Heavy metal content in annually-banded coral Porites lutea at windward and leeward of Tunda Island, Banten bay, West Java Indonesia

N P Zamani1*, Riska2, T Prartono1, A Arman3 and I Wahab1

1Department of Marine Science and Technology, Bogor Agricultural University (IPB University), Bogor, Indonesia
2Haluoleo Kendari University, Kendari, Indonesia
3Center of Isotope and Radiation-Batan, Jakarta, Indonesia

*E-mail: npzamani@gmail.com

Abstract. Longterm fluctuation content of heavy metal concentrations (Sr, Cr, Fe, Zn, and Pb) was traced through the analysis of coral skeletal growth bands of massive coral core Porites lutea. Annual growth band was examined using X radiography. Heavy metal samples were extracted from each yearly layer of the core section. Seven samples of the coral skeleton were analyzed using neutron activation analysis and atomic absorption spectrometry to detect metal concentrations. The oldest layer of coring corals obtained from the windward side started from 1940, while in leeward of the island starting from 1969. All five metals from both sides were still detected until 2014. There was significant increase over time of the four metals (Cr, Fe, Zn, and Pb), while the concentrations of strontium remained relatively stable.

Keywords: coral reef, coral skeleton, environmental change, massive coral, sclerochronology

1. Introduction

Coral has been widely used as indicators of environmental change because it is sensitive to physical and chemical fluctuation in the marine environment (Al-Rousan et al 2007, Jayaraju et al 2009, Chen et al 2010). This evident is observed in the health and physiology of coral polyps (Esselemont 1999, Chan et al 2014) and the physical-chemical characteristics of the skeleton (Fisk and Harriot 1989, Abelson et al 2005). The growth scleractinian have been recognized as a longterm recording of heavy metals pollutants that enter naturally to the marine environment or as a result of human activities such as industrial or organic waste (Huang et al 2003, Edinger et al 2008). Metals will be deposited in the coral skeleton as a result of the structural aragonite incorporation, the inclusion of particulate matter in the framework, and adsorption on the surface of the frame (David 2003, Al-Rousan et al 2007). This metal will remain forever embedded in the coral skeleton as new growth which covers the old framework (Negri and Heyward 2001, Ali et al 2010). Ratio of Sr/Ca, Mg/Ca, U/Ca, B/Ca and δ18O isotopes in coral skeletons have been used to reconstruct sea surface temperature (Beck et al 1992, Gagan et al 2000, Suzuki et al 2001, Fallon et al 2002, Tanaka et al...
2013), whereas Cd/Ca, Mn/Ca and Ba/Ca was used to reconstruct rainfall, and upwelling (Lea et al 1989, Shen et al 1992, Erftemeijer et al 2012). On the other hand, the abundance of heavy metals such as Hg, Pb, Cd, Mn, Cu, Zn and others, in the coral skeleton reflects the influence of anthropogenic and or terrestrial to marine environments such as industrial pollution and waste that may be transported and distributed by currents (Schneider and Smith 1982, Shen et al 1987, Shen and Boyle 1989, Guzman and Jimenez 1992, Koran 2005, Chan et al 2014).

Coral species *P. lutea* commonly used in the research track record of pollutants on limestone skeleton of coral due to growing in tropical regions of Asia-Pacific with the pattern of growth is relatively slow when compared to other organisms (Al Rousan et al 2007, Chen et al 2010, El-Moselhy et al 2014), where the limestone skeleton of coral is a sort of archival footage environmental conditions. Tunda Island located in Banten Bay, which is closed to industrial areas such as Krakatau Steel, recreation area (Anyer) and Sunda Strait which is busy with sea transportation from Java Island to Sumatra Island. In this study the record of heavy metal pollution on the skeleton of coral *P. lutea* is presented annually to determine the concentration of pollutants in each ring of annually coral growth, to see the metal condition both in the windward (the area facing to the wind) and leeward (the relatively calm area which is not facing to the wind) of Tunda Island from the past to the present.

2. Materials and methods

This research was conducted from August 2014 to February 2015. Coral core sampling was carried out on 30 August-4 September 2014 at Tunda Island, Serang District, Banten Province (figure 1). Analysis of (Sr, Cr, Fe, and Zn) content from the annual layer of the coral’s skeleton was made on 8 September 2014 – 2 January 2015 at Laboratory of Application Center Isotopes and Radiation Technology, Center for Nuclear Energy (BATAN), Jakarta.

The circumference analysis of the coring coral used the X-ray tools at Health Laboratory of Nuclear, BATAN, Jakarta. The measurement of heavy metal pollutants used Neutron Activation Analysis (NAA) was used nuclear facilities GA Siwabessy P2TR and gamma spectrometer with a detector High Purity Germanium (HPGe) equipped with Multi-Channel Analyzer (MCA).

![Figure 1](image-url)  
*Figure 1. Map of location for sampling coral *P. lutea* in the direction of the north wind (windward) and the direction of the south wind (leeward) waters of Tunda Island, Banten Province (grey= sea, white= land, triangle symbol= sampling point).*
2.1. Site selection
The sampling point was determined based on the distribution of coral *P. lutea* and the geographical conditions of the island. Point sampling consisted of 2 stations representing facing to open area windward (northern part) and relatively protected area leeward (southern part). Windward locations are more exposed to the waves, while the opposite leeward location in the south is relatively protected by the waves.

2.2. Technical sampling
Sampling was conducted at 3-5 m depth using a hand drill tool connected to a pneumatic air tube to move the submarine pipe stainless steel drill bit attached at one end. The diameter of the drill was 5 cm and a length of 50 cm. Coral reefs in the middle were drilled vertically to get direction and a continuous growth rate (Arman et al 2013). The water was flowed using a pump during drilling which passed through the inside of the stainless steel pipe to remove fine grains of rock eroded by the drill bit. This is to avoid blocking the rotation of the drill bit. After completion of sampling, former drill holes covered with cement to give coral reefs recovery and also to avoid the animal or organism enter into the rock that causes damaged the reef.

2.3. Sample preparation
The coral samples were washed with fresh water for approximately 1-hour using an ultrasonic bath, then dried and taken to the Marine Laboratory, Center for Isotope and Radiation Applications BATAN for further analysis. The samples were cut vertically into the form of slab, with a thickness of 5 mm using a ceramic cutter and further analyzed by X-ray radiography (Arman et al 2013), to determine the age and the rate of linear growth of coral.

2.4. Sample analysis
2.4.1. Coral growth analysis. Age determination on a piece of coral samples (5 mm) was determined through a process images with X-ray radiography apparatus Rigaku Radioflex RF-300EGM2130 KeV for 1 second at a distance of 1 meter. The results of this process are the X-ray film in black and white, which is then converted into a digital format using positive film scanner EPSON V600 (Arman et al 2013). Results were analyzed with software scanners Coral XDS to determine the annual layers (annual band) age of rock, direction, and rate of growth (Helmle et al 2012).

2.4.2. Analysis of total pollutants. After analysis of linear growth, heavy metals were analyzed using Neutron Activation Analysis (NAA) in accordance with the procedure of Malainey (2011) and IAEA (1980). Each ring of coral samples was taken as much as 0.2 g and put into containers of polyethylene. Reference materials for each pollutant materials dried in an oven at 50°C for 24 hours. Samples reefs and reference materials in a closed container. Both samples are irradiated in a reactor with a power of 750 kW with a Thermal Neutron Flux for $10^{13}$ neutron/cm$^2$/sec for 30 minutes. After irradiation, the samples were left for 3 weeks to reduce the radiation exposure of samples.
Gamma spectrometer with high resolution is used to measure the activity of the sample radiation. Enumeration was done for 3600 seconds on both sample and reference materials. For determining the concentration of heavy metals (pollutants) characteristics of gamma energy used were as follows: 320 keV $^{51}$Cr; 514 keV $^{85}$Sr; 1115 keV $^{65}$Zn; and 1099 keV $^{59}$Fe (IAEA 1992).

Pb concentrations were analyzed using Atomic Absorption Spectrometry (AAS). Rock samples that have been crushed as much as 5 grams dissolved using 5 ml HNO$_3$, then stirred. Samples that have been stirred included in the measuring cup 100 ml then added 5 ml of HCl and heated on a steam bath for 15 minutes. Then the sample is filtered using filter paper to the size of 0.40-0.45 μm and added 100 ml of distilled water, then stir again and analyzed by AAS (APHA 2012).

![Figure 3. Annual coral growth tape analysis using digital radiographic approach utilizing X-ray sources and Epson V700 positive film scanning media.](image)

3. Results and discussion

Samplings were carried out at the windward and leeward area of Tunda Island. Lalong (2014) using X-Ray and Coral XDS showed that the samples of coral reefs in the windward area have a circumference of 75 years so that these samples can be drawn from the environment chronologically from 1940 to 2014. The sample size of the colonies of coral reef greater than in samples taken from the leeward, with a number of the smaller circumference. Samples of coral reefs in the leeward area have circumference 46 years, which gives chronological pollutants starting from 1969. Differences between the circumferences of the year due to the different lengths of the sample obtained. The circumference of the core width of the reef is also different, allegedly indicating different growth conditions and are generally related to the water conditions in the future, where water conditions will affect the metabolic processes so that growth from time-to-time is also different.

3.1. Record of Cr, Sr, Fe, Zn, and Pb content

Each type of reef has certain calcification rate each year so that fluctuations of metal concentrations analyzed on the coral skeleton were also vary (Felis and Patzold 2004). Bastidas and Garcia (2004) revealed that the presence of heavy metals in the coral skeleton is a result of detoxification of the coral animals. Coral animals will deposit heavy metals in the cell body to its zooxanthellae and the skeleton. Comparison of heavy metals concentrations of Cr (a), Sr (bk), Fe (c), Zn (d), and Pb (e) in the core area of coral $P.$ lutea windward and leeward was presented in figure 4.

![Figure 4. Comparison of heavy metals concentrations of Cr (a), Sr (bk), Fe (c), Zn (d), and Pb (e) in the core area of coral $P.$ lutea windward and leeward.](image)
presence of Cr, Sr, Fe, and Zn. Pb was not detected because the half-life of Pb is very short so that the content of the radiation of the metal has been depleted during the cooling process in the research reactor. Pb was analyzed by atomic absorption spectrometer (AAS).

Metal concentrations recorded on limestone skeleton *P. lutea* in the windward started from 1940 to 2014 were Cr, Sr, Fe, Zn, Pb. The concentration of Cr, Fe, Zn, and Pb showed a significant improvement over the 75 years, Sr concentrations are relatively similar. Cr concentration measurement results in the range of 4.36 to 10.33 mg/kg/year, with an average concentration of 6.67 mg/kg/year. Sr metal concentrations ranged between 70.42-83.59 mg/kg/year, with an average concentration of 77.24 mg/kg/year. Fe metal concentrations ranged from 4.88-47.70 mg/kg/year, with an average concentration of 26.49. Zn concentrations ranged from 3.28-12.70 mg/kg/year, with an average concentration of 7.16 mg/kg/year, while concentrations of Pb within a period of 75 years ranged from 6.17-14.76 mg/kg/year, with an average concentration 9.69 mg/kg/year.

![Figure 4](image-url)  
*Figure 4. Heavy metal concentrations of Cr (a), Sr (b), Fe (c), Zn (d), and Pb (e) in the skeletal of coral *Porites lutea* windward (blue line) and leeward (red line).*
Metal concentrations were recorded in leeward areas began in 1969 to 2014. The concentration of each metal showed an increasing trend each year. Cr concentration measurement results ranged from 5.11-11.77 mg/kg/year, with an average concentration of 8.54 mg/kg/year. Sr concentration ranges between 70.12-103.5 mg/kg/year, with an average concentration of 83.77 mg/kg/year. Fe metal concentrations ranged between 25.25-43.75 mg/kg/year, with an average concentration of 38.95 mg/kg/year. Zn concentrations ranging from 6.47 to 15.59 mg/kg/year, with an average concentration of 11.70 mg/kg/year, while concentrations of Pb within a period of 75 years ranged between 68.38-17.66 mg/kg/year, with an average concentration 13.33 mg/kg/year. Figure 4 shows of all metals except Sr, have the same pattern of concentration which showed significant improvement.

Metal concentrations located in the leeward area were higher than in the windward. The position of the leeward area faces directly the mainland of Banten bay, and is influenced by anthropogenic activities. The windward areas relatively expose to waves washing the metal from the coral tissue.

Figure 5. Comparison of the concentration ratio of Cr (a), Fe (b), Zn (c), and Pb (d) against Sr, the coral P. lutea core area windward (blue line) and leeward (red line).

Metal concentrations in waters continued to increase indicates an increase in the metal sourced either from the sea or from the land itself. The metal is likely to be carried away by the current. Cr, Fe, Zn, and Pb are also found naturally in seawater composition. The metals used by the coral animals to the process of metabolism and then there were deposited on reefs formed. The deposited metal has undergone bioconcentration by coral animals.

To identify the increase in the metal content of the mainland, the metal concentrations obtained were compared to the value of strontium. This was done to determine the amount of heavy metal that accumulate on the reef every year due to anthropogenic activities on the mainland (David 2003). Profile of metals by the ratio of the Sr can be seen in figure 5.
The concentration of all heavy metals on coral cores of leeward areas was greater than that of windward. This is probably caused by sedimentation patterns and physical factors in Tunda Island waters. Furthermore, the heavy metal content in the north was higher than the next windward-leeward. At the coral core, Fe metal content increases from year to year. The same result was found for Pb, although not as big as Fe. As for Cr and Zn, the pattern of enhancement is almost the same.

Based on the ratio of the value of the Cr, Zn, Fe, Pb to Sr then obtained an increase in the accumulated content of these metals occur after 1960. Whereas in the previous year showed a constant pattern. Under these conditions, it can be assumed that the natural concentration of each metal contained in the reef is the value indicated by each heavy metal before the 1960s.

4. Conclusion

The study shows that coral _P. lutea_ can be used to see changes in the environment of the past to the present, as indicated by an increase in the concentration of contaminants in samples of coral cores profile. This indicates that the region has experienced contamination are likely to come from anthropogenic activities. This influence may vary spatially due to differences in environmental conditions oceanography.

Acknowledgments

We would thank the Directorate General of Higher Education, Ministry of Education and Culture of the Republic of Indonesia, which fund this research. We would also thank Application Center Isotopes and Radiation Technology National Nuclear Agency (BATAN), Jakarta, for using all laboratory for analyzing samples.

References

Abelson A, Olinky R and Gaines S 2005 Coral recruitment to the reefs of Eilat, the Red Sea: temporal and spatial variation, and the possible effects of anthropogenic disturbances _March Pollut. Bull._ 50 576-582

Ali A-ham and M A Hamed Abd El-Azim H 2010 Heavy metals distribution in the coral reef ecosystems of the Northern Red Sea _Helg. March Res._ 65 67-80

Al-Rousan S A, Al-Shioul R N, al-Horani F A and Abu-Hilal A H 2007 Heavy metal contents in the growth bands of Porites corals: record of anthropogenic and human developments from the Jordanian Gulf of Aqaba _March Pollut. Bull._ 54 1912-1922

APHA 2012 _Standard methods for the examination of waters and wastewaters, 22nd ed Part 3000_ (Washington: APHA)

Arman A, Zamani N P and Watanabe T 2013 Studies age determination and the growth rate of coral reefs associated with extreme climate change using X-rays _A Sci. Jour. for The App of Iso Ts. and Rad._ 9 1-10

Bastidas C and Gracia E 1999 Metal content on the reef coral Porites astreoids: an evaluation of river influence and 35 years of sequences _March Pollut. Bul._ 38 899-907

Beck J W, Edwards R L, Ito E, Taylor F W, Recy J, Rougerie F, Joannot P and Henin C 1992 Sea-surface temperature from coral skeletal strontium / calcium ratios _Science_ 257 644-647

Chan I, Hung J J, Peng S H, Tseng L C, Ho T Y and Hwang J S 2014 Comparison of metal accumulation in the azooxanthellate scleractinian coral (_Tubastrea coccinea_) from different polluted environments _March Pollut. Bul._ 85 648-658

Chen T R, Yu K F, Li S, Price G J, Shi Q and Wei G J 2010 Heavy metal pollution recorded in Porites corals from Daya Bay, northern South China Sea _March Environ. Res._ 70 318-326

Cole J E and Fairbanks R G 1990 The Southern Oscillation recorded in the dδ18O of corals from Tarawa Atoll. _Paleoc._ 5 669-683
David C P 2003 Heavy metal concentrations in the growth bands of corals: a record of mine tailings input through time (Island Marinduque, Philippines) Pergamon March Poll. Bul. 46 187-196

Edinger E N, Azmy K, Diegor W and Siregar P R 2008 Heavy metal contamination from gold mining recorded in Porites lobata skeletons, Buyat-Ratototok district, North Sulawesi, Indonesia March Poll. Bul. 56 1553-1569

El-Moselhy K M, Othman A I, Abd El-Azem H and El-Metwally M E A 2014 Bioaccumulation of heavy metals in some tissues of fish in the Red Sea, Egypt Egyp. Jour. of Bas. and App. Scien 1 97-105

Erfemeijer P L, Riegl B, Hoeksema B W and Todd PA 2012 Environmental impacts of dredging and sediment of disturbances on corals: a review March Poll. Bul. 64 1737-1765

Esselemont G, Harriott V J and McConchie D M 2000 Variability of trace metal concentrations within and between colonies of Pocillopora damicornis March Poll. Bul. 40 637-642

Esselemont G 2000 Heavy metals in seawater, marine sediments, and corals from Townsville section, the Great Barrier Reef Marine Park, Queensland Mar. Chem. 71 215-231

Fallon S J, White J C and MacCulloch M T 2002 Porites corals as recorder of mining and environmental impacts: Island Misima, Papua New Guinea Geoc. et Cosm. Act. 66 45-62

Felis T and Patzol J 2004 Climate Reconstruction from Banded Coral Global Environmental Change in the Ocean and on Land ed Shiyomi (Terrapub) pp 205-277

Fisk D A and Harriott V J 1989 The Effects of Increased sedimentation on the recruitment and population dynamics of juvenile corals at Cape Tribulation, North Queensland (Australia: Great Barrier Reef Marine Park Authority)

Gagan M K, Ayliffe L K, Beck J W, Cole J E, Druffel E R M, Dunbar R B and Schrag D P 2000 New views of tropical paleoclimates from corals Quat. Sci. Rev. 19 45-64

Guzman H M and Jimenez C E 1992 Contamination of coral reefs by heavy metals along the Caribbean coast of Central America (Costa Rica and Panama) March Poll. Bul. 24 554-561

Helmle K P, Kohler K E and Dodge R E 2012 Relative Optical Densitometry and The Coral X-Radiograph Densitometry System: Coral XDS., Cambridge, (England Sept. 4-7) (Int. Soc. Reef Studies European Meeting)

Huang D, Shi Q and Zhang Y 2003 Contents of heavy metals in coral Porites in Sanya Bay and their environmental significance Mar. Environ. Sci. 22 35-38

IAEA 1980 Elemental Analysis of Biological Materials: Current Problems and Techniques with Special Reference to Trace Elements (Vienna: International Atomic Energy Agency)

Jayaraju N, Sundara Raja Reddy BC and Reddy K R 2009 Heavy metal pollution in reef corals of Tuticorin Coast, the Southeast Coast of India Soil Sed. Contam. 18 445-454

Koran N 2005 Environmental assessment, documentation and spatial modeling of heavy metal pollution along the Jordan Gulf of Aqaba using coral reefs as environmental indicators [Ph.D. Thesis] (Germany: University of Wurzburg)

Lea D W, Shen G T and Boyle E A 1989 Caroline barium records temporal variability in equatorial Pacific upwelling Nature 340 373-376

Malainey E M 2011 A consumer’s Guide to Archaeological Science: Analytical Techniques (Canada: Brandon University of Manitoba)

Negri A P and Heyward A J 2001 Inhibition of coral fertilization and larval metamorphosis by tributyltin and copper March Environ. Res. 51 17-27

Pastorok R A and Bilyard G R 1985 Effects of sewage pollution on coral-reef communities March Ecol. Prog. Ser. 21 175-189

Patterson C C, Settle D and Glover B 1976 Analysis of lead in polluted coastal seawater Chem. March 4 305-319

Schneider R C and Smith S V 1982 Skeletal Sr content and density in Porites spp. in relation to environmental factors March Biol. 66 121-131

Shen C C, Lee T, Chen C Y, Wang C H, Dai C F and Li L A 1996 The calibration OFD [Sr / Ca] versus sea surface temperature relationship for Porites corals Geoc. et Cosm. Acta. 60 3849-3858
Shen G T and Boyle E A 1989 Determination of lead, cadmium and other trace metals in annually-banded corals Chem. Geol. 67 47-62
Shen G T, Cole J E, Lea D W, Linn J E, McConnaughey T A and Fairbanks R G 1992 Surface ocean variability at Galapagos from 1936 to 1982: Calibration of geochemical tracers in corals Paleoceanography 7 563-588
Suzuki A, Gagan M K, Deckker P D, Omura A, Yukino I and Kawahata H 2001 Last interglacial record of enhanced insolation coral and seawater seasonality 18O enrichment in the Ryukyu Islands, the northwest Pacific Geop. Research Lett. 28 3685- 3688
Tanaka K, Ohde S, Cohen M D, Snidvongs A, Ganmanee M and McLeod C W 2013 Metal contents of Porites corals from Khang Khao Island, Gulf of for Thailand: Anthropogenic input of river runoff into a coral reef from urbanized areas, Bangkok App Geoc. 37 79-86
Wei G, Sun M and Li X B 2000 Nie Mg/Ca, Sr/ Ca and U/ Ca ratios of a Porites coral from Sanya Bay, Hainan Island, South China Sea and their relationships to sea surface temperature Palaeogeogr. Palaeoclimatol. Palaeoecol. 162 59-74