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To cite this article: I Y Ikhsani *et al* 2022 *J. Phys.: Conf. Ser.* **2377** 012039

Flame Atomic Adsorption Spectrophotometer (FAAS) to Assess the Concentration of Heavy Metals (Pb, Cd, Cr, and Zn) in *Porites* Coral from Ambon Bay, Indonesia

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Abstract. The concentration of metals in coral represents environmental changes, monsoonal variation, and human disturbance. Metals in coral were used as a proxy to evaluate the response of coastal areas to climatic and human stresses. In this study, several metals including lead (Pb), cadmium (Cd), chromium (Cr) and zinc (Zn) in *Porites* coral taken from Ambon Bay, Ambon Island, Indonesia, were investigated. The history of metals transient in the most populated island in Maluku Province is documented here from measurements of metals concentration from monthly-banded coral that grew in coastal seawater from 2001 to 2009. The concentration of heavy metals in coral samples was measured using Flame Atomic Adsorption Spectrophotometry (FAAS) method. The results showed metals bioaccumulation (average ± STD) were following decreasing order: Pb (0.96 ± 1.58 µg/g) > Cr (0.15 ± 0.34 µg/g)> Zn (0.11 ± 0.26 µg/g) > Cd (0.007 ± 0.016 µg/g). Moreover, all metals content in the coral showed a remarkable rose from 2001 to 2009 and showed relatively high concentrations during the southeast monsoon for Pb and Cd. Based on the statistical analysis, all metals in Ambon Bay coral were impacted by terrestrial input. In addition, Pb and Cd were also impacted by natural processes that may be associated with their biogeochemical cycle and monsoonal variation.

1. Introduction

A reef-building coral is widely used as a proxy for interpreting past environments due to its sensitivity to physical and chemical changes in the marine environment [1–4]. The massive skeleton of *Scleractinia* coral can provide a long period of information about the environmental condition, for example, sea surface temperature, precipitation, and even pollution that enters the marine environment [3,5–7]. The pollutant, such as metals, might occur in the coral skeleton due to human activities such as fossil fuel burning, shipping, nearshore mining, harbour dredging and sewage discharge [8,9]. These metals are incorporated into the coral skeleton, and the new growth will cover old carbonate surfaces. Furthermore, the metals recorded in the coral skeleton can be correlated with the monsoonal variation, environmental changes, and anthropogenic stresses of the marine environment [10–12].

Ambon Bay plays a vital role in fishery, aquaculture, transportation, and other economically important activities as a coastal area. The population number and industrial activities surrounding Ambon Bay also showed rapid growth in past decades (https://ambonkota.bps.go.id/). The increased industrialization and human population in coastal regions have consequences, particularly for the marine environment. The unplanned and uncontrolled usage of the coastal area decreased the environmental quality of Ambon Bay [13]. Moreover, the transport of pollutants, particularly heavy metals from Ambon Island to the bay is a growing concern due to their toxicity and accumulation in biota and sediment [14–18]. Most of the records about heavy metal pollution in Ambon Bay were obtained from either sediment or biota. Profoundly limited studies about the bioaccumulation of heavy metals in coral skeleton from Ambon Bay. While the life span of *Scleractinia* coral is relatively long (up to hundreds of years) and serves as a long-term environment recorder. Investigation about heavy metal content in the coral skeleton can add valuable insight into the existing knowledge on the evolution of heavy metal pollution in Ambon Bay and even in eastern Indonesia for a longer period.

In this study, we aimed to address the remaining scientific gap about the heavy metal pollution in Ambon Bay recorded by *Scleractinia* coral by focusing on three substantial approaches. Firstly, we characterized the bioaccumulation of selected metals including lead (Pb), cadmium (Cd), chromium (Cr), and zinc (Zn) in the coral skeleton. Secondly, we observed the trend of metal concentration and correlation between those metals in the coral sample. Lastly, we elucidated the geochemical behaviour and possible sources for each metal.

2. Methods

2.1. Description of sampling location

In this study, *Porites* coral was taken from Ambon Bay located in Ambon Island, Maluku Province as seen in Figure 1. Ocean Data View (ODW) software was used to visualize the sampling station [19]. Ambon Island is the place of Maluku province's capital city, Ambon City. As the capital city of Maluku province, Ambon City developed to become a small area with rapid population growth.

Furthermore, as a gate to Ambon City, Ambon Bay has an essential role for Maluku province and even the eastern Indonesia area region. Ambon Bay is a location for the economy, tourism, fisheries, marine culture, transportation, and industrial activities. Topographically, Ambon Bay has a unique marine setting. Ambon Bay is a single bay that consists of two regions, inner and outer regions. A shallow sill with a maximum depth of about 12 m separates both regions. The inner Ambon Bay has a smaller area (± 6 km^2) and shallower depth (40 m) than the outer region which has an area of about 100 km^2 with an average depth of more than 100 m.

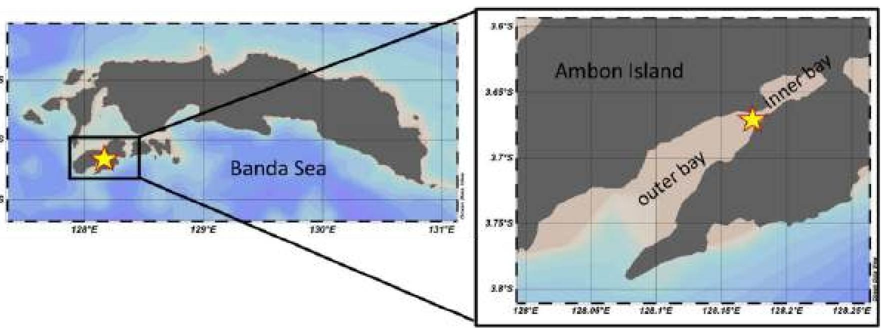

Figure 1. The sampling location is marked by a star symbol [20].

2.2. Coral sample and metal analysis

Porites coral specimen was collected from approximately 3 meters depth in October 2009 using a pneumatic drilling pistol. The preliminary processes in coral sample preparation including cleaning, X-ray scanning, and linear growth analysis have been done in a previous study [20]. The *Porites* sample contained coral skeletons growing from 2001 to 2009, covering nine years of record [20]. The X-radiograph of the skeletal slab of the *Porites* coral is provided in Figure 2.

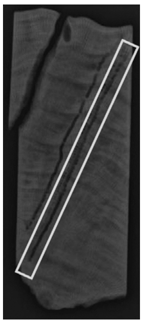

Figure 2. The X-radiograph of the skeletal slab of the *Porites* coral from Ambon Bay. The box enclosed with white line indicates the sub-sampling section to prepare the coral powder sample.

Coral powder samples were collected carefully using a 1 mm bit drilling along the coral's growth axis from the top core to the bottom core for metal analysis. The coral powder was then placed in a mini tube, numbered, and ordered from the first to last sample. Approximately 0.5 g of coral powder was weighed precisely and placed in an acid-cleaned vial. The coral powder then digested with 1 mL of 2% (v/v) nitric acid (HNO_3) solution, filtered through a 0.45 µm membrane filter and diluted to 50 mL with 2% (v/v) HNO_3. Metals concentration in the coral skeleton was determined using a flame atomic absorption spectrophotometer (FAAS, Shimadzu model AA 7000) in the AAS laboratory of Research Centre for Geotechnology, Bandung, Indonesia. The FAAS result data were then converted to µg/g dry weight coral powder since the metals concentrations were determined from the digested solid sample. For quality assurance of analytical data, blanks containing matrix and acid that were used for digestion were analysed at the beginning of the round of analyses. To assure the accuracy and precision of measurement, replications were done 5 times for obtaining a mean and standard deviation < 5%.The detection limits of FAAS were 0.01 mg/L for Cr and Zn, 0.05 mg/L for Cd, and 0.05 mg/L for Pb. In addition, all apparatus were acid-cleaned prior to use. Moreover, ultra-high purity water (Merck Millipore) and analytical grade of HNO_3 (Merck Co. Inc.) were used without further purification.

2.3. Statistical analysis
The statistical analysis and data visualization were performed using Microsoft Excel 2010 and IBM SPSS 24. IBM SPSS 24 software was performed to evaluate the correlation between each metal. Principal Component Analysis (PCA) was also used to evaluate the grouping of analysed metals to assess the geochemical behaviour and suspected sources.

3. Results and Discussions
3.1. Pb, Cd, Cr, and Zn concentration
The concentration of metals in the bands of coral slab samples is shown in Figure 3A – 3D. Each band was assumed to represent about three months period. Generally, all analysed metals showed higher values on the younger bands than the older bands. However, there were also significant differences among their distribution in each period. For example, gradual increase was observed for Pb from the youngest to the oldest slabs (Figure 3A). On the other hand, Cr and Zn in coral skeleton showed relatively flat profiles before the year 2008 and rocketed in the last three bands (Figure 3C and 3D). While for cadmium, generally showed an increasing trend for ten years record, even though some fluctuation occurred in the band older than 2007 (Figure 3B).

Furthermore, metals bioaccumulation in coral skeleton were following decreasing order: Pb > Cr > Zn > Cd. The average values were 0.96 ± 1.58 µg/g, 0.15 ± 0.34 µg/g, 0.11 ± 0.26 µg/g, and 0.007 ± 0.016 µg/g, for Pb, Cr, Zn and Cd respectively. The Pb concentration ranged from not detected to 5.6 µg/g, the highest value recorded in the period July-September 2008. The highest value of Cd was 0.06

µg/g during April-June 2007. The concentration of Cr remained low from the oldest subsampling to April-June 2008, then reached the highest value of 1.5 µg/g in October-December 2008. Similar to Cr, Zn also showed low concentration before April-June 2008, and then increased drastically afterwards. The highest Zn was 1 µg/g, recorded on the last band during January-March 2009.

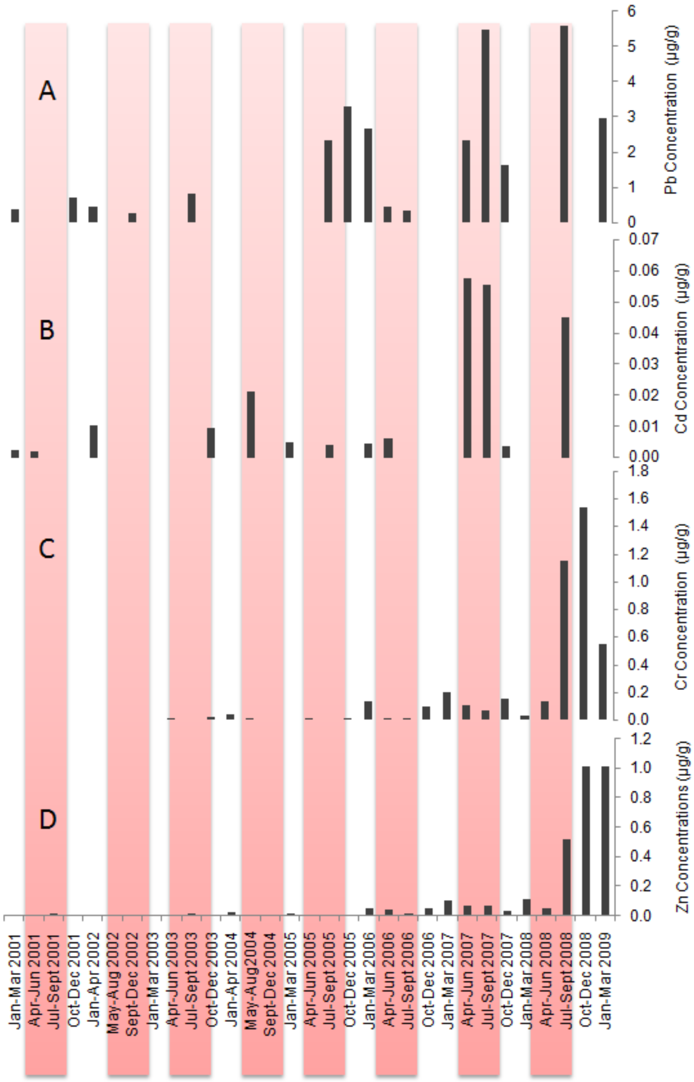

Figure 3. The concentration of Pb (A), Cd (B), Cr (C), and Zn (D) in µg/g dry wt in *Porites* coral of Ambon Bay (the pink background represent southeast monsoon).

3.2. Results of correlation analysis

The correlation between metals in the coral skeleton were tested and analysed using Pearson correlation. There were six possible combinations between two metals, and out of these only two pairs showed significant correlation. Pb & Cd and Cr & Zn showed strong correlations with Pearson correlations were 0.678 & 0.868, respectively. In contrast, as Pb has a strong correlation with Cd, it showed a weak correlation (Pearson correlation <0.5) with Cr and Zn. Similarly, Cd also showed weak correlation with Cr and Zn.

Furthermore, PCA was used to determine the geochemical behaviour and suspected sources of each metal. PCA sampling adequacy prior to PCA was calculated by the Kaiser-Meyer-Olkin (KMO) test. KMO statistic values was 0.502, indicated satisfactory of PCA value. Varimax rotation was applied in the factor analysis to evaluate the factoring processes. The rotation formed two final factors; the first factor accounted for 55.81% of the total variance is Pb and Cd. While the second factor is Cr and Zn and they accounted for 33.5% of the total variance. The distribution and both factors after varimax rotation was provided in Figure 4.

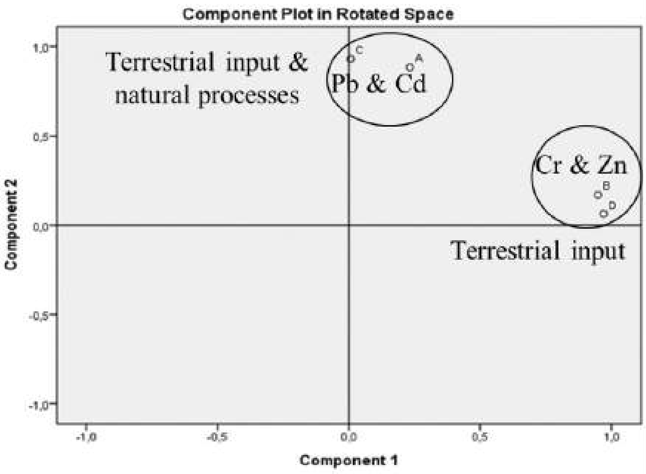

Figure 4. Distribution of factors of PCA analysis result;. Note: A, B, C, and D in the figure indicated Pb, Cr, Cd, and Zn, respectively.

The metal content on coral's band represents their historical level of ambient seawater because metals are incorporated into coral's skeleton in proportion to their concentration in ambient seawater. In this study, *Porites* coral in Ambon Bay recorded that metals concentration increased within the year 2001 to 2009. During that time, the rose of Cr bioaccumulation has the most significant value (14-fold), followed by Zn (10-fold), Cd (7-fold) and Pb (6-fold).

Interestingly, during the analyzed coral's lifespananalyzed coral's lifespan, the human population in Ambon City also increased from 220.988 people in 2001 to 284.809 in 2009 (https://ambonkota.bps.go.id/). Parallel to the population growth, the demand for residential land also increased. The total area of built-land in Ambon City was 675 hectares in 2003 and increased to 921 hectares in 2009 [21]. On the other hand, all analysed metals in this study were widely used in human activities. Pb is widely used in gasoline and diesel fuel [22-23], Cd, Cr, and Zn are commonly used in the paint manufacturing, electrical, and agricultural industries [24]. The increase of metal concentration in the *Porites* coral of Ambon Bay thus might be related to the increased of anthropogenic disturbance including urban waste and industrial activities around the bay. The similar trend were reported previously in coral from other areas such as Gulf of Aqaba, Jordan [25]; Sabah, Malaysia [26]; Bermuda, North Atlantic Ocean, central Indian Ocean including Chagos Archipelago, western Sumatra, and Strait of Singapore [27].

Furthermore, statistical analysis was used to understand metals geochemical behaviour and suspected sources. Pb and Cd showed strong correlation in both Pearson and PCA analysis. On the other hand, Cr strongly correlated with Zn. For further identification of metals geochemical behaviour and retrospect origin, we overlaid the metal concentration data with monsoonal periods (Figure 3). Ambon Bay is generally impacted by two different monsoon, southeast and northwest monsoon. The southeast monsoon or rainy season occurs from April to September, while the northwest monsoon or dry season occurs from November to March [28]. The period southeast monsoon indicated by pink coloured background in Figure 3.

Based on the Figure 3A and 3B, the concentration of Pb and Cd were relatively higher during southeast monsoon than northwest monsoon. On the other word, both Pb and Cd showed a seasonal pattern. Pb and Cd enter the marine environment through the riverine transport and atmospheric deposition [24,29-30]. The sampling site is located close to the docking area, populated residence area, ferry ship port, and traditional market. Therefore, higher precipitation during the southeast monsoon might deliver more Pb and Cd from Ambon Island into the Ambon Bay. In addition, high precipitation during southeast monsoon might also dilute the aerosol contained Pb and Cd and deposited it in the surface water of Ambon Bay. These reasons lead to the tendency of higher Pb and Cd bioaccumulation in the coral sample during southeast monsoon. The high concentration of Cd during southeast monsoon might also be affected by the water from Banda Sea that is dragged into the coastal area through the upwelling process [31]. During the southeast monsoon, the deep water from the Banda Sea enters Ambon Bay. This water is characterized by its cooler temperature and high macronutrients content [32-33]. Since Cd has an analogous biogeochemical cycle to macronutrients [34], the upwelled water mass might also bring metal including Cd [35]. However this hypothesis should be confirmed by further study. Taken together, the geochemical behaviours of Pb and Cd in coral from Ambon Bay most likely be influenced by the combination of terrestrial input and natural processes associated with monsoonal variation.

Unlike Pb and Cd, Zn and Cr did not show seasonal pattern (Figure 3C and 3D) but exhibited dramatically increasing trends from half of the 2008 to 2009. Zn is an important micronutrient for phytoplankton growth [36-37]. However, it become toxic in high concentration [38]. Similarly, high concentration of Cr may also be toxic for marine microorganism [39-40]. Zn and Cr occur naturally in marine environment however human activities increased their concentration. Cr and Zn are commonly used in paint and dyes, electronic device and battery [8,41]. Zn is also used as fertilizer and fungicides [42]. Therefore, the presence of Cr and Zn in coral skeleton from Ambon bay was likely associated with terrestrial input such as urban sewage, agriculture and industrial activities.

Although all metal concentrations in Ambon Bay's coral showed increasing trends, it was lower than the metal content in coral from other tropic areas at relatively comparable period. Table 1 shows the comparison of metal concentration in *Porites* coral from several tropical places that FAAS analysed. A report from Payar Island documented the average of Pb and Cr concentrations in *Porites* coral were 32.2 and 5.6 μg/g [43] These values were more than 30 times higher than the of Pb and Cr concentrations in this study. Higher Zn concentration in *Porites* coral obtained from three islands around Malaysia Peninsular, Tioman, Rendang, and Langkawi Islands was reported by [44]. Relatively lower metals concentration in coral from Ambon Bay, indicated lesser metals loads into Ambon Bay than in other compared areas.

Table 1. The average of metals concentration (in μg/g) in *Porites* coral obtained in this study and other places. The bracketed values indicated the range of metal concentrations.

Ref.	Location	Period	Pb	Cd	Cr	Zn
This study	Ambon Bay	2001-2009	0.96 (ND-5.6)	0.007 (ND-0.06)	0.15 (ND-1.5)	0.11 (ND-1)
[43]	Payar Island	1992-1996	32.2 (<1-96)	3.8 (3-7)	5.6 (2-12)	16.8 (13-24)
[44]	Tioman Island	1996-2004	-	-	-	23.73
	Rendang Island	1996-2005	-	-	-	39.96
	Langkawi Island	1999-2005	-	-	-	118.03

ND: below the detection limit

4. Conclusion

This study highlighted the ability of *Scleractinia* coral as an environmental recorder. Within nine years of record, the coral showed changes in several metals concentration in Ambon Bay drastically. From 2001 to 2009, the newest band showed that chromium concentration rocketed to 14-fold higher than the oldest band, followed by zinc (10-fold), cadmium (7-fold), and lead (six-fold). The increased of human population and activities might be responsible for the rose of metals concentration in coral skeleton from Ambon Bay. Statistical analysis suggested that Pb & Cd and Cr & Zn have similar geochemical behaviour and possible sources. Moreover, Pb and Cd showed seasonal variation. Pb and Cd concentration in coral skeleton tended to be higher during southeast monsoon than northwest monsoon. This suggested that natural processes associated with monsoonal variation also affected the geochemical behaviour of Pb and Cd.

5. Acknowledgments
The authors are thankful to the Centre for Deep Sea Research-LIPI for the research apprenticeship permit and to Research Centre for Geotechnology-LIPI for a chance to conduct research in AAS and micro preparation laboratories. This research was supported by the research project of the Research Centre for Geotechnology-LIPI in Seribu Island No.4408.001. 014.H DIPA No. 079.01.2.017152/2016. The LPDP also supported this research through BPI program.

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