MALAYSIAN JOURNAL OF ANALYTICAL SCIENCES

Published by The Malaysian Analytical Sciences Society

ISSN 1394 - 2506

ANALYSIS OF HEAVY METAL CONCENTRATIONS IN BALLAST WATER AND SEAWATER AT TANJUNG PELEPAS PORT

(Analisis Kandungan Kepekatan Logam Berat dalam Air Balast dan Air Laut di Pelabuhan Tanjung Pelepas)

Jacqueline Chong Kar Xin[1], Sharina Abu Hanifah[1,2]*, Nor Aishah Salleh[2], Normazida Rozi[1], Norfaizan Padli[2]

[1]*Centre for Advanced Materials and Renewable Resources, Faculty of Science and Technology*
[2]*Centre for Water Research and Analysis, Faculty of Science and Technology*
Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia

**Corresponding author: sharina@ukm.edu.my*

Received: 31 March 2018; Accepted: 17 April 2019

Abstract

Ballast water is water kept in the ballast tank of ships in order to increase its stability and balance during shipping. Although it helps in maintaining the ships' stability and safety, the exchange of ballast water causes the spreading of heavy metals present in the ballast tank to the surrounding seawater. Therefore, this research aims to investigate the spreading of heavy metals from ballast water taken from numerous countries and released at the Port Tanjung Pelepas. A comparison was done between seawater and ballast water samples using inductively coupled plasma optical emission spectrometer (ICP-OES) and the data were statistically analysed using Microsoft Excel. The results showed that Fe and Zn were detected at high concentrations in ballast water, while Fe was also highly concentrated in seawater. Besides that, this study found out that changes in weather is one of the factors that contribute to the differences in heavy metal concentrations in seawater.

Keywords: seawater, ballast water, heavy metals, statistical analysis

Abstrak

Air balast ialah air yang dibawa oleh sesebuah kapal dalam tangki balast untuk meningkatkan kestabilan dan keseimbangan semasa pelayaran. Akan tetapi, sistem pertukaran air balast juga akan menyebabkan kandungan logam berat dalam tangki balast tersebar kepada air persekitaran iaitu air laut. Oleh itu, kajian ini bertujuan untuk mengenalpasti penyebaran logam berat dalam air balast yang diambil dari pelbagai negara dan dilepaskan ke Pelabuhan Tanjung Pelepas. Perbandingan di antara sampel air persekitaran iaitu air laut dengan air balast telah dilakukan dengan menggunakan alat spektrometer pancaran plasma gandingan aruhan (ICP-OES) dan data yang diperoleh dianalisis secara statistik oleh Microsoft Excel. Hasil kajian menunjukkan bahawa Fe dan Zn dikesan mempunyai kepekatan paling tinggi dalam air balast manakala Fe pula mempunyai kepekatan paling tinggi dalam air laut. Selain itu, kajian ini juga mendapati bahawa perubahan cuaca merupakan salah satu faktor kepada perbezaan kepekatan logam berat air laut.

Kata kunci: air laut, air balast, logam berat, analisis statistik

Introduction

Malaysia is one of the countries that are rich with coastal areas and islands. These coastal areas have become potential areas for strong development. Rapid development does not only occur in land areas, but also in coastal areas and islands, particularly due to developments in the tourism, industry and agriculture sectors. Nevertheless, improper development planning has caused coastal areas to be exposed to pollution from heavy metals. This is a serious matter as heavy metals contained in seawater cannot be easily removed and can consequently affect the quality of seawater as well as food chains, which will then affect human and aquatic life [1].

Heavy metals constitute of metallic elements that have a relative density of 5 times higher than water which density is 1 g/cm^3 [2]. Heavy metals are also considered as trace elements as they are only found in trace concentrations (less than 10 ppm). Heavy metals are one of the anthropogenic pollutants in water [3]. Its mean that the toxicity of heavy metals exposed to the environment is attributable to human activities such as industrial and agricultural activities. Indirectly, industrial activities such as burning coal at power plants, nuclear power plant operations and plastic manufacturing have released heavy metals to the environment. Not only manufacturing activities, agricultural activities also give an impact through the use of arsenic insecticides. Naturally, there are several types of heavy metals needed by aquatic life in seawater such as copper (Cu), zinc (Zn), iron (Fe), manganese (Mn) and nickel (Ni). However, there are also heavy metals that are not directly needed by aquatic life and can have toxic effects on aquatic ecosystems such as cadmium (Cd), mercury (Hg), lead (Pb) and arsenic (As) [4].

In addition, ballast water carried by ships in their ballast tanks to enhance stability and balance during navigation can also be a cause of seawater pollution as it contains thousands of aquatic species as well as heavy metals that are transferred into the ship and then discharged out into the seawater before the cargo is loaded. It is impossible to neglect the harmful consequence of the physiochemical parameters of ballast water, such as the presence of heavy metals which has an adverse effect on marine life [5]. The International Maritime Organization (IMO) is a United Nations (UN) organisation responsible for safeguarding shipping safety and preventing pollution from ships. Under the IMO, there is a committee responsible for the management of ballast water. The Marine Environment Protection Committee (MEPC) established in 2004 was assigned to set rules for ballast water exchange management systems. Ballast water exchange systems have the potential to spread dangerous organisms classified as Invasive Aquatic Species (IAS) such as cholera (*Vibrio cholerae*) and toxic algae that can kill various types of marine life. In addition, the ballast water exchange system can also cause the spread of heavy metals in ballast tanks from one area to another [6]. The presence of heavy metals in the sea will certainly endanger marine life and thus give a negative impact on humans through the intake of seafood in their daily diets [7].

Thus, the present study attempts to analyse the distribution of heavy metals in seawater in the coastal areas of Tanjung Pelepas Port (Johor Bahru, Malaysia) and its correlation with ballast water originating from various parts of the world and discharged in the port area. The study chooses to focus on this area as this location is surrounded by nearby villages, industries, and development activities. Moreover, it is Malaysia's largest port. Every day, ships release ballast water that may contain heavy metals directly to this coastal area. This may increase the existing concentration of heavy metals in the surrounding seawaters. Aquatic organisms living in the seawater may accumulate these heavy metals. Villagers living nearby also depend on this coastal area for their daily consumption. The heavy metal pollution problem can thus affect humans' health through the food chain. Thus, investigation on this area is important. The data collected will be compared with the heavy metal concentrations set by the Malaysia Marine Water Quality Criteria and Standard (IMWQS) in order to evaluate the degree of contamination in this area.

Materials and Methods

Study area

This study uses seawater samples taken from ships' ballast water and the seawater surrounding Tanjung Pelepas Port. Samples of seawater were taken from four different areas situated along the Tanjung Pelepas Port, Johor. In addition, eight samples of ballast water were also obtained. Sampling for seawater was performed twice, while sampling for ballast water was done once. The yellow marks in Figure 1 show the surrounding waters' sampling areas. Table 1 shows the locations of study stations for the surrounding water, and Table 2 shows the sampling information of ballast water taken from ships originating from eight different countries.

Figure 1. Sampling locations at the Tanjung Pelepas Port (Source: Google Maps)

Table 1. Location of research stations for seawater according to the coordinates and description of the location

Station	Coordinate	Description of Location
1	N 1°19'29.91" E 103°33'23.40"	Station is an entrance point for ships to the Tanjung Pelepas Port.
2	N 1°19'53.19" E 103°33'14.08"	Station 2 is located along the Tanjung Pelepas Port.
3	N 1°20'19.36" E 103°33'1.41"	Station 3 is also an area along the Tanjung Pelepas Port but it is near the end of the port area.
4	N 1°20'40.27" E 103°32'41.39"	Station 4 is adjacent to a mangrove swamp area with a distance of 100 m.

Table 2. Information regarding ballast water sampling

Ship	Ship Name	Type of Ship	Origin of the Ship	Location of Ballast Water Collection	Retention Time (days)	Sampling Section
1	*Maersk Warsaw*	Container Ship	Portugal	Sihanoukville, Cambodia	6	Manhole
2	*MSC London*	Container Ship	Panama	South of China Sea (Open Sea)	2	Manhole
3	*Areopolis*	Container Ship	Monrovia, Liberia	Arboleas, Spain	5	Manhole
4	*MSC New York*	Container Ship	Panama	Rotterdam	40	Manhole
5	*MV. Olympia*	Container Ship	Marshall Island	Yangon	3	Manhole
6	*Ever Loading*	Container Ship	London	Jeddah	6	Manhole

Table 2 (cont'd). Information regarding ballast water sampling

Ship	Ship Name	Type of Ship	Origin of the Ship	Location of Ballast Water Collection	Retention Time (days)	Sampling Section
7	*SM Qingdao*	Container Ship	Liberia	South Africa	14	Manhole
8	*Ever Laden*	Container Ship	Panama	Suez Canal	25	Manhole

Sample collection

Plastic sample bottles were used for sampling. Before sampling, all of the bottles were immersed in detergent for one night and then rinsed with tap water. Firstly, these bottles were rinsed with 10% nitric acid, followed by tap water and deionised water. 1 L of the surrounding water samples were taken from each area. This means that there were four 1 L sample bottles for each area. For ballast water, samples were taken from eight different ballast tanks of ships coming from overseas. For each ship, 500 mL of water sample was obtained. Samples of the surrounding waters and ballast water were taken at depths of two to three metres from the sea level.

Measurement of physical and chemical parameters

The physical and chemical parameters of seawater should be measured directly after received of samples. The physical parameter measured was temperature (˚C). For chemical parameters, pH, salinity, dissolved oxygen and conductivity were measured *in situ*. These parameters were measured using a multimeter tool.

Sample preservation and digestion

The samples were filtered under a vacuum filtration method using a 0.45 μm membrane acetate cellulose. After that, the samples were treated to obtain a pH of less than 2 by adding 3 mL of nitric acid (1 + 1) into the 1 L sample. After the samples were preserved with nitric acid, they were kept in a chiller room at 4 ˚C. The samples can be stored for about 6 months [8].

100 mL of sample was taken from each station and heated to a temperature range from 70 to 80 ˚C. The water samples were heated until the volume of water was reduced to between 20 to 25 mL. This heating procedure must be done in a condition where no boiling occurs. After heating, 5 mL of ambient water samples for each station were taken and diluted with 1% nitric acid to 50 mL using a volumetric flask. A ratio of 1:10 was used for the dilution. After discharge, samples were sent to ICP-OES for heavy metal analysis. All these processes were performed for the other surrounding water and water ballast samples [9].

Analysis of data

Two types of preserved samples were digested and diluted before they were delivered to the inductively coupled plasma optical plasma emission spectrometer (ICP-OES) to measure their heavy metal concentration. The data obtained were analysed using Microsoft Excel software. ANOVA was further used to check if the means of two or more groups were significantly different from each other.

Results and Discussion

Physical and chemical analysis of seawater and ballast water samples

For the first and second sampling of seawater (surrounding waters), the pH range was recorded from 7.50 to 8.11. Referring to Scientific America, the average pH for seawater is 8.10. According to Doney et al., the reduction in pH is due to the absorption of carbon dioxide by seawater which is also known as 'sea acidification' [10]. A temperature range from 29.80 to 31.80 ˚C was recorded when the sampling was performed. Conductivity values from 45.68 to 50.53 mS/m and salinity values from 26.55 to 29.22 g/L were measured. The level of dissolved oxygen obtained was from 2.45 to 3.77 mg/L. Dissolved oxygen is the amount of oxygen contained in seawater for aquatic life. Based on the Malaysia Standard Water Quality Criteria and Standards (IMWQS), the standards dissolved oxygen determined for the port area should be 3 mg/L. However, the dissolved oxygen values of the first and second sampling did not reach the standard for seawater samples.

For ballast water sampling, a higher range of pH 2.00 to 6.89 was recorded. The pH values of the ballast water samples from all ships were lower than the pH values of the first and second seawater samples. This distinction may be due to the ships' water samples which came from foreign countries such as the Philippines, Africa and Cambodia. Therefore, their pH values were different than that of the Malaysian seawater because pH value depends on the activities carried out in the surrounding sea area. The temperature was recorded to range from 11.42 to 31.02 ˚C as sampling was carried out in the ship's ballast tank. The measured temperatures for all ballast water samples were also lower than the temperature of seawater at the Tanjung Pelepas Port as the ballast water was stored in ballast tanks within the range of 2 to 40 days. They have not been exposed to sunlight, thus causing the temperatures to decline.

On the other hand, seawater is out in the open and exposed to sunlight, thus its temperature was higher than the ballast water. The ballast water samples had also come from other countries which were likely experiencing winter, thus causing the ballast water's temperature to be lower. The levels of soluble oxygen measured ranged from 0.05 to 0.27 mg/L. The same explanation for temperature can also be applied to the value of dissolved oxygen in ballast water which was lower than the level of dissolved oxygen in the seawater taken at the port. Ballast water that is stored in closed ballast tank is not exposed to air like seawater. Additionally, the ballast water's conductivity was recorded ranging from 16.79 to 58.43 mS/m and the salinity ranged from 9.82 to 38.91 g/L. The conductivity and salinity values depend on weather and the fact that the ballast water samples had originated from overseas.

Analysis of heavy metal concentrations in seawater

Tables 3 and 4 show the levels of heavy metal concentrations that were detected in the first and second seawater samples, in which 11 types of heavy metals were studied. It was reported that it was raining on the second sampling day while the skies were sunny on the day of the first sampling. The difference in weather during sampling caused a difference in data between the two samples. Heavy metals such as Ag, Cr, Fe, Mn, Pb, Zn, Se and As showed higher concentrations in the first sampling compared to in the second sampling. Based on the study of relationship between season types and heavy metal concentrations of Lake Isikli in Turkey, they explained that heavy metal concentration decreases during rainy days as a result of a seawater dilution compared to seawater under hot weather [11]. In hot weather, the seawater temperature will increase and cause evaporation, thus increasing its heavy metal concentrations.

Table 3. Concentration of heavy metals during first sampling in seawater

Station	**Heavy Metal (mg/L)**										
	Ag	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**	**Se**	**As**
1	0.011	*nd*	0.028	0.026	0.171	0.020	0.014	0.019	0.055	0.070	0.003
2	0.022	*nd*	0.029	*nd*	0.158	0.031	*nd*	0.013	0.029	0.079	0.006
3	0.001	*nd*	0.032	*nd*	*nd*	0.015	*nd*	0.011	0.035	0.074	0.003
4	*nd*	*nd*	0.028	*nd*	*nd*	0.012	*nd*	0.011	0.025	0.065	*nd*

nd means not detected

Table 4. Concentration of heavy metals during second sampling in seawater

Station	Heavy Metal (mg/L)										
	Ag	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**	**Se**	**As**
1	0.008	*nd*	0.023	*nd*	0.038	0.009	*nd*	0.012	0.019	0.072	*nd*
2	0.010	*nd*	0.020	*nd*	0.024	0.008	*nd*	0.004	0.032	0.072	*nd*
3	0.004	*nd*	0.020	*nd*	0.027	0.008	*nd*	0.008	0.022	0.063	*nd*
4	0.005	*nd*	0.020	*nd*	0.027	0.008	*nd*	0.006	0.017	0.083	0.003

nd means not detected

Comparison of heavy metal concentrations in seawater between first and second sampling

A one-way ANOVA analysis was conducted to determine the significant differences between these two sampling due to weather differences occurring during the first and second sampling. The alpha value, α used for ANOVA analysis was 0.05. Results from ANOVA analysis for first and second sampling are summarised in Table 5.

Table 5. ANOVA analysis during the first and second sampling of seawater

Type of Heavy Metal	Ag	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	Se	As
Comparison between the 1st and 2nd sampling	-	*nd*	*	*nd*	-	*	*nd*	-	-	-	-

nd means not detected, * symbol means significant difference

The result of the ANOVA analysis shows that only heavy metals Cr and Mn showed significant differences between first and second sampling. The ANOVA analysis cannot be performed for Cd, Cu and Ni because their concentrations cannot be detected. For example, the concentrations of Cd cannot be detected for the first and second sampling, while for Cu and Ni, concentrations can only be detected from station 1 for the first sampling, while no data was obtained for all areas during the second sampling. Therefore, data comparison using ANOVA cannot be conducted. For the remaining heavy metals; Ag, Fe, Pb, Zn, Se and As, there were no significant differences observed.

Correlation analysis between physical and chemical parameters of heavy metal concentrations in seawater and ballast water samples

First sampling of seawater

Table 6 shows the correlation analysis performed to determine the relationship between the concentration of heavy metals and the physical and chemical parameters measured for the first sampling. A positive r value indicates that it is positively correlated. This means that if one of the value increases, the other value will also increase. A negative r value indicates that it is negatively correlated, which means that if one of the valueincrease, the other value decrease.

Based on Table 6, Ag has a significant and positive correlation with the other heavy metals i.e. Fe, Mn, As and Se because it has an r value that exceeds 0.70, but it also has a negative correlation with pH with an r value of -0.71. This means that if the concentration of Ag increases, then Fe, Mn, As and Se concentrations also increase, but the pH value will decrease. There was no r value calculated for Cd because no readings for Cd were detected from all four stations during the first sampling. Cr also gives a negative correlation with conductivity, while Cu shows a positive correlation with dissolved oxygen.

Fe shows a positive correlation with the temperature, conductivity and dissolved oxygen parameters. However, it has a negative correlation with pH. Mn also shows a positive correlation with Se and As, but shares a negative correlation with pH. Furthermore, Ni also has positive correlations with Pb, Zn, conductivity and dissolved oxygen, while Pb shows positive correlations with Zn, temperature, conductivity and dissolved oxygen.

Table 6. Correlation analysis between physicochemical parameters and concentration of heavy metals during the first sampling of seawater

DO (mg/L)	Sal. (g/L)	Cond. (mS/m)	Temp. (˚C)	pH	As	Se	Zn	Pb	Ni	Mn	Fe	Cu	Cr	Ag	
0.55	-0.28	0.68	0.67	-0.71**	0.79*	0.72*	0.15	0.48	0.19	0.98*	0.88*	0.19	-0.42	1.00	**Ag**
-0.15	-0.65	-0.78**	-0.09	0.04	0.19	0.33	-0.26	-0.56	-0.53	-0.24	-0.61	-0.53	1.00		**Cr**
0.76*	-0.03	0.81*	0.62	-0.53	0.02	-0.25	0.95	0.95	1.00	0.03	0.62	1.00			**Cu**
0.78*	-0.21	0.94*	0.81*	-0.80**	0.62	0.44	0.56	0.83	0.62	0.79*	1.00				**Fe**
0.50	-0.39	0.53	0.65	-0.70**	0.87*	0.84*	0.03	0.34	0.03	1.00					**Mn**
0.76*	-0.03	0.81*	0.62	-0.53	0.02	-0.25	0.95*	0.95*	1.00						**Ni**
0.88*	-0.17	0.92*	0.79*	-0.73	0.30	0.03	0.92*	1.00							**Pb**
0.86*	-0.31	0.69	0.74*	-0.66	0.17	-0.09	1.00								**Zn**
0.42	-0.76**	0.09	0.60	-0.68	0.96*	1.00									**Se**
0.65	-0.80	0.32	0.79*	-0.85	1.00										**As**
-0.95	0.74*	-0.65	-0.99	1.00											**pH**
0.98*	-0.70	0.69	1.00												**Temp. (˚C)**
0.73*	0.04	1.00													**Cond. (mS/m)**
-0.62	1.00														**Sal. (g/L)**
1.00															**DO (mg/L)**

*Significant positive correlation has been shown
**Significant negative correlation has been shown

In addition, Zn shows positive correlation with the temperature and dissolved oxygen parameters, but Se has a negative correlation with salinity and As shows a significant correlation with temperature. Finally, pH shows a significant correlation with salinity. In addition, dissolved oxygen shows a positive correlation with temperature and conductivity.

Second sampling of seawater

Table 7 shows the correlation analysis performed to determine the relationships between the concentration of heavy metals and the physical and chemical parameters measured during the second sampling of seawater. From the table, Ag shows a positive correlation with dissolved oxygen, while the correlations between Cd, Cu and Ni with the other parameters cannot be determined as these three heavy metals cannot be detected in the second sampling. Cr shows positive correlations with Fe, Pb, salinity, dissolved oxygen, and especially with Mn because its r value is 1.00

(fully correlated). Fe shows positive correlations with Mn and Pb, while Mn shows positive correlations with Pb, salinity and dissolved oxygen. In addition, Se also shows a positive correlation with As, but has a negative correlation with temperature. As also shows negative correlations with all physical and chemical parameters, and ultimately, all parameters displayed positive correlations with each other.

Table 7. Correlation analysis between physicochemical parameters and concentration of heavy metals during the second sampling of seawater

DO (mg/L)	Sal. (g/L)	Cond. (mS/m)	Temp. (˚C)	pH	As	Se	Zn	Pb	Mn	Fe	Cr	Ag	
0.76*	0.64	0.59	0.62	0.54	-0.42	0.08	0.68	-0.16	0.30	0.08	0.30	1.00	**Ag**
0.78*	0.71*	0.69	0.44	0.68	-0.33	-0.04	-0.35	0.88*	1.00*	0.97*	1.00		**Cr**
0.62	0.57	0.56	0.29	0.55	-0.22	-0.03	-0.54	0.95*	0.97*	1.00			**Fe**
0.78*	0.71*	0.69	0.44	0.68	-0.33	-0.04	-0.35	0.88*	1.00				**Mn**
0.49	0.52	0.53	0.28	0.55	-0.29	-0.25	-0.60	1.00					**Pb**
0.32	0.36	0.36	0.60	0.34	-0.55	-0.34	1.00						**Zn**
-0.28	-0.53	-0.58	-0.70*	-0.64	0.86	100							**Se**
-0.71**	-0.87**	-0.89**	-0.97*	-0.91**	1.00								**As**
0.92*	0.99*	1.00*	0.96*	1.00									**pH**
0.85*	0.95*	0.95*	1.00										**Temp. (˚C)**
0.94*	1.00*	1.00											**Cond. (mS/m)**
0.96*	1.00												**Sal. (g/L)**
1.00													**DO (mg/L)**

*Significant positive correlation
** Significant negative correlation

Ballast water sampling

Table 8 shows the correlation analysis conducted to determine the relationship between the concentration of heavy metals and the physical and chemical parameters measured for the ballast water sampling. Based on Table 8, r values of 0.00 were obtained for Cd, As and Ni because these heavy metals cannot be detected in the ballast water. Fe has strong and positive correlations with Mn, Pb, Zn and dissolved oxygen, but has negative correlations with the pH, conductivity and salinity parameters. Mn also has the same relationship as Fe. Pb and Zn show positive correlations with Zn and dissolved oxygen, but show negative correlations with other parameters except temperature. Finally, the pH parameter shows positive correlations with salinity and conductivity, but is negatively correlated with dissolved oxygen.

Table 8. Correlation analysis between physiochemical parameters and heavy metal concentrations in ballast water

DO (mg/L)	Sal. (g/L)	Cond. (mS/m)	Temp. (˚C)	pH	As	Se	Zn	Pb	Mn	Fe	Cu	Cr	Ag	
0.39	-0.41	-0.42	0.25	-0.59	0.00	-0.35	0.59	0.66	0.55	0.58	-0.28	0.19	1.00	**Ag**
0.45	-0.34	-0.34	0.03	-0.35	0.00	0.48	0.14	0.25	0.14	0.25	0.50	1.00		**Cr**
0.23	-0.09	-0.08	0.20	0.15	0.00	0.58	-0.15	-0.09	-0.13	-0.08	1.00			**Cu**
0.85*	-0.93**	-0.94**	0.08	-0.97**	0.00	-0.37	0.99*	0.99*	0.99*	1.00				**Fe**
0.82*	-0.91**	-0.92**	0.06	-0.95**	0.00	-0.42	1.00*	0.98*	1.00					**Mn**
0.83*	-0.87**	-0.89**	0.04	-0.95**	0.00	-0.33	0.98*	1.00						**Pb**
0.81*	-0.92**	-0.93**	0.11	-0.96*	0.00	-0.46	1.00							**Zn**
-0.24	0.35	0.35	-0.57	0.38	0.00	1.00								**Se**
0.00	0.00	0.00	0.00	0.00	1.00									**As**
-0.80**	0.93*	0.94*	-0.10	1.00										**pH**
0.20	-0.24	-0.24	1.00											**Temp. (˚C)**
-0.81**	1.00	1.00												**Cond. (mS/m)**
-0.80**	1.00													**Sal. (g/L)**
1.00														**DO (mg/L)**

*Significant positive correlation
** Significant negative correlation

Comparison of heavy metal concentrations between the first sampling of seawater and ballast water

The concentration of heavy metals in the first and second sampling cannot be predicted in order to show comparison with ballast water samples due to the significant differences in the levels of Cr and Mn. Therefore, the first sampling which was obtained on a sunny day was compared with the ballast water sampling as shown in Table 9.

Table 9. ANOVA analysis for the first sampling of surrounding water and ballast water

Type of Heavy Metal	Ag	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	Se	As
Comparison between first sampling of seawater and ballast water sampling	-	*nd*	*	-	-	-	*nd*	-	-	-	*nd*

nd means not detected, * symbol means significant difference

Based on the results of the ANOVA analysis, it can be seen that only Cr shows a significant difference between the first sampling of seawater and ballast water. The concentrations of Cd for both sampling cannot be detected; therefore, the ANOVA test for Cd cannot be performed. As for Ni and As, their concentrations cannot be detected in the ballast water sampling, thus the ANOVA test cannot be performed in comparison with seawater. There are no significant differences between both sampling for Ag, Cu, Fe, Mn, Pb, Zn and Se.

Concentration of heavy metals in ballast water

Table 10 shows the concentration of heavy metals for the ballast water samples which had originated from overseas. Eight types of ballast water samples were obtained in this study. Zn and Fe had the highest concentrations among the 11 types of heavy metals in all ballast water samples. The Malaysia Standard Water Quality Criteria and Standard (IMWQS) has set the standards for some heavy metals such as Cd, Cr, Cu, As, Pb and Zn.

Table 10. Heavy metal concentrations in ballast water

Ship	**Heavy Metal (mg/L)**										
	Ag	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**	**Se**	**As**
1	0.000	*nd*	0.009	*nd*	0.173	0.009	*nd*	0.008	1.136	0.039	*nd*
2	0.003	*nd*	0.019	*nd*	0.058	*nd*	*nd*	0.007	0.036	0.051	*nd*
3	0.000	*nd*	0.019	0.002	0.176	0.004	*nd*	0.009	0.136	0.080	*nd*
4	0.015	*nd*	0.018	*nd*	0.037	*nd*	*nd*	0.010	0.085	0.054	*nd*
5	0.002	*nd*	0.021	0.021	0.139	0.001	*nd*	0.007	0.137	0.068	*nd*
6	0.000	*nd*	0.019	*nd*	0.014	0.000	*nd*	0.005	0.043	0.044	*nd*
7	0.014	*nd*	0.021	0.003	3.224	0.057	*nd*	0.035	9.067	0.040	*nd*
8	0.000	*nd*	0.022	0.025	0.270	0.004	*nd*	0.010	0.160	0.072	*nd*

nd means not detected

The first ship which ballast water had originated from Cambodia showed a Zn level of 1.136 mg/L and a Fe level of 0.173 mg/L. These two types of metals had the highest concentrations in all types of heavy metals studied, and Zn had exceeded the concentration level determined by the Malaysian standard of 100 ppb (0.100 mg/L). When the Zn concentration levels were compared between the ballast water sample and the surrounding seawaters at Tanjung Pelepas Port, the Zn concentration in the seawater was still at a safe level of less than 100 ppb for all four sampling stations. Ballast water from the second ship had originated from South China Sea (Open Sea). The Fe and Zn concentrations for the second ship were also lower than other ships at 0.058 mg/L (Fe) and 0.036 mg/L (Zn). However, Zn concentration did not exceed the prescribed limit set by the Malaysian government. One of the reasons is that this ballast water sample was taken from the open sea, unlike water taken from port areas which are home to many activities such as shipping and other industrial activities that may contribute to the increase in heavy metal concentration.

The third ship which originated from Spain also had high concentrations of Fe and Zn at 0.176 mg/L and 0.136 mg/L respectively. The concentration of Zn exceeded the standard set by the Malaysian government. However, the concentrations of Zn and Fe in the sample taken from the fourth ship which came from the Rotterdam Port, Netherland did not exceed the standard set by Malaysia. The concentrations of Zn and Cu in the sample from the fifth ship which came from Yangon Port, Myanmar had also exceeded the Malaysian standards. The standard set by the Malaysian government for Cu is 10 ppb, however 21 ppb of Cu was detected in the sample from the fifth ship.

In addition, the concentration of Fe in the sample from the sixth ship was lower compared to other ships at only 0.014 mg/L. However, the Zn and Se levels of the sample recorded the highest concentrations. However, the values recorded for the sample from the sixth ship still did not exceed the Malaysian standard level. The sample from the seventh ship which originated from South Africa had the highest concentrations of Zn and Fe among all ships that were studied. The concentrations of Zn and Fe were detected at 9.067 mg/L and 3.224 mg/L. Zn concentration far exceeded the standards set by the Malaysian government. Based on the current sampling observation, the ballast water sample from the seventh ship was the muddiest and dirtiest of all ballast water samples collected. Ballast water from the eighth ship which originated from the Suez Canal Port in Egypt contained Zn levels exceeding the specified standard at a concentration of 0.160 mg/L, and its concentration of Fe was 0.270 mg/L. Cu was also present in the ballast water sample at a concentration of 0.025 mg/L. As for Cd, Ni and As, these heavy metals could not be traced in all ballast water samples. Cd was not found in all four stations for the first and second sampling of seawater. Ni and As could not be detected in some stations for both seawater sampling. The remaining heavy metals were still at a safe level as they did not exceed the specified standards.

Based on the concentration of detected heavy metals, Fe and Zn are the most detected metals in all ballast water samples. One of the factors of high Zn concentration is Zn has been widely used for corrosion protection in ships. Ballast water is seawater taken from the surrounding waters of a port and stored in a ballast tank made of iron. Thus, corrosion will occur due to the high level of salinity. During the ship building process, the surface of the ballast tank, cargo tank and other parts of the ship are coated with a Zn layer of nearly 120 µm thickness. This corrosion prevention method is a type of cathode protection where galvanization is done using Zn [12] Given that Zn is an important component of ships, therefore it explains why its concentration is one of the highest for heavy metals in ballast water.

The increase in Fe concentration levels of all samples may be due to the corrosion process. Corrosion occurs due to electrochemical processes where seawater which has ionic content attracts ions from other substances such as ion Fe^{2+} which may be withdrawn from the surface of the ballast tank. Seawater also has a high salinity level, and this will affect the conductivity of water. Then, Cl^- ions will enter the passive iron surface and try to pull ions inside the ballast tank by breaking the surface's passivity. The corrosion rate for iron in seawater is within the range of 0.1 to 0.3 mm/y, but it may increase to 2 to 4 mm/y if the seawater is contaminated with other corrosive materials. Thus, that may be the cause of high Fe concentrations in the collected seawater [13].

The first sampling (no rain occurring) was chosen to be compared to the ballast water samples because during a sunny day, dilution of seawater will not occur and affect the results. The concentrations of heavy metals such as Ag, Mn, Pb As and Se detected in the aquatic environment were higher due to the industrial activities happening around the port area. Cu and Ni can only be found at Station 1. Additionally, Fe, Pb, Zn and Cu concentrations were also high at Station 1. The concentration of Cu which was found only at Station 1 had exceeded the standards set by Malaysia. This may be due to ballast water discharge from ships entering the Tanjung Pelepas Port. Based on the information obtained during the sampling activity, ships release some ballast water before entering the port area because it helps stabilise the ship when anchored at port. Station 1 is an entry point into the port. The discharge of ballast water will cause heavy metals to spread from the ships' ballast water to Station 1 through natural phenomena such as high tide and low tide. The phenomena may contribute to the high concentration of some heavy metals at Station 1. Using this comparison, it is evident that Fe and Zn had the highest concentrations. As for the concentration of Pb that was higher in seawater than the ballast water, it was due to the smoke released by ships anchored at Tanjung Pelepas Port.

Furthermore, it can be seen that Zn and Cu were the two types of heavy metals that had exceeded the standards set by Malaysia in both seawater and ballast water. Zn and Cu are minerals required by the human body, but excessive amounts can cause health problems such as skin diseases and anaemia. The concentration of Fe was also very high in both types of samples, although it is not listed in the Malaysian standard. Fe is also an important element for the human body especially in the blood, but if it exceeds the limit, it will become a radical that is capable to do damage to human tissue cells. Based on the information collected during the sampling activity, a nearby area designated for fishing activity and mussel farming can be affected as the heavy metal content in both ballast water and seawater can be very hazardous and affect not only the water quality at the port but also the marine life and subsequently, humans through seafood consumption.

Conclusion

In conclusion, the weather factor can be one of the causes affecting the concentration of heavy metals in seawater. From the ANOVA analyses, it can be proved that the concentrations of Cr and Cd in both types of samples showed a significant difference. Furthermore, Fe showed the highest concentration of heavy metals in the aquatic environment. Fe and Zn showed highest concentrations in ballast water, thus have the potential to affect the water quality at Tanjung Pelepas Port through the ballast water release process. The cargo or container loading activities carried out within the port area requires the discharge of ballast water before the process to ensure the stability of the ships. Through this process, the concentration of heavy metals in ballast water will be spread out to the port area. Therefore, this research has provides a feasible reference for future studies of onsite monitoring of water quality at the port and contribute to the idea in developed a simple, rapid and sensitive method for an onsite monitoring activity at the port such as sensor in order to control the release of heavy metals at the port area all around the world.

Acknowledgement

I would like to extend my appreciation to Universiti Kebangsaan Malaysia (UKM) Bangi, Selangor for providing the research grant GUP-2016-061 and GUP-2018-025. I would also like to thank the Marine Science UKM research group for their kind help in collecting the seawater and ballast water samples needed for this study.

References

1. Hsiang Tan, W., Tair, R., Aishah, S., Ali, M., Talibe, A., Sualin, F. and Payus, C. (2016). Distribution of heavy metals in seawater and surface sediment in coastal area of Tuaran, Sabah. *Transactions on Science and Technology*, 3(12): 114-122.
2. Tchounwou, P. B., Yedjou, C. G., Patlolla, A. K. and Sutton, D. J. (2012). Heavy metals toxicity and the environment. *National Institutes of Health Public Access*, 101: 133-164.
3. Naser, H. A. (2013). Assessment and management of heavy metal pollution in the marine environment of the Arabian Gulf: A review. *Marine Pollution Bulletin*, 72(1): 6–13.
4. Tavakoly Sany, S. B., Salleh, A., Rezayi, M., Saadati, N., Narimany, L. and Tehrani, G. M. (2013). Distribution and contamination of heavy metal in the coastal sediments of Port Klang, Selangor, Malaysia. *Water, Air, and Soil Pollution*, 224(4): 1476.
5. Nosrati-Ghods, N., Ghadiri, M. and Früh, W.-G. (2017). Management and environmental risk study of the physicochemical parameters of ballast water. *Marine Pollution Bulletin*, 114(1): 428–438.
6. International Maritime Organization. (2017). Ballast Water Management. Access from http://www.imo.org/en/OurWork/Environment/BallastWaterManagement/Pages/Default.aspx [Access online 10 October 2017]
7. Yunus, S. M., Hamzah, Z., Wood, A. K. and Ahmad. (2015). Assessment of heavy metals in seawater and fish tissues at Pulau Indah, Selangor, Malaysia. *AIP Conference Proceedings*, 1659: 050007.
8. Greenberg, A. E., Clesceri, L. S. and Eaton, A. D. (1992). Standard methods for the examination of water and wastewater. United States of America: American Public Health Association.
9. Noor, A. A. H., Farah, F. M. Z., Mohd, I. I. and Nik, A. N. A. (2015). Assessment of selected heavy metals in seawater and sediment at Klang coastal area Malaysia. *Malaysian Journal of Analytical Sciences*, 19(4): 730-738.
10. Doney, S. C., Fabry, V. J., Freely, R. A., Kleypas, J. A. (2009). Ocean acidification: The other CO_2 problem. *Annual Review of Marine Science*, 1(1): 169-192.
11. Tekin-özan, S. and Aktan, N. (2012). Relationship of heavy metals in water, sediment and tissues with total length, weight and seasons of *Cyprinus carpio* L., 1758 from Işikli Lake (Turkey). *Pakistan Journal of Zoology, 44*(5), 1405–1416.
12. BMT Defense Services (2009). The feasibility of a corrosion resistant ship. Access from https://www.bmtdsl.co.uk/media/1058725/BMTDSL-Corrosion-Resistant-Ship-Whitepaper.pdf[Access online 22 Mei 2018].
13. Aldez, B., Ramirez, J., Eliezer, A., Schorr, M., Ramos, R. and Salinas, R. (2016). Corrosion assessment of infrastructure assets in coastal seas. *Journal of Marine Engineering and Technology*, 15(3): 124-134.