

Metal Contents and Pb Isotopes in the Surface Seawater of the Gulf of Prigi, Indonesia: Detection of Anthropogenic and Natural Sources

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In order to investigate the anthropogenic and natural sources of metals in the Gulf of Prigi, Indonesia, it was analyzed their metal contents and Pb isotopes of surface seawater together with sediment, grouper fish, mosh, seaweed, soil, and sharp grass for protecting the environmental pollution of the study area. Samples were leached using a microwave digestion technique. Metal (Ca, Fe, Mn, Cu and Pb) concentrations and ²⁰⁶Pb, ²⁰⁷Pb and ²⁰⁸Pb in the leached solutions were analyzed using inductively coupled plasma-mass spectrometry (ICP-MS). The level concentrations of Ca (491436 µg kg⁻¹), Fe (12123 µg kg⁻¹), Mn (37.2 µg kg⁻¹), Cu (84.0 µg kg⁻¹) and Pb (34.5 µg kg⁻¹) in the surface seawater were low compared with those of background seawater levels issued by World Health Organization (WHO). The range of Pb isotope ratios (²⁰⁷Pb / ²⁰⁶Pb = 0.7966-0.9945 and ²⁰⁸Pb / ²⁰⁶Pb = 2.2600-2.8243) in surface seawater was higher in the plotted Pb growth curve suggesting unpolluted Pb reflected by natural sources such as mineral sources or lithogenic from marine sediment.

Keywords: seawater, Pb isotopes, metals, Gulf of Prigi, natural sources

Introduction

Seawater is primarily used to inform the anthropogenic and natural sources of elements (including metals). Assessment of metal contents affected by physical, chemical and biological characteristics of surface seawater are vital substances as a major health controlling the living organism surrounding the sea. Variations of anthropogenic and natural sources are caused by mobilization of metal due to fresh water and pollutant from rivers, precipitation, and evaporation processes in the sea forming their geochemical fractions. Some researchers investigated the metal contents, stable isotopes and their geochemical fractions of sediment in the river adjacent sea for monitoring seawater pollution.¹⁻⁶

The status of seawater can be monitored using their level of metal contents in water, sediment, seaweed, coral reefs and then identified to investigate their source of metal contents using stable isotopes analysis, such as δ¹¹B, δ¹⁸O, δ¹³C, δ¹⁵N and Pb isotope ratios (²⁰⁸Pb / ²⁰⁶Pb vs. ²⁰⁷Pb / ²⁰⁶Pb). The contaminant of [F⁻] in seawater is reflected by the F / Ca in non-symbiotic corals (*Flabellum* sp.).³ Using the two stable isotopes (δ¹¹B) with their composition, such as ¹⁰B (ca. 20%) and ¹¹B (ca. 80%), provided the important information on the global geochemical cycle and metals mobility. The fractionations of ¹¹B released the dominant boron species of B(OH)₃ and B(OH)₄⁻ incorporating into marine carbonates (corals) which reflected the history of seawater records and level of pH associated with the coral growth. The pattern of two cyclic changes in δ¹⁸O and δ¹³C in coral aragonite indicates an annual change in seawater salinity.⁷ Stable

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isotopes of $\delta^{13}\text{C}$ and $\delta^{15}\text{C}$ showed enrichment in muscle (0.5 and 1.3%), liver (1.3 and 1.0%), and whole fish tissues of brown-marbled groupers (*Epinephelus fuscoguttatus*).⁸ However, the use of stable isotopes of $\delta^{11}\text{B}$, $\delta^{18}\text{O}$, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ cannot distinguish anthropogenic and natural sources. To address this, previous studies have recommended using Pb isotope ratios ($^{208}\text{Pb}/^{206}\text{Pb}$ vs. $^{207}\text{Pb}/^{206}\text{Pb}$) as reflecting the anthropogenic and natural sources.^{4,5,9,10}

The use of Pb stable isotope analysis in seawater is based on the premise that Pb isotopes are introduced as “fingerprints” of each anthropogenic or natural source of Pb, which can have unique isotopic ratio values. Pb has four main isotopes: ^{208}Pb (52%), ^{206}Pb (24%), ^{207}Pb (23%) and ^{204}Pb (1%), while radiogenic isotopes ^{206}Pb , ^{207}Pb and ^{208}Pb are produced as the decay of ^{238}U , ^{235}U and ^{232}Th , respectively. The ^{204}Pb is the only primordial stable isotope with a constant abundance on the Earth.⁴ The abundance of Pb isotopes in a sample strictly depends on the concentrations of primordial Pb, U and Th and the lengths of the closed system, i.e., half-lives ($t^{1/2}$) of the parent isotopes. The three radioactive isotopes ^{210}Pb ($t^{1/2} = 22$ years), ^{212}Pb ($t^{1/2} = 10$ h) and ^{214}Pb ($t^{1/2} = 26.8$ min) are commonly used in determining the history and sources of anthropogenic Pb inputs into the environment.^{11,12} Furthermore, ^{210}Pb , for its convenient half-life, is widely used for dating of seawater, glacial ice, recent sediments and peat deposits.^{13,14}

The isotopic composition of Pb is not significantly affected by physico-chemical fractionation processes. Pb isotopes provide an efficient tool for determining the sources and pathways of Pb pollution.^{15,16} The isotopic composition of Pb in the Earth (and especially in seawater) is commonly expressed as ratios $^{206}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$, with the latter being the most preferred since it can be determined precisely and the abundances of these isotopes are relatively vital. However, normalization to ^{204}Pb ($^{206}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$) yields the largest variability between reservoirs. Furthermore, the abundance of ^{207}Pb has slightly changed with time compared to ^{206}Pb because most ^{235}U has already decayed, while ^{238}U still has a relatively high abundance on the earth and seawater.¹⁷ For example, while old Pb ores are generally characterized by low $^{206}\text{Pb}/^{207}\text{Pb}$ ratios (1.06-1.10), more recent samples containing more radiogenic Pb (originating from U and Th decay) reflect higher $^{206}\text{Pb}/^{207}\text{Pb}$ ratios (> 1.18).^{18,19} For the use of Pb isotopes to “track” the origin of contamination, the values of $^{206}\text{Pb}/^{207}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ are more commonly compared with the ^{204}Pb . ^{204}Pb does not change its value and is not of much interest as to distinguish between ratio values. The use of Pb isotope ratios have been studied in many sites for tracking the origin of contamination in plants, mammals,

river sediment and ocean water.^{4,5,10} The growth curves of the Pb isotopes have been applied in many cases to address Pb pollution.⁹ The growth curve can be expressed using the ratios $^{208}\text{Pb}/^{206}\text{Pb}$ against $^{207}\text{Pb}/^{206}\text{Pb}$, or $^{206}\text{Pb}/^{207}\text{Pb}$. Some researchers widely used $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ because the ^{206}Pb isotope is more abundant than ^{207}Pb and is therefore more suitable as a reference isotope. In addition, $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ are chosen for practical reasons including more frequent use of this previous research for similar locations and materials.^{4,5,9,10}

The Gulf of Prigi, Indonesia, is one of the business centers for fisheries, recreation, and ecotourism on the southern coast of Java Island. The position of this Gulf is directly adjacent to the Indian Ocean, which has many coastal areas and the great potential for mobilization of metals and nutrients in seawater. All of anthropogenic and natural activities can contribute metals such as Ca, Fe, Mn, Cu and Pb in seawater. Those metals are essentially required for living organisms in specific concentration, but possibly produce high toxic effects in high concentrations. Some metals such as Pb, Zn, Cu, Fe and Mn are extremely toxic owing to their toxicity, persistent and bio-accumulative nature to induce multiple organ damage, even at lower levels of exposure. Because of activities in the Gulf of Prigi associated with environmental and health protections, the monitoring of metal contents in its surrounding seawater is quite imperative in order to investigate their sources. Here, we firstly report the level of metal contents and investigate the Pb isotopes in seawater associated with anthropogenic and natural sources in the Gulf of Prigi. In addition, we continue detecting their sources using the application of $^{208}\text{Pb}/^{206}\text{Pb}$ vs. $^{207}\text{Pb}/^{206}\text{Pb}$ with the modelling single stage one on the Pb growth curves.

Experimental

Sample collection and pretreatment for analysis

A total of 24 samples of surface seawater were collected from the southern part of the Gulf of Prigi, from January to July 2017 (Figure 1, Table 1).

In order to investigate the source of anthropogenic and natural sources, we also collected the sediment, grouper fish, moss, seaweed, soil, and sharp grass surrounding the gulf. All samples were collected in the surroundings of the floating home, which is located in the middle of the Gulf of Prigi. During seawater sampling, temperature (T), pH, electrical conductivity (EC), and turbidity were measured at several sites (samples SW1 up to SW24) using water quality checker (WQC) 22A. Salinity of surface seawater was measured by salinometer Atago S-28E. Sulfate concentrations in seawater

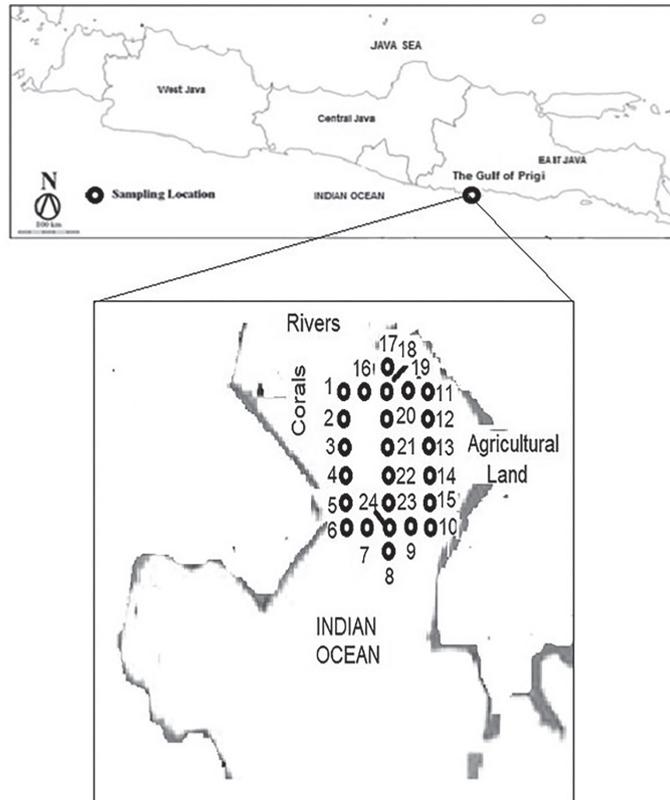


Figure 1. Map showing sampling locations of surface seawater in the middle of the Gulf of Prigi.

Table 1. Physical and chemical parameters of surface seawater in the Gulf of Prigi

Sample	Temperature / °C	Salinity / ‰	DO / (mg L ⁻¹)	EC / mS	pH	COD / (mg L ⁻¹)	Turbidity / (NTU)	Sulfate / ppm	BOD / (mg L ⁻¹)
SW1 ^a	30.1	3.40	6.30	3.15	6.70	94	0.24	16.2	2.92
SW2	30.1	3.40	6.96	3.48	6.70	35	0.38	29.5	ND
SW3	30.1	3.40	14.2	7.10	6.60	7582	0.29	25.2	12.3
SW4	30.1	3.40	7.59	3.80	6.60	95	0.26	21.9	ND
SW5	30.2	3.40	11.6	5.78	6.70	1621	0.37	17.9	ND
SW6	30.6	3.40	15.6	7.79	6.70	125	0.27	14.9	ND
SW7	30.2	3.40	13.1	6.53	6.70	4706	0.27	22.7	ND
SW8	30.3	3.40	12.9	6.45	6.30	3198	1.55	18.1	4.63
SW9	30.2	3.40	14.3	7.13	6.80	3038	0.68	15.5	2.86
SW10	30.2	3.40	13.3	6.63	6.70	3118	0.40	13.7	11.6
SW11	30.2	3.40	8.85	4.43	6.70	417	0.34	9.20	19.5
SW12	30.1	3.40	13.4	6.70	6.60	4938	0.38	14.5	0.03
SW13	30.1	3.40	13.1	6.56	6.70	2656	0.11	12.0	3.78
SW14	30.0	3.40	13.7	6.84	6.70	3438	0.28	14.0	2.47
SW15	30.1	3.40	13.7	6.87	6.40	3898	0.37	12.9	2.47
SW16	30.1	3.40	14.9	7.47	6.40	3778	0.43	11.7	1.85
SW17	30.0	3.50	15.5	7.77	6.40	2080	0.41	10.5	7.36
SW18	29.9	3.20	2.80	1.40	6.50	2420	0.53	75.9	6.83
SW19	30.0	3.50	1.46	44.5	6.57	2720	0.56	50.2	14.9
SW20	29.9	3.20	2.10	43.6	6.51	2500	0.40	22.6	5.67
SW21	29.9	3.20	12.7	43.6	6.57	2860	0.53	63.7	11.0
SW22	29.9	3.20	2.09	44.6	6.56	2460	0.53	61.4	1.34
SW23	30.1	3.40	2.75	44.4	6.56	3020	0.55	68.5	0.43
SW24	30.3	3.60	1.78	44.8	6.59	2840	0.39	68.5	1.81

^aSeawater. DO: dissolved oxygen; EC: electrical conductivity; COD: chemical oxygen demand; NTU: nephelometric turbidity unit; BOD: biological oxygen demand; ND: not determined.

were determined by colorimetry. Chemical oxygen demand (COD) was measured using dichromate reflux technique standard method. Dissolved oxygen (DO) and biological oxygen demand (BOD) in seawater were determined by the Winkler method. The chlorophyll *a* was determined by spectroscopic method at 32 spot locations (SP1 to SP32) for detecting natural sources and then mapping using the Surfer 10.0 software²⁰ (Figure 2).

For seawater analysis, the chromatography column was prepared before sample digestion. The column was attached by glass wool at the end of column prior to filling the slurry (1 g Chelex-100 resin containing 100-200 mesh Na form in NH_4OH solution). The filled resin column was conditioned at pH 7 using $\text{CH}_3\text{COONH}_4$ to convert the active sites of the resin into ammonium form for reducing the potential interference of the salt matrix in seawater analysis.²¹ After exiting the resin, 7 mL of the sample in a 120 mL Teflon-perfluoroalkoxy (PFA) microwave digestion vessel were digested using a closed microwave oven system (CEM MARS 6). We used ultrapure grade HNO_3 (69%, specific gravity 1.42, Fluka) for digesting cycles at 10-15 min and then analyzing for Ca, Fe, Mn, Cu, and Pb using inductively coupled plasma mass spectrometry (ICP-MS).

The accuracy of the method was confirmed by analyzing certified reference materials (LGC-6187 and BCR-141R), revealing good agreement (recoveries = 81-122%) between the certified and the measured values.²²

Sediment, grouper fish, moss, seaweed, soil, and sharp grass samples were dried in an oven at ca. 70 °C until they were completely dried (approximately 12 h). The dried samples were kept in a clean plastic, then ground and homogenized in an agate mortar and sifted through a polyethylene sieve of less than ca. 50 μm . All plastic, hair, wood, and paper were removed from samples. Finally, the fine-grained fraction samples were also kept enclosed in a clean plastic bag to prevent contamination. We used the total leaching metal contents for these samples using microwave digestion,⁶ as follows: 10.0-11.0 mg of dry sediment, grouper fish, moss, seaweed, soil, and sharp grass samples were leached with 1 mL of HNO_3 (15.3 M) in 7 mL vials, subjected to continuous shaking for 24 h, put in a sonic bath for 30 min and centrifuged for 10 min, respectively. The supernatant solution was then put in a sonic bath for 30 min and then centrifuged at 100 rpm for 10 min. After the resultant residue was heated to 110 °C, 3 drops of HF and 3 drops of HNO_3 (15.3 M) were added,

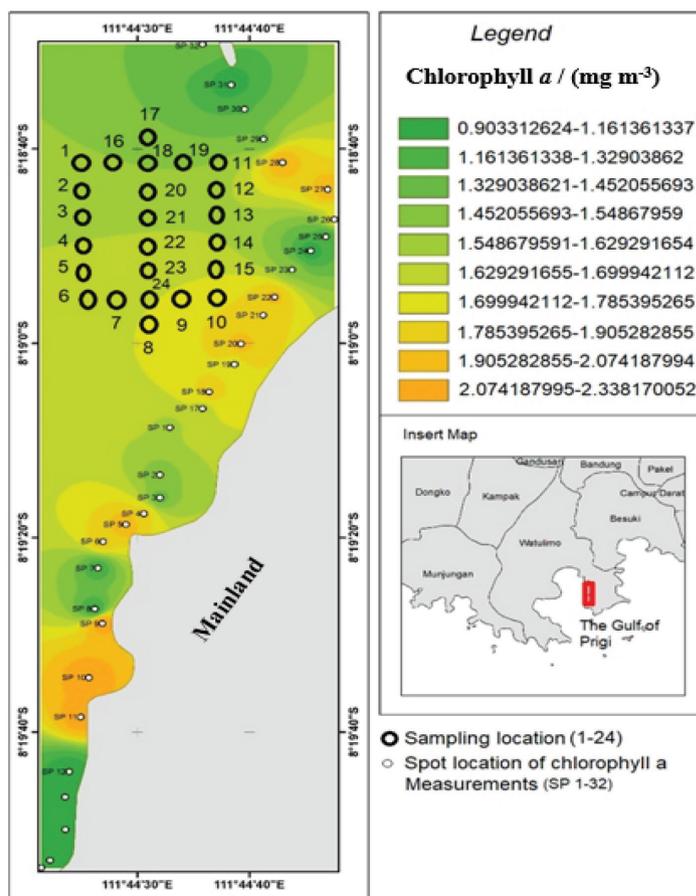


Figure 2. Map of chlorophyll *a* distributions in the Gulf of Prigi.

and it was heated again until dry. Then the residue was dissolved and diluted with 1 mL 1% HNO₃ five times. The total leached supernatant and residue samples were finally mixed and poured into a 7 mL polyethylene tube for ICP-MS analysis.

ICP-MS analysis

Total concentrations of Ca, Fe, Mn, Cu, Fe and Pb isotopes in leached solutions of seawater, sediment, grouper fish, moss, seaweed, soil, and sharp grass samples were analyzed by ICP-MS (NexION 300, PerkinElmer). The concentrations of ICP-MS-68B standard solution A were set to be 0.25, 0.50, 0.75, 1, 10 and 100 µg L⁻¹. The sample uptake rate of ICP-MS was ca. 0.1 mL min⁻¹ adjusted by micro flow perfluoro-alkoxy (PFA) nebulizer. The operation for integration was 3 s *per* mass and radio frequency (RF) power was 1.3 kW, while reflected power was smaller than 1.0 W. The flow rates of the plasma and nebulizer gas (argon) were 16.0 and 1.0 L min⁻¹, respectively.

All samples were counted three times *per* run. The concentration of metals was determined using a calibration method with correlation coefficient (r²) ranging from 0.99 to 1.00. Analyses in the leached solutions were converted and calculated on a dry weight basis. The detection limits of Ca, Fe, Mn, Cu, and Pb were found to be 0.10, 0.10, 0.10, 0.68, and 0.30 g mL⁻¹, respectively. The precision of the method was evaluated by standard certified reference material of coastal seawater (CASS-4) and the results varied between 0.7 and 1.3% (relative standard deviation; RSD) (n = 5).²³

Index of pollutant (anthropogenic) and natural assessment of metal in seawater

Pollution load index (PLI)

We modified the PLI to assess the metal contents data in seawater using the background values.²⁴ The mathematical equation using PLI can be written as follows:

$$PLI = \sqrt[4]{\frac{(Fe)}{(Fe)b} \times \frac{(Mn)}{(Mn)b} \times \frac{(Cu)}{(Cu)b} \times \frac{(Pb)}{(Pb)b}} \quad (1)$$

where 4 is the number of measured metal contents in seawater collected from the study area. The terms $\frac{(Fe)}{(Fe)b}$, $\frac{(Mn)}{(Mn)b}$, $\frac{(Cu)}{(Cu)b}$, $\frac{(Pb)}{(Pb)b}$ indicate the highest concentration of measured metals for each site *per* their metal background (b). Polluted sample (anthropogenic) is indicated by PLI value > 1, while unpolluted (natural) is specified by PLI < 1.^{5,25}

Index of the non-carcinogenic/chronic risk (hazard quotient, HQ)

The HQ is measured to estimate the non-carcinogenic or chronic risk of seawater in the Gulf of Prigi. If the value of HQ is lower than 1, it is assumed to be safe, whereas HQ greater than 1 indicates chronic risk.^{5,26,27} The HQ is expressed by applying the following equation:

$$HQ = ADD / RfD \quad (2)$$

where average daily dose (ADD) is defined here as $ADD = C_m \times IR / BW$. C_m, IR and BW are the measured concentration of metal in seawater samples, the water ingestion rate (2 L day⁻¹) and the average Indonesian's body weight (65 kg), respectively. The reference dose (RfD) is the data of the oral toxicity reference dose values.²⁸ The value of RfD is given as follows: Fe = 0.07 mg kg⁻¹ day⁻¹, Mn = 1.4 × 10⁻¹ mg kg⁻¹ day⁻¹, Cu = 3.7 × 10⁻² mg kg⁻¹ day⁻¹, and Pb = 3.6 × 10⁻² mg kg⁻¹ day⁻¹.

Results and Discussion

Chemical-physical parameters and metal contents of surface seawater (SW samples)

Analytical results of SW1-SW24 at the study site are listed in Table 1. Water temperature at different sites varied from 29.9-30.6 °C during the day on the sampling date (January-June 2017), while air temperature was ca. 30 °C. According to the East Java meteorological observatory, water temperature of seawater in the Gulf of Prigi ranged from 29-30 °C during the last 10 years. Our temperature data implies that the observation was performed on one of the hottest days in the year, whereby it has a large influence on climate and weather surrounding the region of East Java. The high temperature of seawater was possibly affected by the interaction between atmosphere and the Indian Ocean.

Seawater salinity of SW1-SW24 ranged from 32.0-36.0 psu (practical salinity units) and it increased with elevating surface water temperature (Table 1). The high salinity of SW1-SW24 (34.0-36.0 psu), except for SW18, SW20, SW21 and SW22, was possibly governed by the high evaporation of surface water in the Gulf of Prigi at day time. The salinity of oceanic water ranged from 33.6-34.1 psu,²⁹ which is comparatively lower than our observation (32.0-36.0 psu). The salinity of seawater above 30.0 psu may increase the tolerance of corals against the high temperature effects and cover by high light intensity.²⁹

The DO, specific conductance (EC), pH, COD, turbidity, sulfate, and BOD values in SW1-SW24 ranged

from 6.50-8.50 mg L⁻¹, 1.40-44.8 mS m⁻¹, 6.30-6.80 mg L⁻¹, 35-7582 mg L⁻¹, 0.11-1.55 nephelometric turbidity units (NTU), 9.20-75.9 mg L⁻¹, and not detected-19.5 mg L⁻¹, respectively (Table 1). DO contents of SW1-SW24 were higher than the average of saturation state of seawater 70-87%.²⁹ DO value above 6.50 mg L⁻¹ indicates no water pollution.²⁴ The high contents of DO in SW1-SW17 suggest that the condition of seawater in the Gulf of Prigi may provide enough oxygen for respiration and decomposition of organic matters in seawater. Therefore, the floating home at the SW1-SW17 possibly can be used as the media of natural sources for increasing the fish, coral, lobster, and shrimp productivities.

EC in SW reflects the competition of ionic composition in seawater, e.g., when Ca²⁺, Fe³⁺, Mn²⁺, Cu²⁺, and Pb²⁺ ions competed with SO₄²⁻ ion (Table 1, Figure 3). All values of EC in SW, except for SW1, SW2, SW4, SW11 and SW18, were found in the range of typical drinking water (5-50 mS m⁻¹).²⁴ EC of SW1, SW2, SW4, SW11 and SW18 were recorded at ca. 5 mS m⁻¹ related with the average of EC of seawater in the world's oceans.³⁰ The data can be used as a typical way to monitor and treat in low quality water (e.g., water rich with sodium, boron and fluorides) as well as in high quality irrigation water (e.g., adequately fertilized water with appropriate nutrient concentrations and ratios). EC is related to pH values in seawater. The measured pH at SW1-SW24 tended to be relatively stable within the range of 6-7. The pH in SW probably was affected by acid solutions such as H₂CO₃, HNO₃, H₂SO₄, and H₃PO₄ using cation exchange reactions and C, H, O, N, and S or biogeochemical cycles in surface seawater.

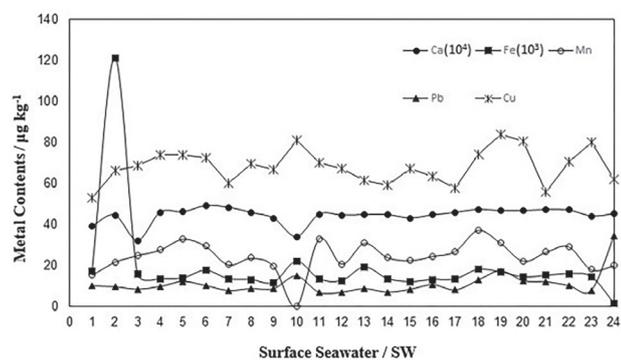
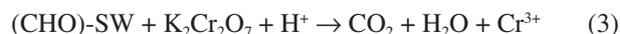


Figure 3. Distributions of metal contents of surface seawater in the sampling locations in the Gulf of Prigi.

The COD values of SW1-SW5, SW11 and SW17 are categorized as very low (below 2100 mg L⁻¹) (Table 1).³¹ We suggest that the index reflected no water pollution by organics due to high seawater quality discharge from river runoff. Such lower value of COD in seawater indicates the little oxygen required for the chemical oxidation of

organic matter. We used K₂Cr₂O₇ as the strong chemical oxidant for COD test. The possible chemical reaction can be written as follows:



For the case of turbidity, all values in SW1-SW24 were recorded below 1 NTU, except for SW8 (1.55 NTU). It might be caused by a wide variety of suspended particles and the effect of ocean turbidity through the Indian Ocean currents. Such low turbidity in SW1-SW24 might support the photosynthesis process. The acceptable and permissible limits of turbidity in water are 1 and 5, respectively.³⁰ One of the parameters to influence turbidity is sulfate content in seawater. SW1-SW24 contained sulfate ions and most of these ions are also slightly soluble in seawater. Sources of sulfate ions were possibly produced by oxidation process of their ores, such as CaSO₄, PbSO₄ and Fe₂(SO₄)₃ or by products of industrial waste associated with river runoff. All of the sulfate values in SW were found in the range of the values in desirable limit (200 mg L⁻¹) and permissible limit (400 mg L⁻¹) in natural water. Moreover, the BOD values in SW1-SW24 were found below 10 mg L⁻¹, except for those in SW3, SW10, and SW11. BOD value less than 10 mg L⁻¹ are categorized as low contamination.²⁴ The low of BOD values may also suggest that the biodegradability of dissolved organic matter slightly occurred in SW.³²

In order to investigate the ecological characteristics of seawater in the Gulf of Prigi, we report the distribution of chlorophyll a along the sampling points (Figure 2). As shown in Figure 2, concentrations of chlorophyll a were found to vary between 0.90-2.34 mg m⁻³ from sea surface to Indian Ocean in ca. 18.5 m.

The range of concentrations of chlorophyll a were 1.45-1.54 mg m⁻³, observed for SW1-SW3, SW12, SW13, SW20 and SW21. For SW8-SW10 and SW16-SW19 it was detected between 1.69-1.78 and 1.55-1.63 mg m⁻³, respectively, while SW4-SW7, SW14, SW15, and SW22-SW24 were found to be 1.63-1.70 mg m⁻³. The concentration of chlorophyll a measured in this research is the same range of chlorophyll a concentrations at the surface seawater as in the previous study.^{33,34} The variability of chlorophyll a-enriched reflected the good ecological conditions of marine systems in the Gulf of Prigi and such variability was possibly affected by the changes in the physical and chemical characteristics of the marine environment, such as terrestrial runoff, mass corals bleaching, temperature, wind stress and the Indian Ocean Dipole (IOD). Seasonal and inter-annual variability of phytoplankton biomass in the eastern part of the gulf, which is influenced by mixing of fresh water discharges

(estuary) with Indian Ocean, may also contribute to the high distribution of chlorophyll a concentrations in the Gulf of Prigi. Several studies reported the positive relationship between chlorophyll a with phytoplankton biomass and fish abundance in natural water bodies.³⁵⁻³⁷ The abundance of chlorophyll in seawater governs the invasion of populations of grouper fish. Our observations of enriched chlorophyll in seawater indicates the Gulf of Prigi tends to be a natural source and provides nutrient for marine organisms. Therefore, it is significantly required to conduct permanent and serious effort of protect this natural source from anthropogenic inputs which may cause the pollution in the water bodies of the gulf.

The concentrations of Ca, Fe, and Mn ranged from 243917-504518, 1181-2270, and not detected-44.8 $\mu\text{g kg}^{-1}$, respectively, and those of Cu and Pb ranged from 41.2-99.2 and 6.00-35.2 $\mu\text{g kg}^{-1}$, respectively. As listed in Table 2

and shown in Figure 3, the highest Ca concentration (491436 $\mu\text{g kg}^{-1}$) was found in SW6. In SW1-SW24, the averages of Ca concentrations were recorded as multifold higher than the respective permissible limit set by WHO.²⁴

Ca enrichment in seawater suggests the possible leaching of Ca and its dissolution at low pH in surface seawater from coral skeletons or aragonite (CaCO_3) surrounding the Gulf of Prigi. Input of acids to leach CaCO_3 caused the pollutant input through river, contributing HNO_3 , H_2SO_4 (including H_2S), H_3PO_4 and other organic acids. In addition, the source of mineral and organic acids was emitted by rock weathering process surrounding rivers, agricultural activities, fertilizer use, livestock, sewage treatment plant, and soil dust. The chemical reaction can be written as follows:



Table 2. Metal contents and isotopic Pb of surface seawater samples and their related materials in the Gulf of Prigi

Sample	Ca / ($\mu\text{g kg}^{-1}$)	Fe / ($\mu\text{g kg}^{-1}$)	Mn / ($\mu\text{g kg}^{-1}$)	Cu / ($\mu\text{g kg}^{-1}$)	Pb / ($\mu\text{g kg}^{-1}$)	²⁰⁶ Pb / ($\mu\text{g kg}^{-1}$)	²⁰⁷ Pb / ($\mu\text{g kg}^{-1}$)	²⁰⁸ Pb / ($\mu\text{g kg}^{-1}$)	
SW1-1-2017	395701	1714	16.4	51.6	10.8	12.0	11.2	10.0	
SW1-2-2017	383231	1758	15.2	56.4	9.60	10.4	10.8	9.20	
SW1	SW1-3-2017	394148	1665	14.0	50.4	9.60	12.8	9.60	8.40
	range	383231-395701	1665-1758	14.0-16.4	50.4-56.4	9.60-10.8	10.4-12.0	9.60-11.2	8.40-10.0
	mean \pm SD	391027 \pm 5549	1712 \pm 38.0	15.2 \pm 0.98	52.8 \pm 2.59	10.0 \pm 0.56	11.7 \pm 0.99	10.5 \pm 0.68	9.20 \pm 0.65
SW2-1-2017	457884	1218	22.4	52.0	10.0	10.0	10.8	9.20	
SW2-2-2017	426165	1203	23.2	99.2	8.80	9.60	10.0	8.40	
SW2	SW2-3-2017	451121	1216	19.2	47.6	9.60	10.0	10.4	9.20
	range	426165-457884	1203-1218	19.2-22.4	47.6-99.2	8.80-10.0	9.60-20.0	10.0-10.8	8.40-9.20
	mean \pm SD	445057 \pm 13641	12123 \pm 6.65	21.6 \pm 1.73	66.3 \pm 23.4	9.47 \pm 0.50	9.87 \pm 0.19	10.4 \pm 0.33	8.93 \pm 0.38
SW3-1-2017	357233	1480	26.0	67.6	6.40	7.20	8.00	5.60	
SW3-2-2017	356593	1700	23.2	69.2	6.80	7.60	8.40	6.80	
SW3	SW3-3-2017	243917	1518	25.6	69.6	11.6	12.4	12.8	10.8
	range	243917-357233	1480-1700	23.2-26.0	67.6-69.2	6.40-11.6	7.20-12.4	8.00-12.8	5.60-10.8
	mean \pm SD	319248 \pm 53267	1566 \pm 96.0	24.9 \pm 1.24	68.8 \pm 0.86	8.27 \pm 2.36	9.07 \pm 2.36	9.73 \pm 2.17	7.73 \pm 2.22
SW4-1-2017	450100	1387	21.2	76.4	9.60	10	11.2	8.80	
SW4-2-2017	471437	1268	22.0	72.8	10.0	10.8	11.2	9.20	
SW4	SW4-3-2017	455911	1370	39.6	73.2	9.20	10.4	10.4	8.40
	range	450100-471437	1268-1387	21.2-39.6	72.8-76.4	9.60-10.0	10.0-10.8	10.4-11.2	8.40-9.20
	mean \pm SD	459149 \pm 9007	1342 \pm 52.6	27.6 \pm 8.49	74.1 \pm 1.61	9.60 \pm 0.33	10.4 \pm 0.33	10.9 \pm 0.38	8.80 \pm 0.33
SW5-1-2017	471872	1251	24.0	64.8	16.8	21.2	16.8	15.2	
SW5-2-2017	433418	1504	37.2	76.4	10.0	10.8	11.2	9.20	
SW5	SW5-3-2017	475868	1378	37.6	81.2	9.60	9.60	12.0	8.80
	range	433418-175868	1251-1504	24.0-37.6	64.8-81.2	9.60-16.8	9.60-21.2	11.2-16.8	8.80-15.2
	mean \pm SD	460386 \pm 19139	1378 \pm 103	32.9 \pm 6.32	74.1 \pm 6.88	12.1 \pm 3.30	13.9 \pm 5.21	13.3 \pm 2.47	11.1 \pm 2.93
SW6-1-2017	494898	1823	28.8	84.8	8.40	8.80	9.20	7.60	
SW6-2-2017	474832	1683	27.2	70.4	11.6	12.0	12.4	10.8	
SW6	SW6-3-2017	504578	1728	32.4	62.4	10.4	10.8	11.6	10.0
	range	474832-504578	1683-1823	27.2-32.4	62.4-84.8	8.40-11.6	8.80-12.0	9.20-12.4	7.60-10.8
	mean \pm SD	491436 \pm 12388	1745 \pm 58.4	29.5 \pm 2.17	72.5 \pm 9.27	10.1 \pm 1.31	10.5 \pm 13.2	11.1 \pm 1.36	9.47 \pm 1.36

Table 2. Metal contents and isotopic Pb of surface seawater samples and their related materials in the Gulf of Prigi (cont.)

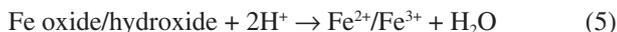
Sample	Ca / ($\mu\text{g kg}^{-1}$)	Fe / ($\mu\text{g kg}^{-1}$)	Mn / ($\mu\text{g kg}^{-1}$)	Cu / ($\mu\text{g kg}^{-1}$)	Pb / ($\mu\text{g kg}^{-1}$)	^{206}Pb / ($\mu\text{g kg}^{-1}$)	^{207}Pb / ($\mu\text{g kg}^{-1}$)	^{208}Pb / ($\mu\text{g kg}^{-1}$)	
SW7-1-2017	486108	1367	18.8	65.2	7.20	7.60	8.00	6.40	
SW7-2-2017	481603	1263	20.8	54.8	7.20	7.60	8.40	6.40	
SW7	SW7-3-2017	483232	1385	21.2	60.4	8.40	8.80	9.20	7.60
	range	481603-486108	1263-1385	18.8-20.8	54.8-65.2	7.20-8.40	7.60-8.80	8.00-9.20	6.40-7.60
	mean \pm SD	483648 \pm 1863	1338 \pm 53.8	20.3 \pm 1.05	60.1 \pm 4.25	7.60 \pm 0.57	8.00 \pm 0.57	8.53 \pm 0.50	6.80 \pm 0.57
SW8-1-2017	480704	1336	22.4	83.6	11.6	12.0	13.2	10.8	
SW8-2-2017	463877	1324	26.0	72.8	6.80	7.60	8.80	6.00	
SW8	SW8-3-2017	427609	1223	22.4	52.0	7.20	7.60	8.40	6.40
	range	427609-480704	1223-1336	22.4-26.0	52.0-83.6	6.80-11.6	7.60-12.0	8.40-13.2	6.00-10.8
	mean \pm SD	457397 \pm 22155	1294 \pm 50.7	23.6 \pm 1.70	69.5 \pm 13.1	8.53 \pm 2.17	9.07 \pm 2.07	10.1 \pm 2.17	7.73 \pm 2.17
SW9-1-2017	427528	1154	23.2	59.2	7.60	8.80	8.80	6.96	
SW9-2-2017	438574	1159	18.4	74.0	8.80	8.80	10.0	8.40	
SW9	SW9-3-2017	422733	1163	17.2	67.2	9.20	9.20	11.2	8.80
	range	422733-438574	1154-1163	17.2-23.2	59.2-74.0	7.60-9.20	8.80-9.20	8.80-11.2	6.96-8.80
	mean \pm SD	429612 \pm 6633	1159 \pm 3.68	19.6 \pm 2.59	66.8 \pm 6.05	8.53 \pm 0.68	8.93 \pm 0.19	10.0 \pm 0.98	8.05 \pm 0.79
SW10-1-2017	338060	2198	ND	71.2	15.2	15.6	16.4	14.8	
SW10-2-2017	333377	2270	ND	92	16.8	16.8	18.0	16.0	
SW10	SW10-3-2017	341945	2098	ND	79.6	12.4	12.8	12.8	11.6
	range	333377-338060	2098-2198	ND	71.2-92.0	12.4-16.8	12.8-16.8	12.8-16.4	11.6-16.0
	mean \pm SD	337794 \pm 3503	2189 \pm 70.5	ND	80.9 \pm 8.54	14.8 \pm 1.82	15.1 \pm 1.68	15.7 \pm 2.17	14.1 \pm 1.86
SW11-1-2017	461338	1454	19.6	70.4	6.80	7.60	8.00	6.00	
SW11-2-2017	456853	1337	44.8	57.6	7.20	7.20	8.40	6.40	
SW11	SW11-3-2017	429206	1202	34.8	82.8	6.00	6.40	7.20	4.80
	range	429206-461338	1202-1454	34.8-44.8	57.6-82.8	6.00-7.20	6.40-7.60	7.20-8.40	4.80-6.40
	mean \pm SD	449132 \pm 14208	1331 \pm 103	33.1 \pm 10.4	70.3 \pm 10.3	6.67 \pm 0.50	7.07 \pm 0.50	7.87 \pm 0.50	5.73 \pm 0.68
SW12-1-2017	450698	1237	20.0	53.6	6.80	7.20	7.60	6.00	
SW12-2-2017	411602	1291	21.2	91.2	7.20	7.20	8.00	6.80	
SW12	SW12-3-2017	473009	1216	20.8	56.8	6.40	6.80	7.60	5.60
	range	411602-450698	1216-1237	20.0-21.2	53.6-91.2	6.40-7.20	6.80-7.20	7.60-8.00	5.60-6.80
	mean \pm SD	445103 \pm 25380	1248 \pm 31.6	20.7 \pm 0.50	67.2 \pm 17.0	6.80 \pm 0.33	7.07 \pm 0.19	7.73 \pm 0.19	6.13 \pm 0.50
SW13-1-2017	435524	1902	30.4	49.2	8.00	8.00	9.20	7.60	
SW13-2-2017	449208	1917	28.0	73.6	9.60	10.0	10.8	8.80	
SW13	SW13-3-2017	455268	1914	34.4	61.6	8.00	8.40	9.20	7.20
	range	435524-455268	1902-1917	28.0-34.4	49.2-61.6	8.00-9.60	8.00-10.00	9.20-10.8	7.20-8.80
	mean \pm SD	446667 \pm 8258	1911 \pm 6.48	30.9 \pm 2.64	61.5 \pm 9.96	8.53 \pm 0.75	8.80 \pm 0.86	9.73 \pm 0.75	7.87 \pm 0.68
SW14-1-2017	448677	1303	29.2	65.2	6.80	6.80	7.60	6.40	
SW14-2-2017	457742	1363	21.2	58.0	7.20	7.60	8.80	6.40	
SW14	SW14-3-2017	436122	1375	21.6	54.4	6.40	6.40	8.00	5.60
	range	436122-457742	1303-1375	21.2-29.2	54.4-65.2	6.40-7.20	6.40-7.60	7.60-8.80	5.60-6.40
	mean \pm SD	447514 \pm 8865	1347 \pm 31.5	24.0 \pm 3.68	59.2 \pm 4.49	6.80 \pm 0.33	6.93 \pm 0.50	8.13 \pm 0.50	6.13 \pm 0.38
SW15-1-2017	426328	1204	21.6	63.2	7.20	8.80	8.80	6.40	
SW15-2-2017	416834	1092	20.8	68.0	6.80	7.20	7.60	6.00	
SW15	SW15-3-2017	449282	1286	24.8	70.4	10.4	10.8	11.6	9.60
	range	416834-449282	1092-1286	20.8-24.8	63.2-70.4	6.80-10.4	7.20-10.8	7.60-11.6	6.00-9.60
	mean \pm SD	430815 \pm 13621	1194 \pm 79.5	22.4 \pm 1.73	67.2 \pm 2.99	8.13 \pm 1.61	8.93 \pm 1.47	9.33 \pm 1.68	7.33 \pm 1.61

Table 2. Metal contents and isotopic Pb of surface seawater samples and their related materials in the Gulf of Prigi (cont.)

Sample	Ca / ($\mu\text{g kg}^{-1}$)	Fe / ($\mu\text{g kg}^{-1}$)	Mn / ($\mu\text{g kg}^{-1}$)	Cu / ($\mu\text{g kg}^{-1}$)	Pb / ($\mu\text{g kg}^{-1}$)	^{206}Pb / ($\mu\text{g kg}^{-1}$)	^{207}Pb / ($\mu\text{g kg}^{-1}$)	^{208}Pb / ($\mu\text{g kg}^{-1}$)
SW16-1-2017	467998	1342	32.0	79.2	11.2	11.6	12.8	10.0
SW16-2-2017	417512	1181	19.2	58.4	12.8	13.2	13.6	12.4
SW16-3-2017	451264	1371	22.4	52.8	7.60	8.00	9.20	7.20
range	417512-467998	1181-1371	19.2-32.0	52.8-79.2	7.60-12.8	8.00-13.2	9.20-13.6	7.20-12.4
mean \pm SD	445591 \pm 20998	1298 \pm 83.6	24.5 \pm 5.44	63.5 \pm 11.4	10.5 \pm 2.17	10.9 \pm 2.17	11.9 \pm 1.91	9.88 \pm 2.12
SW17-1-2017	461581	1278	28.8	66.4	7.60	8.40	8.80	6.80
SW17-2-2017	417123	1266	26.0	59.6	7.20	7.60	8.80	6.40
SW17-3-2017	494272	1430	26.0	47.2	8.80	8.80	9.60	8.40
range	417123-494272	1266-1430	26.0-28.8	47.2-66.4	7.60-8.80	7.60-8.40	8.80-9.60	6.40-8.40
mean \pm SD	457659 \pm 31618	1325 \pm 74.6	26.9 \pm 1.32	57.7 \pm 7.95	7.87 \pm 0.68	8.27 \pm 0.50	9.07 \pm 0.38	7.20 \pm 0.86
SW18-1-2017	480205	1850	34.8	68.8	13.6	14.8	14.8	12.4
SW18-2-2017	439805	1594	40.0	90.0	12.4	12.4	13.6	11.6
SW18-3-2017	498864	1924	36.8	64.0	12.0	12.4	13.2	11.2
range	439805-498864	1594-1924	34.8-40.0	68.8-90	12.0-13.6	12.4-14.8	13.2-14.8	11.2-12.4
mean \pm SD	472958 \pm 24649	1789 \pm 141	37.2 \pm 2.14	74.3 \pm 11.3	12.7 \pm 0.68	13.2 \pm 1.13	13.9 \pm 0.68	11.7 \pm 0.50
SW19-1-2017	447355	1569	30.0	112	16.4	16.8	18.0	15.6
SW19-2-2017	488894	1838	28.8	71.2	17.6	18.0	18.8	17.2
SW19-3-2017	463299	1595	34.0	68.8	18.0	19.6	18.8	17.2
range	447355-488894	1569-1838	28.8-34.0	68.8-112	16.4-17.6	16.8-19.6	18.0-18.8	15.6-17.2
mean \pm SD	466516 \pm 17110	1667 \pm 121	30.9 \pm 2.22	84.0 \pm 19.8	17.3 \pm 0.68	18.1 \pm 1.15	18.5 \pm 0.38	16.7 \pm 0.75
SW20-1-2017	448386	1328	21.2	76.4	13.2	13.6	14.0	12.8
SW20-2-2017	489382	1507	23.6	88.4	12.8	13.6	14.0	12.4
SW20-3-2017	461535	1445	21.6	76.8	11.2	11.6	12.4	10.4
range	461535-489382	1328-1507	21.2-23.6	76.4-88.4	11.2-13.2	11.6-13.6	12.4-14.0	10.4-12.8
mean \pm SD	466434 \pm 17091	1427 \pm 74.2	22.1 \pm 1.05	80.5 \pm 5.56	12.4 \pm 0.86	12.9 \pm 0.94	13.5 \pm 0.75	11.9 \pm 1.05
SW21-1-2017	467996	1482	26.4	51.2	10.0	10.8	11.6	9.20
SW21-2-2017	476123	1551	26.8	67.2	12.4	12.4	14.0	11.6
SW21-3-2017	473227	1472	26.4	48.4	13.6	14.8	14.8	12.4
range	467996-476123	1472-1551	26.4-26.8	48.4-67.2	10.0-13.6	10.8-14.8	11.6-14.8	9.20-12.4
mean \pm SD	472449 \pm 3363	1502 \pm 35.1	26.5 \pm 0.19	55.6 \pm 8.28	12.0 \pm 1.50	12.7 \pm 1.64	13.5 \pm 1.36	11.1 \pm 1.36
SW22-1-2017	464937	1732	33.2	79.6	8.00	8.00	9.60	7.60
SW22-2-2017	470217	1438	26.4	79.6	10.4	10.8	12.4	9.60
SW22-3-2017	473586	1571	28.0	52.4	12.0	12.4	13.6	11.2
range	464937-473586	1438-1732	26.4-28.0	52.4-79.6	8.00-12.0	8.00-12.4	9.60-13.6	7.60-11.2
mean \pm SD	469580 \pm 3560	1580 \pm 120	29.2 \pm 2.90	70.5 \pm 12.8	10.1 \pm 1.64	10.4 \pm 1.82	11.9 \pm 1.68	9.47 \pm 1.4
SW23-1-2017	425572	1430	17.6	86.0	8.40	8.80	10.0	7.60
SW23-2-2017	438180	1404	18.4	71.2	6.80	7.20	8.00	6.00
SW23-3-2017	457844	1481	17.6	83.6	8.00	8.40	9.60	7.20
range	425572-457844	1404-1481	17.6-18.4	71.2-86.0	6.80-8.40	7.20-8.80	8.00-10.0	6.00-7.60
mean \pm SD	440532 \pm 13279	1438 \pm 32.0	17.9 \pm 0.38	80.3 \pm 6.49	7.73 \pm 0.68	8.13 \pm 0.68	9.20 \pm 0.86	6.93 \pm 0.68
SW24-1-2017	482662	1310	18.8	41.2	34.8	35.6	35.6	34.4
SW24-2-2017	425914	1231	22.0	71.6	35.2	36.4	34.0	35.2
SW24-3-2017	445132	1289	18.8	73.2	33.6	35.2	33.2	35.2
range	425914-482662	1289-1310	18.8-22.0	41.2-73.2	34.8-35.2	35.2-36.4	33.2-35.6	34.4-35.2
mean \pm SD	451236 \pm 23566	1277 \pm 33.4	19.9 \pm 1.51	62.0 \pm 14.7	34.5 \pm 0.68	35.7 \pm 0.50	34.3 \pm 0.99	34.9 \pm 0.38
WHO ²⁴	200000	300	400	2000	10	-	-	-

SW1-SW24: Surface seawater samples 1-24; SWx-y-2017: sample No. y (y = 1-3) of the surface seawater sample x (x = 1-24) collected in 2017; SD: standard deviation; ND: not detected; WHO: World Health Organization.

The highest average of Fe concentration ($1213 \mu\text{g kg}^{-1}$) was found in SW2 with the overall concentrations ranging from $1203\text{-}1218 \mu\text{g kg}^{-1}$. Fe concentrations of the study area (SW1-SW24) were shown to be extremely higher than their permissible level.²⁴ The source of Fe was possibly leached from the Fe oxide/hydroxide in the mineral sediment of seawater as nodules and crusts. Concomitantly, the concentration of Fe^{2+} or Fe^{3+} increases with decreasing pH. The chemical reaction is written as:



The highest Mn concentration ($44.8 \mu\text{g kg}^{-1}$) was noticed in SW18. As listed in Table 2 and Figure 3, all of the seawater samples (SW1-SW24) show lower concentrations of Mn than the permissible value ($400 \mu\text{g kg}^{-1}$).²⁴ Mn concentrations in the study area were also found to be lower than those reported previously²⁷ in the surface water and sub-surface water samples of Bucha and surrounding areas of Mohammad agency, northern Pakistan. Mn was possibly deposited near the seafloor and then removed by weathering. As shown in Figure 3, the pattern of the concentrations of Mn and Cu are relatively similar, except for SW10. For SW10, located at the end area of sampling sites close to Indian Ocean, the lowest concentration of Mn maybe affected by the high dissolution of MnO_2 to the ocean. The highest average concentration of Cu ($84.0 \mu\text{g kg}^{-1}$) was noticed in SW19. At the SW1-SW24 sampling sites, Cu contents are lower in comparison to their respective permissible limit set by WHO ($2000 \mu\text{g kg}^{-1}$).²⁴ The low levels of Cu suggest that they were originated most likely from natural occurrence. The source of Cu comes from the cobalt-bearing mineral, such as chalcopyrite, bornite and chalcocite.^{38,39} The high mean concentration of Pb (up to $34.5 \mu\text{g kg}^{-1}$) at SW24 exceeded the background value of WHO ($10.0 \mu\text{g kg}^{-1}$).²⁴ However, the Pb concentrations of surface seawater samples at SW1-SW24 were close to

the standard Pb value by WHO,²⁴ except for SW18-SW21, and SW24 (Table 2 and Figure 3). Additionally, the Pb and Ca in SW1-SW24 show a similar pattern, indicating the cooperation with sulfate ionic in surface seawater.

In order to assess the pollutant or natural sources, we used the indexes of PLI and HQ. As listed in Table 3, the highest Fe, Mn, Cu, and Pb concentrations are recorded at SW2 ($12123 \mu\text{g kg}^{-1}$), SW18 ($37.2 \mu\text{g kg}^{-1}$), SW19 ($84 \mu\text{g kg}^{-1}$) and SW24 ($34.5 \mu\text{g kg}^{-1}$), respectively. The calculated PLI values for each site were less than 1 (0.859), suggesting no anthropogenic inputs. HQ values were also calculated to monitor the highest metals at SW2, SW19 and SW24. People living in the surroundings of the Gulf of Prigi encouraged the average ADD values to be 0.38 (Fe), 0.001 (Mn), 0.003 (Cu) and $0.001 \mu\text{g kg}^{-1}$ (Pb). The HQ assessments at the highest concentration of metals at each sites have $\text{HQ} < 1$ for all elements, i.e., Fe (0.005), Mn (8.18×10^{-6}), Cu (6.98×10^{-5}) and Pb (2.95×10^{-5}), indicating low risk in surface seawater.

Figure 4 shows Pb isotopes data for all samples (SW1-SW24). We successfully measured and combined total Pb content vs. ^{206}Pb , total Pb content vs. ^{207}Pb , and total Pb content vs. ^{208}Pb . Simulated total Pb content in seawater ranges from $5\text{-}20 \mu\text{g kg}^{-1}$, with one outlier at $35 \mu\text{g kg}^{-1}$ (Figure 4).

There is a correlation between total Pb content with ^{206}Pb , ^{207}Pb , and ^{208}Pb . The correlation coefficients of total Pb content vs. ^{206}Pb , ^{207}Pb , and ^{208}Pb were 0.9961, 0.9947, and 0.9981, respectively. The similar pattern plots among ^{206}Pb , ^{207}Pb , and ^{208}Pb suggest the source of Pb in surface seawater initiated from the decay of parent rock, such as ^{238}U , ^{235}U , and ^{237}Th . The natural sources of U and Th cooperating with Pb isotopes were generally from stones and mineral sources in sediment around the Gulf of Prigi. Our results reflect the evolution of U-Th-Pb isotope system in the leached sedimentary rock, which provides for evaluation of the sources of the Pb isotope composition of the seawater.

Table 3. PLI and HQ assessments of metals in seawater

Assessment	Fe	Mn	Cu	Pb
Metal ^a / ($\mu\text{g kg}^{-1}$)	12123 (SW2)	37.2 (SW18)	84 (SW19)	34.5 (SW24)
b / ($\mu\text{g kg}^{-1}$)	300	400	2000	10
Metal b ⁻¹	40.4	0.093	0.042	3.45
		PLI = 0.859		
ADD	0.373	0.001	0.003	0.001
RfD	70	140	37	36
HQ	0.005	8.18×10^{-6}	6.98×10^{-5}	2.95×10^{-5}

^aThe data in parentheses indicate the number of seawater sample. PLI: pollution load index; b: metal (Fe, Mn, Cu or Pb) content in the background reference; ADD: dose-response data; RfD: reference dose; HQ: hazard quotient.

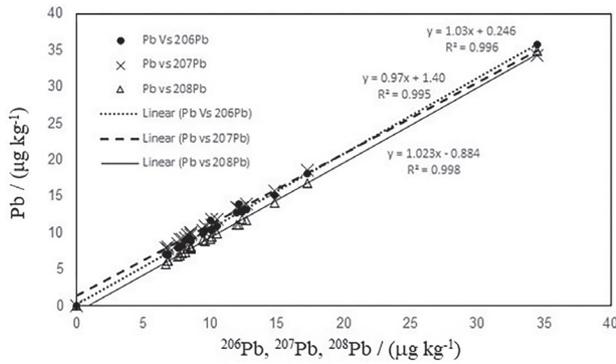


Figure 4. Pb contents vs. Pb isotope in seawater.

Pb isotope ratios of seawater from the Gulf of Prigi

Pb isotope ratios growth curve for detection of sources of Pb mines

Pb isotope ratios can be used to reflect time-dependent decay process and provide information on the age of

material associated with Pb content. The modelling growth curve of the Pb is produced by plotting on the line of Pb ore mined in the world. In order to apply the modelling of growth curve of Pb isotope ratios in seawater of the Gulf of Prigi, we calculated the data of Pb isotopes references from various mines around the world, in combination with the age of the different ore Pb published previously (Table 3 and Figure 5).⁴⁰ As listed in Table 4, the third column from the right indicates the geological age of the ore Pb contents. Using a single-stage model of Russell and Reynolds,⁴⁰ we predict the value of Pb isotope ratios for different ages according to the decay of unstable U and Th into the stable end-product Pb isotopes. ²³⁸U decays comprise 14 steps to produce ²⁰⁶Pb as the stable end-product, with half-life of 4.468×10^9 years. ²³⁵U decays to ²⁰⁷Pb and ²³²Th decays to ²⁰⁸Pb with half-lives of 0.7038×10^9 and 14.010×10^9 years, respectively. ²⁰⁴Pb is the only naturally-occurring stable isotope of Pb that is not radiogenic, thus its abundance does not change over time.

Table 4. Ore lead isotope ratios and geological ages

Reference sample	²⁰⁶ Pb / ²⁰⁴ Pb	²⁰⁷ Pb / ²⁰⁴ Pb	²⁰⁸ Pb / ²⁰⁴ Pb	Geological age / Ma	²⁰⁸ Pb / ²⁰⁶ Pb	²⁰⁷ Pb / ²⁰⁶ Pb
Daylight	12.4310	14.0650	32.2700	3000-3200	2.5959	1.1314
French Bob's	12.4610	14.0770	32.2850	3000-3200	2.5909	1.1297
Geneva Lake	14.0020	14.8700	33.7160	> 2500	2.4079	1.0620
Cobalt; upper end of mixing line	14.8570	15.1480	34.4120	2120	2.3162	1.0196
Sudbury Errington mine Toronto No. 359	15.4890	15.3030	35.3380	1900	2.2815	0.9880
Southwest Finland	15.6760	15.3280	35.2330	ca. 1700	2.2476	0.9778
Broken Hill	16.0030	15.3900	35.6600	ca. 1660	2.2283	0.9617
	16.0070	15.3970	35.6750		2.2287	0.9619
Mount Isa	16.1080	15.4540	35.8340	1500-1700	2.2246	0.9594
	16.1200	15.4540	35.8500		2.2239	0.9587
McArthur River	16.1560	15.4740	35.8870	ca. 1500	2.2213	0.9578
Sullivan	16.5260	15.5040	36.1950	> 1300	2.1902	0.9382
Balmat	16.9060	15.5250	36.4490	1080	2.1560	0.9183
	16.9350	15.5050	36.4230		2.1508	0.9156
Captains Flat	18.0650	15.6140	38.1570	425	2.1122	0.8643
Cobar, CSA Mine	18.1050	15.6260	38.1610	410-420	2.1078	0.8631
	18.1780	15.6290	38.1180		2.0969	0.8598
Bathurst	18.2040	15.6550	38.1220	450	2.0942	0.8600
	18.3780	15.6020	38.3620		2.0874	0.8489
White Island ^a	18.7720	15.5980	38.6620	0	2.0596	0.8309
Manitauwadge Wilroy No. 332	13.2860	14.4110	33.1190	–	2.4928	1.0847
No. 371	13.3600	14.4270	33.1930	–	2.4845	1.0799
Mississippi Galena-38a	13.2110	14.4010	33.0690	–	2.5031	1.0901
Geco vein No. 372 ^a	29.8700	17.5480	46.9490	–	1.5718	0.5875
Flin Flon No. 648 ^a	15.3150	15.1060	34.8460	–	2.2753	0.9864
Mine No. 660 ^a	15.7450	15.2280	35.2970	–	2.2418	0.9672
Chisel Lake mine No. 652 ^a	15.3870	15.1160	34.9400	–	2.2707	0.9824
Snake Lake No. 660 ^a	15.7090	15.2560	35.1760	–	2.2392	0.9712

^aNot included in calculations for the growth curve development. –: geological age of present day.

The Pb isotope ratios $^{206}\text{Pb} / ^{204}\text{Pb}$, $^{207}\text{Pb} / ^{204}\text{Pb}$ and $^{208}\text{Pb} / ^{204}\text{Pb}$ were calculated using the following equations:

$$^{206}\text{Pb} / ^{204}\text{Pb} = X = a + \alpha V(1 - e^{-\lambda t}) \quad (6)$$

$$^{207}\text{Pb} / ^{204}\text{Pb} = Y = b + V(1 - e^{-\lambda' t}) \quad (7)$$

$$^{208}\text{Pb} / ^{204}\text{Pb} = Z = c + W(1 - e^{-\lambda'' t}) \quad (8)$$

where t is assumed from the present; a , b and c are the present day ratios; V is the present day value of $^{235}\text{U} / ^{204}\text{Pb}$; α is the present day value of $^{238}\text{U} / ^{235}\text{U}$; W is the present day value of $^{232}\text{Th} / ^{204}\text{Pb}$; and λ , λ' , λ'' are the decay constants. The decay constants used are $\lambda = 0.155125 \times 10^{-9} \text{ year}^{-1}$, $\lambda' = 0.98485 \times 10^{-9} \text{ year}^{-1}$, $\lambda'' = 0.49475 \times 10^{-10} \text{ year}^{-1}$, and $\alpha = ^{238}\text{U} / ^{235}\text{U} (\text{present}) = 137.88$. We used the following values using the new decay constants and the corrected Pb isotope ratios of Table 4: $a = 18.465 \pm 0.074$, $b = 15.642 \pm 0.010$ and $c = 38.057 \pm 0.095$, whereas $V = 0.066413 \pm 0.00085$ and $W = 36.058 \pm 0.132$.

We chose the time for every 0.1×10^9 years from present day to 1.5×10^9 years in order to produce the lead growth curve according with the range value of Pb isotope ratios of seawater in the Gulf of Prigi. The calculated Pb isotope ratios are listed in Table 5.

As mentioned above, ^{204}Pb is not a radiogenic isotope and it has therefore become more common to convert the ratios $^{207}\text{Pb} / ^{206}\text{Pb}$ and $^{208}\text{Pb} / ^{206}\text{Pb}$ in the Pb isotope ratio calculation. The calculated $^{208}\text{Pb} / ^{206}\text{Pb}$ and $^{207}\text{Pb} / ^{206}\text{Pb}$ ratios as a function of time (Table 5) are plotted in Figure 5. The growth curve shows the calculated values, where the end of curve at lower values to the left represents the present day. The line of growth curve was calculated and made from the values of Pb isotope ratios of the Pb ores in the

world (Table 5 and Figure 5). As shown in Figure 4, we finally normalized from the predicted line calculations in the Pb growth curve. This Figure can be used to monitor the value of Pb isotope ratios in seawater of the Gulf of Prigi for detecting their originating mine sources.

Pb isotope ratios in the samples of the Gulf of Prigi

In order to investigate the anthropogenic and natural sources, we detected and treated calculation of Pb isotope ratios in seawater of the Gulf of Prigi. Seawater samples (SW1-SW24) as a group show a wide range in $^{207}\text{Pb} / ^{206}\text{Pb}$ (2.2600-2.8243) and $^{208}\text{Pb} / ^{206}\text{Pb}$ (0.7966-0.9945) (Table 6). Figure 5 shows the patterns and variations of Pb isotope ratios from SW1 to SW24. The SW1-SW24 samples extend from the typical Pb-polluted growth curve. These results indicate that source of unpolluted Pb in seawater of the Gulf of Prigi may be originated from natural sources including fresh water and mineral resources in sediment of the Gulf of Prigi.

Figure 5 shows clearly the distinguished Pb isotope ratios of seawater group and the group of natural samples, except for SW1, SW5, SW10, SW11, SW22 and SW24. As shown in Figure 5, Pb isotope ratios of SW1-SW24 commonly reflect 4 groups of seawater such as 1-SW (SW3, SW4, SW7, SW8, SW23), 2-SW (SW16, SW17, SW21), 3-SW (SW7, SW9, SW13, SW15) and 4-SW (SW2, SW6, SW18, SW19, SW20). The $^{207}\text{Pb} / ^{206}\text{Pb}$ ratios in groups 1-SW-4-SW ranged between 0.8094-0.8692 or 1.1505-1.2355 ($^{206}\text{Pb} / ^{207}\text{Pb}$) for 1-SW, 0.8320-0.8560 or 1.1682-1.2019 ($^{206}\text{Pb} / ^{207}\text{Pb}$) for 2-SW, 0.8182-0.8566 or 1.164-1.222 ($^{206}\text{Pb} / ^{207}\text{Pb}$) for 3-SW and 0.8679-0.8923 or 1.1207-1.1522 ($^{206}\text{Pb} / ^{207}\text{Pb}$) for 4-SW. These interval

Table 5. Calculated Pb isotope ratio development, using single-stage model 1

time $\times 10^9$ / year	$^{206}\text{Pb} / ^{204}\text{Pb}$	$^{207}\text{Pb} / ^{204}\text{Pb}$	$^{208}\text{Pb} / ^{204}\text{Pb}$	$^{207}\text{Pb} / ^{206}\text{Pb}$	$^{208}\text{Pb} / ^{206}\text{Pb}$
0.1	18.3218	15.6351	38.3282	0.8534	2.0919
0.2	18.1765	15.6275	38.1484	0.8598	2.0988
0.3	18.0288	15.6192	37.9678	0.8663	2.1060
0.4	17.8788	15.6099	37.7863	0.8731	2.1135
0.5	17.7265	15.5997	37.6039	0.8800	2.1213
0.6	17.5718	15.5885	37.4206	0.8871	2.1296
0.7	17.4147	15.5761	37.2363	0.8944	2.1382
0.8	17.2551	15.5624	37.0512	0.9019	2.1473
0.9	17.0930	15.5473	36.8651	0.9096	2.1567
1.0	16.9284	15.5306	36.6782	0.9174	2.1667
1.1	16.7612	15.5122	36.4903	0.9255	2.1771
1.2	16.5914	15.4919	36.3014	0.9337	2.1880
1.3	16.4190	15.4695	36.1116	0.9422	2.1994
1.4	16.2439	15.4447	35.9209	0.9508	2.2114
1.5	16.0660	15.4175	35.7292	0.9596	2.2239

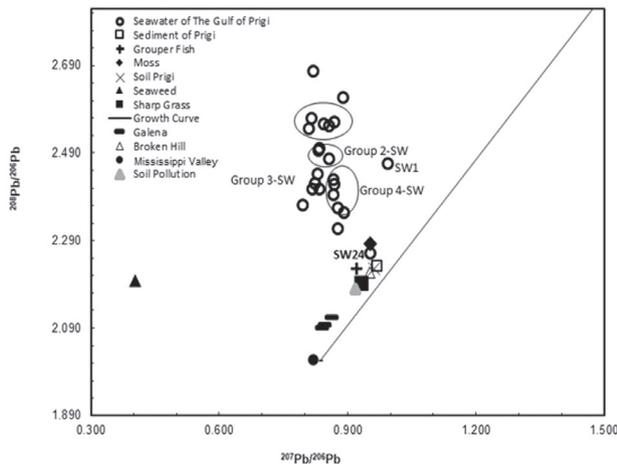


Figure 5. Pb isotope ratios of seawater, sediment, grouper fish, moss, soil, seaweed and sword grass including natural and anthropogenic sources in the Gulf of Prigi. The line shows the Pb growth curve.⁴⁰

values are in agreement with the previous study,⁴¹ which shows the Pb isotopic composition of tidal flat sediments (human-unaffected, with geogenic $^{206}\text{Pb} / ^{207}\text{Pb}$ ca. 1.2 and nearshore and offshore suspended particulate matter $^{206}\text{Pb} / ^{207}\text{Pb}$ ca. 1.172 and 1.166, respectively). The variation of $^{206}\text{Pb} / ^{207}\text{Pb}$ from 1-SW to 4-SW is consistent with Pb enrichment factors ($\text{EF} < 1$) with respect to a background marine sediment $^{206}\text{Pb} / ^{207}\text{Pb}$ value of ca. 1.2, as reported previously.⁴² We suggest the groups 1-SW-4-SW of surface seawater were characterized by small difference in range values of the $^{207}\text{Pb} / ^{206}\text{Pb}$ ratios, indicating their environmental substances related with original Pb leached by regional marine sediment and geogenic variations. The most Pb in surface seawater leached by unpolluted marine sediment is derived from weathered bedrocks and their isotopic compositions of Pb are mostly influenced by the decay of ^{238}U to ^{206}Pb . In addition, Pb isotopes of SW1, SW5, SW10, SW11 and SW22 reflected the areas with different source materials, such as the natural resources and Pb dissolved components (Figure 5). In the future, the integrated characteristic of stable isotopes of Pb and $^{87}\text{Sr}/^{86}\text{Sr}$ can be used as tracer for geographic variation to support natural sources for environmental protection.

Pb isotope ratios in our natural samples group, such as sediment, grouper fish, moss, seaweed, soil, and sharp grass, were investigated to understand their relation with seawater of the Gulf of Prigi. As listed in Table 6, the range of their Pb isotope ratios ($^{207}\text{Pb} / ^{206}\text{Pb} = 0.4033\text{-}0.9667$ and $^{208}\text{Pb} / ^{206}\text{Pb} = 2.1918\text{-}2.2253$) were also higher in the plotted Pb growth curve (Figure 5). Pb isotope ratios of seawater for SW24 agreed well to that in the natural samples group, except for the Pb isotope ratios of seaweed ($^{207}\text{Pb} / ^{206}\text{Pb} = 0.4033 \pm 0.176$ and $^{208}\text{Pb} / ^{206}\text{Pb} = 0.4033 \pm 0.0293$). This result shows that Pb

Table 6. Pb isotope ratios of known and natural or anthropogenic sources

Sample	$^{208}\text{Pb} / ^{206}\text{Pb}$	$^{207}\text{Pb} / ^{206}\text{Pb}$	Reference
Seawater			
SW1	2.4642 ± 0.0713	0.9945 ± 0.0297	a
SW2	2.3945 ± 0.026	0.8679 ± 0.0226	a
SW3	2.5559 ± 0.0618	0.8447 ± 0.0439	a
SW4	2.5599 ± 0.0364	0.8692 ± 0.0614	a
SW5	2.616 ± 0.1019	0.8911 ± 0.2290	a
SW6	2.4171 ± 0.0313	0.8703 ± 0.0209	a
SW7	2.5516 ± 0.0124	0.8566 ± 0.0327	a
SW8	2.5680 ± 0.0553	0.8159 ± 0.0320	a
SW9	2.4060 ± 0.0950	0.8182 ± 0.1099	a
SW10	2.3157 ± 0.0256	0.8787 ± 0.0368	a
SW11	2.6771 ± 0.0716	0.8205 ± 0.0577	a
SW12	2.4991 ± 0.0672	0.8355 ± 0.0341	a
SW13	2.4193 ± 0.0484	0.8252 ± 0.0368	a
SW14	2.8243 ± 0.2210	0.9098 ± 0.2301	a
SW15	2.4409 ± 0.0539	0.8300 ± 0.0651	a
SW16	2.4065 ± 0.0387	0.8356 ± 0.0603	a
SW17	2.4945 ± 0.0761	0.8324 ± 0.0556	a
SW18	2.4289 ± 0.0498	0.8680 ± 0.0493	a
SW19	2.3540 ± 0.0396	0.8923 ± 0.0586	a
SW20	2.3644 ± 0.0227	0.8773 ± 0.0228	a
SW21	2.4764 ± 0.0528	0.8567 ± 0.0648	a
SW22	2.3708 ± 0.0320	0.7966 ± 0.0516	a
SW23	2.5431 ± 0.0700	0.8094 ± 0.0168	a
SW24	2.2600 ± 0.0136	0.9537 ± 0.0357	a
Sediment	2.2332 ± 0.0077	0.9667 ± 0.0168	a
Grouper fish	2.2265 ± 0.0346	0.9213 ± 0.0292	a
Moss	2.2811	0.9537	a
Seaweed	2.1993 ± 0.176	0.4033 ± 0.0293	a
Soil	2.2253 ± 0.0256	0.9615 ± 0.0164	a
Sharp grass	2.1918	0.9316	a
Natural sources			
Natural galena ore	2.091-2.118	0.8394-0.8654	Wijaya <i>et al.</i> ⁵
Anthropogenic sources, Pb products and ore deposit			
Leaded gasoline			
Broken Hill	2.2182	0.952	Mukai <i>et al.</i> ⁹
Mississippi Valley	2.0172	0.82	
Municipal solid waste incinerators			
Incinerator fly ash	2.200-2.120	0.867-0.870	Hansmann and Koppel ¹⁰
Soil pollution	2.180	0.908	Wijaya <i>et al.</i> ⁵

^aThis study.

in seawater could contribute and transport to the grouper fish, moss, soil, and sharp grass and might also be affected by coastal sediment of Prigi (Figure 5).

In order to detect anthropogenic sources, Pb isotope ratios in seawater were plotted in the Pb growth curve, indicating Pb ore mined in the world. As shown in Figure 5, we also plotted the Pb isotope ratios of Broken Hill mine ($^{207}\text{Pb} / ^{206}\text{Pb} = 0.952$ and $^{208}\text{Pb} / ^{206}\text{Pb} = 2.2182$) and Mississippi Valley ($^{207}\text{Pb} / ^{206}\text{Pb} = 0.820$ and $^{208}\text{Pb} / ^{206}\text{Pb} = 2.0172$) ores

in the additive of gasoline to increase the octane ratio of fuel. Their Pb isotopic compositions of ores in leaded gasoline presents a wide range of Pb isotope ratios and exhibit different ranges compared to those of seawater (Figure 5).

Pb isotope ratios of soil were also chosen as one of anthropogenic sources in order to detect its fingerprint in seawater. The Pb leached from agricultural soil may contribute in the seawater (Figure 1).

The value of Pb isotope ratios in soil pollution ($^{207}\text{Pb} / ^{206}\text{Pb} = 0.9080$ and $^{208}\text{Pb} / ^{206}\text{Pb} = 2.180$) was more radiogenic comparing to that in soil surrounding the Gulf of Prigi ($^{207}\text{Pb} / ^{206}\text{Pb} = 0.9615$ and $^{208}\text{Pb} / ^{206}\text{Pb} = 2.2253$) (Figure 5).

The Pb isotope of soil at Prigi was closer to seawater (SW-24) comparing with that in soil pollution. This result indicates that the Pb isotope ratios of soil pollution did not agree well with that of seawater. In order to detect the sources of atmospheric pollution input in seawater, we added the value of Pb isotope ratios of municipal solid waste incinerator. The municipal solid waste incinerator was well known as the source of pollution in seawater of the Gulf of Thailand and other countries.^{5,15,43} The range of Pb isotope ratios in the incinerator fly ash ($^{207}\text{Pb} / ^{206}\text{Pb} = 0.867-0.870$ and $^{208}\text{Pb} / ^{206}\text{Pb} = 2.200-2.120$) was very far from the Pb isotope ratios in seawater.

Table 5 and Figure 5 also show the value of Pb isotope ratios of geologic material such as galena (PbS). The range of Pb isotope ratios of galena ($^{207}\text{Pb} / ^{206}\text{Pb} = 2.091-2.118$ and $^{208}\text{Pb} / ^{206}\text{Pb} = 0.8394 \pm 0.8654$) falls completely within that of seawater. These results indicated that the leaded gasoline, soil pollution, incinerator fly ash, and galena did not contribute to the concentrations of Pb that were present in seawater.

Conclusions

In the Gulf of Prigi, the majority of physico-chemical parameters including temperature, salinity, DO, EC, pH, COD, turbidity, sulfate, BOD, chlorophyll a and metal contents of Ca, Fe, Mn, Cu, Pb isotopes in surface seawater samples were found within the permissible limits set by WHO. The relationship between total content of Pb and their Pb isotopes showed that the Gulf of Prigi receives contributions from natural sources reflected from parent rock such as U and Th. The investigation of $^{208}\text{Pb} / ^{206}\text{Pb}$ and $^{207}\text{Pb} / ^{206}\text{Pb}$ falls completely with the Pb growth curve and anthropogenic sources corresponding to the predominant unpollution by natural-leached Pb from marine sediment. This study, by investigating surface seawater from the Gulf of Prigi, revealed that this gulf is a potential dwelling for

opening and increasing the productivities of fish, shrimp, corals, lobster and associated marine products for the public welfare. The use of Pb isotopes in seawater of the Gulf of Prigi is an effective approach for environmental monitoring associated with its interaction with Indian Ocean.

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