	Nature	1	31.4	7.18	29.5	5.77
24.	OK	Nature	1	31.4	7.05	28.8	5.40
25	PI	Nature	3.5	30.2	7.6	29.6	6.24
26	LS	Nature	1.5	30.8	7.4	28.7	6.12
27	IZ	Nature	2	30.3	8.0	28.7	4.03
28	HL	Nature	1	30.3	8.0	33.5	6.16
29	C 8	Nature	2.5	30.6	7.7	33.7	3.51
30	PP	Nature	37	30.5	7.4	32.4	4.29
31	S	Nature	6.5	30.6	6.2	7.7	6.52
32	NG	Nature	2	30.8	7.9	32.1	5.8

Note : NA (Not Available)

The passenger vessel of S, that has dead weight of 1,400 tons and berthed on December 19th 2014, has 11 of ballast water tank. They have total ballast water capacity of 818 tons. Sample was collected from ballast water tank number 61, starboard and port side tank. The tanks are interconnected. Her ballast water capacity was 76.3 tons. The ballast water origin is from Jakarta dockyard waters, oil polluted waters. The high content of TSS shows that ballast water contains high level of mud.

The passenger vessel of B, DWT of 1450 tons, was berthed on December 18th 2015. She has 11 ballast water tank with the total capacity of 819.3 tons. Sample is collected from ballast water tank number 32 (port side and starboard side tank). It has capacity of 218 tons. Ballast water origin is from Pontianak.

The passenger vessel of L, with DWT of 1,400 tons, was berthed on January 7th 2015. She also has 11 ballast water tank with the total capacity of 819.3tons. Sample is colleted from Double Bottom Deep tank number 32 (port side and starboard tank). She has ballast water capacity of 218.6 tons, its ballast water from Pontianak. Ce 1 vessel that loads rice is also from the same waters.

The fertilizer carriers of J and SB are from the same port of origin, Palembang. The vessels have dead weight of 11,615 and 9,237.4 tons respectively. Sample of ballast water from each of the vessel is collected from ballast water tank number 4 (port side) and number 3 (starboard side). While another fertilizer carrier, A, is from Jakarta.

Heavy metal is metal with the density of five gr cm^{-3}or more. It has atom number from 22 to 96 [6]. The characterictics of heavy metal are, it has bigger gravitational specification (more than 4), it has atom number responds of specific biochemistry on living organism [12]. The source of heavy metal pollutants are from natural and artificial sources. The natural source is from the coastal area (from rivers and coastal abrasion due to wave activity), metal released from volcanoes activity, and chemistry process. The artificial source is from industrial process of mining activity.

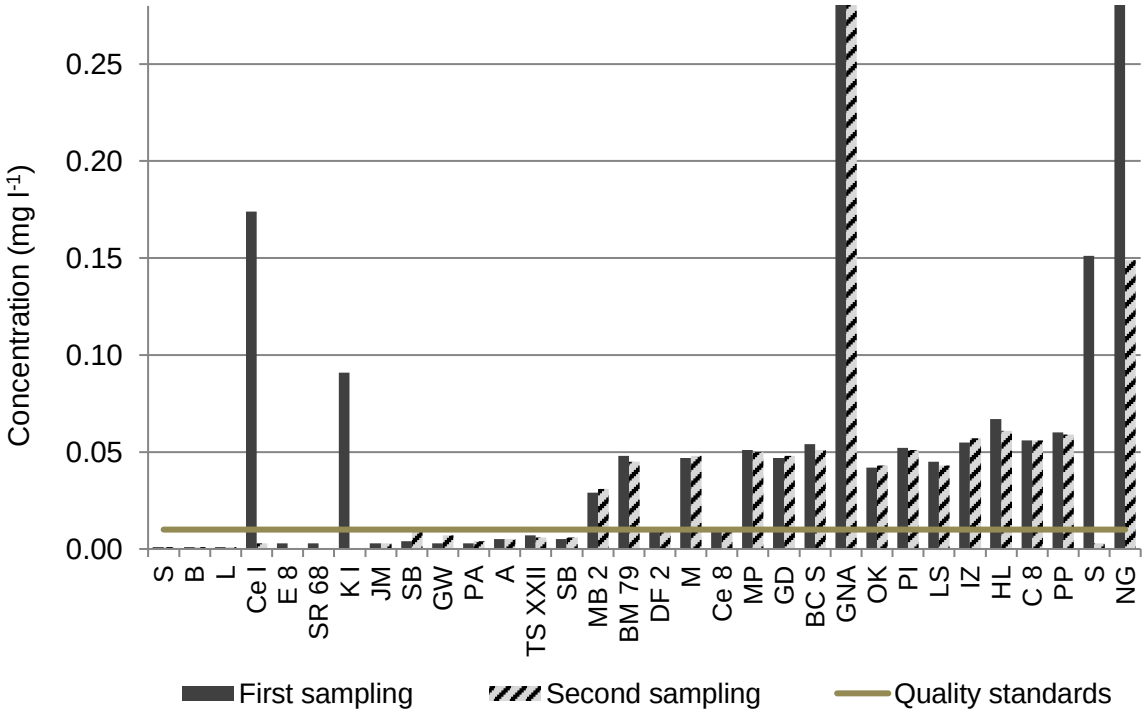


Figure 3. Cd concentration in ballast water of commercial vessels

Kadmium is widely spread out in the nature. The type of metal is mostly used in indutries as a stabilizer and alloy for battery industries, airplanes, weapons, and materials for welding. In waters, Cd solubility in certain concentration can be kill waters biota. In the concentration of 0.005-0.15 ppm, crustaceans

will be dead in 24-504 hours. In the concentration of 0.003-18 ppm, insects will be dead in 24-672 hours. In the concentration of 1.092-1.104 ppm, carps will be dead in 96 hours [13].

Kadmium concentration in ballast water of the vessel researched is from 0,001 to 0,46 mg l^{-1}. Passengger or Ro-Ro vessels studied are S, B, L, K1, and DF2. All of them still follow the quality standard, except K1 vessel. She exceeds the quality standard because there is only little water volume in the ballast water tank of the vessel. The vessel with Cd concentration of 0,003 to 0,057 mg l^{-1} are JM, SB, A, MP, OK, PI and IZ. Among other vessels that are from the same port, C8 and S also have the highest Cd content. TS XXII and GW tankers have Cd content of 0,003-0,007 mg l^{-1}. In addition, PA and SB vessels have Cd content of 0,003-0,006 mg l^{-1}. The Cd content in those vessels still fulfil the a standard required, except for C1 that is from Pontianak. The highest Cd content level in this research is in GNA on shipping dockyard because its ballast water is in minimum condition. NG vessel has the highest Cd content, it from Merak-polluted waters (Figure 3).

Zinc is plenty in nature. The level of Zinc in earch crust is about 70 mg kg^{-1}. The level of Zinc in waters is about 0.01 mg l^{-1}.Zinc is an essential source for living things. It can help enzime to work properly, it becomes an agent in transferring hydrogen in plant's photosynthesis, it has a part in protein fromation. Zinc is widely used in industries of iron and steel, paint, rubber, textile, paper and pulp [13].

The concentration of Zinc dissolved in ballast water of commercial vessels is 0.001 to 2.464 mg l^{-1}. DF2, it is a passenger vessel with the highest concentration of Zinc as well as it has content that of 21 times higher than quality standard, because there is only little volume that can be examined. OK has the highest content of Zn amomg all fertilizer carriers from same port. For container vessels and tankers, Zn content in SB and TS XXII exceeds the quality standard, about 0.56 to 0.65 mg l^{-1}. The content of high Zinc in ballast water of the vessels can be caused by age of the vessels. The passenger vessels, B and L are 21 years old. The fertilizer carriers, A and S, are about 29 to 30 years old, while the other vessels are about 10 years old. The second possibility is the origin port, has the highest concentration i.e. NG is from Merak waters (Figure 4).

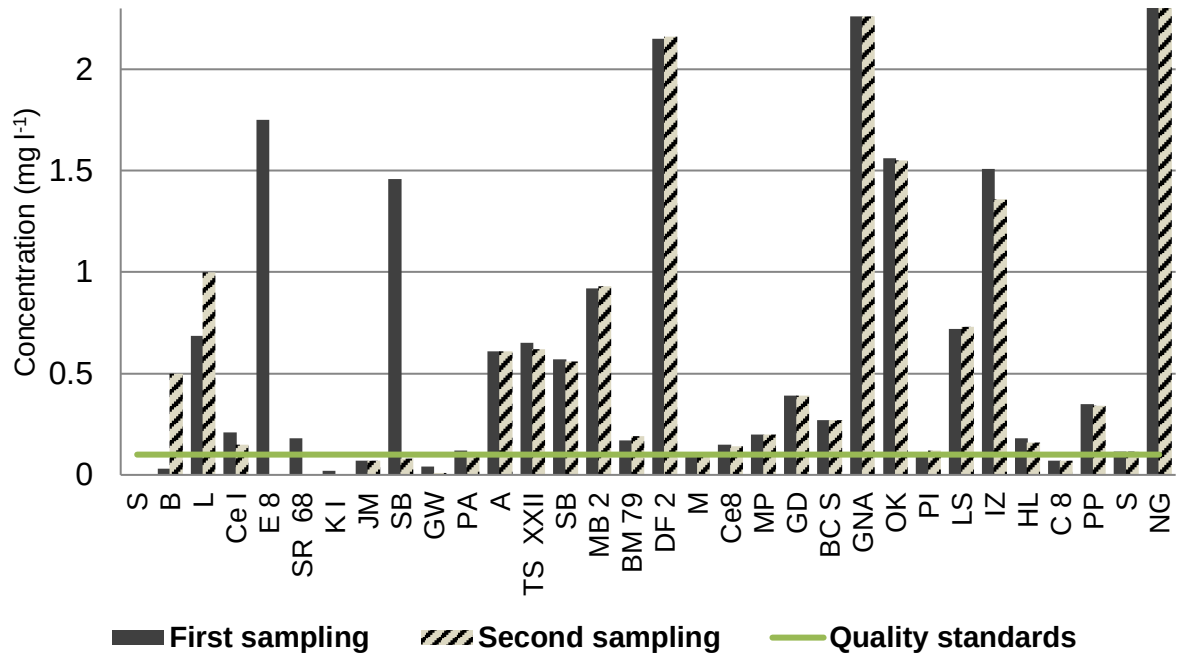


Figure 4. Zn concentration in ballast water of commercial vessels

The study shows the mean concentration of heavy metals of Cd and Zn respectively in a ballast tanks of commercial vessels are 0.04894 ± 0.07874 mg l^{-1} and 0.59122 ± 0.70373 mg l^{-1}. It shows that mean content of Cadmium from the ballast water of commercial ships is 49 times higher than the Bay of Jakarta and Cisadane estuaries, and 16 times higher than the Bangka waters. The mean content of Zinc in the ballast water of commercial ships showed 84 times higher than the Bay of Jakarta, 197 times higher than Cisadane estuaries and 147 times higher than the Bangka waters (Table 2).

Heavy metal pollution in the middle of Jakarta Bay in June and September 2003 was dominated by Zinc metal in order of Zn>Cu>Cd. Tanjung Priok port area becomes a place for vessels to dump their ballast water, industry and domestic wastes [14] (Table 3). The sample of ballast water from Tanjung Priok port is collected from A, GNA, M and MB2 vessels. The ballast water was dominated by Zinc with the average level of 0.9725 mg l^{-1}. It has exceeded the quality standard of the port 0.1 mg l^{-1} [17].

Table 2. Comparison of Research on Commercial Vessels and Other Research

Vessels/Waters	Metal concentration (mgl^{-1})		References
	Cd	Zn	
Vessels	0.001-0.46	0.001-2.464	Tjahjono, 2016*
Jakarta bay	< 0.001	< 0.001-0.007	Lestari & Edward, 2004
Cisadane estuaries	< 0.001-0.001	< 0.001-0.003	Rochyatun *et. al.*, 2006
Bangka waters	< 0.0001-0.003	0.001-0.004	Arifin, 2011

Table 3. Comparison of heavy metals (Zn and Cd) (mg l^{-1}) in sediments in the Bay of Jakarta and commercial vessels from Jakarta

Parameter	Research location (mg l^{-1})	
	Middle of Jakarta bay	Vessels from Jakarta
Zn	71.13-230.54	NA
Cd	0.001-0.28	0.005-0.282

Note : NA (Not Available)

4.Conclusion

The result of the study shows that the Cd content of ballast water vessels is a about 0.001-0.46 mg l^{-1}, and Zn is 0.001-2.464 mg l^{-1}. Heavy metal content of ballast water vessels are in order Zn>Cd. It happens because the vessels are quite old. It is also influenced by sea water of origin port. The content of heavy metal in the ballast water vessels shows that the vessels have not conducted ballast water exchange before entering to Tanjung PTES. The more frequency vessels entry and more dead weight, more dangerous the ballast water discharged into the port waters. It will put the marine environment around the port in danger.

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give permission to the technicians on board, and the staffs of Regional Health Laboratories Semarang in analyzing the samples.

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Glossary and Abbreviation

1. Portside : the left-hand side of or direction from a vessel, facing forward
2. Starboard : right-hand side of or direction from a vessel, facing forward
3. GM : measurement of the initial static stability of a floating body. It is calculated as the distance between the centre of gravity of a ship (G) and its meta center (M). A larger meta centric height implies greater initial stability against overturning.
4. Listing : the degree to which a vessel heels (leans or tilts) to either port or starboard. A listing vessel is stable and at equilibrium, but the distribution of weight aboard (often caused by uneven loading or flooding) causes it to heel to one side.
5. LPG : Liquid Petroleum Gas
6. Ro-Ro vessel : Roll-on/roll-off vessel, vessels designed to carry wheeled cargo, such as cars, trucks, semi-trailer trucks, trailers, and railroad cars, that are driven on and off the ship on their own wheels or using a platform vehicle, such as a self-propelled modular transporter.
7. Even-keel : balance condition of vessel with the same between forward (bow) and after (stern) draft.

8. Draft : the vertical distance between the waterline and the bottom of the hull (keel), with the thickness of the hull included; in the case of not being included the draft outline would be obtained. Draft determines the minimum depth of water a ship can safely navigate.
9. Dead weight : the difference between the displacement and the lightweight at any givin draft, measured in ton. Deadweight is the weight of cargo, fuel, stores, etc. That a vessel can carry.
10. DWT : Dead Weight Ton (ton)
11. TSS : Total Suspended Solid (mg l^{-1})
12. DO : Dissolved Oxigen (mg l^{-1})
13. MT : Metric Ton

Sources of Glossary and Abbreviation

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