# Distribution and sources of polycyclic aromatic hydrocarbons (PAHs) in coastal waters of the Timor Sea

Dede FALAHUDIN<sup>1\*</sup>, Khozanah MUNAWIR<sup>1</sup>, Zainal ARIFIN<sup>2</sup> and Gabriel A. WAGEY<sup>3</sup>

<sup>1</sup> Organic Chemistry Lab, Research Centre for Oceanography (RCO)-LIPI, Indonesia

\*E-mail: dede.falahudin@lipi.go.id

<sup>2</sup> Marine Ecotoxicology Lab, Research Centre for Oceanography (RCO)-LIPI, Indonesia

<sup>3</sup> Arafura Timor Sea Expert Forum (ATSEF) Secretariat, Ministry of Fisheries and Marine Affairs, Indonesia

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**Abstract** — Studies of polycyclic aromatic hydrocarbons (PAHs) was carried out during Arafura and Timor Seas Ecosystem Action (ATSEA) Cruise on 10–16 May 2010. The objective of the study was to determine the concentration of total PAHs and to identify the potential source of contamination in the Timor Sea. Fifteen priority PAHs based on U.S. Environmental Protection Agency (U.S. EPA) were analyzed at the Research Center for Oceanography, Indonesian Institute of Sciences (RCO-LIPI) laboratory from 12 stations along the coastal waters of the Timor Island. Our study showed that total concentration of PAHs ranged from 54.5 to 213.7  $\mu$ g/l with an average of 99.8  $\mu$ g/l in seawaters, and ranged from 23.6 to 24.5 mg/kg dry weight (dw) in sediments. Potential sources of PAHs at Timor Sea came from petroleum, petroleum combustion, and organic material combustion.

Key words: polycyclic aromatic hydrocarbons (PAHs), Timor Sea, ATSEA, ratio analysis

## Introduction

The Timor Sea waters have unique characteristics because its location covers the Sahul continental shelf of north coast of Australia, part of the Timor shelf and the Timor Through which reaches depths of over 3,300 m (Wagey and Arifin 2008). The Timor Sea waters are the site of important oil fields, and there has been exploration for deposits on the Sahul Shelf off the northwest coast of Australia (Morrison and Delaney 1996). Oil drill activities and related industries may cause contaminations of heavy metals and persistent organic pollutants (POPs) that could have potential impact to marine resources.

Polycyclic aromatic hydrocarbons (PAHs) are a group of persistent organic pollutants (POPs) which consist of two or more rings of benzene and are resistant to oxidation and hydrophobic in nature (Zakaria et al. 2009). Aqueous solubility, vapor pressure and partition coefficient of octanol-water and organic carbon-water are important factor influencing environmental behavior for the PAHs. Various PAHs with high molecular weight are known to have significant toxicities. Moreover, PAHs have shown to be carcinogenic and mutagenic to marine life and human (WHO 2006). They are mainly derived from petrogenic source (crude oil and petroleum product) and pyrogenic source formed by incomplete combustion of organic matter (e.g., wood, coal, and grass). Beside that, PAHs are also derived from natural sources such

or use of unique compound as molecular markers and using difference in thermodynamic stability among PAHs species to

ference in thermodynamic stability among PAHs species to distinguish pyrogenic and petrogenic PAHs (Saha et al. 2009). Ratio diagnostic model based on difference in thermodynamic stability has been used to determine the origin of PAHs by several researchers to estimate the sources of PAHs in a water, sediments and biota. Furthermore, principal component analysis (PCA) and hierarchical cluster analysis (HCA) have been employed to distinguish individual PAHs among more sources of PAHs (Yunker and Macdonal 1995, Wenchuan et al. 2002, Yunker et al. 2002, Mostafa et al. 2003, Jinshu et al. 2004, Nemr et al. 2004, Nemr et al. 2006, Opuene et al. 2009, Jun Luo et al. 2008, Grigoriadou et al. 2008, Hiller et al. 2010).

as oil seeps, biogenesis, and volcano (Yunker et al. 2002,

mine their sources and migration (Hiller et al. 2010). There

are several approaches to determine PAHs sources such as

Characterization of PAHs has been conducted to deter-

Burns et al. 2010, Saha et al. 2009, Opuene et al. 2009).

The objectives of our study are first to determine PAHs concentration in seawaters and sediments, and second to distinguish the source of PAHs contaminants in the Timor Sea waters.

## **Materials and Methods**

Field study was carried out during Arafura and Timor

Seas Ecosystem Action (ATSEA) Cruise on 10–16 May 2010 by R/V Baruna Jaya VIII. Twelve samples of surface seawater (Stns 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, and 13) and two samples of sediments (Stns 12 and 13) were taken in the Timor Sea (Fig. 1, Table 1).

Surface seawater samples were taken using stainless steel water sampler at less than 1.0 meter depth, stored in dark bottles of 2.5 L volume, then immediately filtered by 0.45  $\mu$ m glass fiber filters (Whatman GF/C) and stored at 4°C during transport to laboratory for analysis (Hutagalung and Rozak 1997). The sediments were taken using a box corer, and then the surface sediments were sampled by an aluminum spoon. The sediments were then put into a glass bottle and covered with aluminum foil and finally stored in a refrigerator at 4°C for further analysis.

PAHs were analyzed at laboratory as follows; the raw extracts were dried from water by passing through Na<sub>2</sub>SO<sub>4</sub>,

and evaporated until 1 ml. Furthermore, the sediment samples as 40 g were dried in the oven at 50°C overnight, puree mashed in a mortar. After Na<sub>2</sub>SO<sub>4</sub> was added, soxhlet extraction was carried out for 8 h with 120 ml dichloromethane (DCM). The raw extracts were evaporated until 1 ml. The concentrated extract from water and sediments samples was then cleaned up using alumina chromatographic column with 4 g aluminum oxide WB 5 basic (SIGMA). After the conditioning of the column with 10 ml DCM and hexane, a concentrated extract was transferred into the column, and eluted with 4% diethyl ether in hexane, and evaporated again until 1 ml.

The cleaned samples were separated and fractionated using silica gel chromatographic column with silica gel Merck 7754 as much as 4 g. That column was conditioned before use with 10 ml DCM and hexane. Non-polar fraction (F1) was eluted by hexane for analysis of pesticide, saturated



Fig. 1. Location of sampling PAHs research on ATSEA Cruise 2010 (St. 1–13).

Table 1. Sampling stations of PAHs during ATSEA Cr	uise.
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Name of	Position		Dopth (m)	Time of Sampling		Sample	
Station	Latitude (LS)	Longitude (BT)	Deptil (III) —	Date	Time (GMT)	Water	Sediment
Station 1	-10°31.011′	123°43.968′	272	10-May-10	18:24	Х	
Station 2	-10°55.478′	123°58.055′	2000	10-May-10	23:10	Х	
Station 3	-10°25.102′	124°51.090'	1939	11-May-10	9:34	Х	
Station 4	-10°01.772′	124°37.184′	746	11-May-10	15:05	Х	
Station 5	-09°23.030′	125°50.940'	1029	12-May-10	7:06	Х	
Station 6	-09°43.893′	126°07.907′	2584	25-May-10	15:05	Х	
Station 7	-09°09.055′	126°51.623′	1589	13-May-10	10:00	Х	
Station 8	-08°50.899′	126°51.487′	1583	13-May-10	7:17	Х	
Station 9	-08°29.229′	127°256.767′	2016	13-May-10	20:35	Х	
Station 10	-08°47.405′	129°14.310′	1615	14-May-10	9:40	Х	
Station 12	-08°25.007′	131°16.029′	1506	15-May-10	7:17	Х	Х
Station 13	-08°53.266′	131°43.331′	339	15-May-10	15:38	Х	Х

hydrocarbon; and polar fraction (F2) was eluted by 10% diethyl ether in hexane for analysis of PAHs. The polar fraction (F2) was analyzed using GC/FID (gas chromatography-flame ionization detector) analyses. The GC/FID separation using HP1 capillary column ( $12 \text{ m} \times 0.2 \text{ mm}$  I.D.,  $0.33 \mu \text{m}$  film thickness) with a GC oven temperature program: oven temperature 60°C for 2 min, heated to 280°C at 10°C/min, and then hold for three minutes at 300°C. Injector temperature was set to be at 240°C with helium as carrier gas. The GC-FID was calibrated with QTM PAHs standard mixture (QTM PAH mix 479330-U Supelco) (EPA Methods 8001, 1986, Holden and Marsden 1969, Greve and Grevenstuk 1975, Duinker and Hillebrand 1978).

Data analysis was conducted for calculating concentration of total PAHs and individual PAHs, composition of diagnostic ratio, performing principal component analysis (PCA) and hierarchical cluster analysis (HCA) using SPSS version 16.00. Diagnostic ratio to assess PAHs sources are phenanthrene/anthracene (Phe/Ant), fluoranthene/pyrene (Flu/Pyr), indeno(123-cd) pyrene/(indeno(123-cd)pyrene+benzo(ghi) pyrylene) (InP/(InP+BghiP)), fluoranthene/(fluoranthene+ pyrene) (Flu/(Flu+pyr)), benzo(a)pyrene/(benzo(a)pyrene+ chrysene) (BaP/(Bap+Chr)), anthracene/(anthracene+ phenanthrene) (Ant/(Ant+Phe)), anthracene/178 (Ant/178) and benzo(a)anthracene (BaA/228) (Yunker and Macdonald 1995, Yunker et al. 2002).

### Results

Fifteen PAHs analyzed in this study were categorized as the US-EPA pollutant priority. These were naphthalene (Naph), acenaphthylene (Acethy), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene

Table 2.	Concentration	$(\mu g/l)$	of PAHs in	seawater	of the Timor Sea
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PAHs Compound		St 1	St 2	St 3	St 4	St 5	St 6
Naphthalene	Naph	0.33	nd	0.33	0.29	0.27	0.26
Acenaphthylene	AceThy	nd	nd	nd	nd	Nd	nd
Acenaphthene	Ace	0.32	0.34	0.27	0.27	0.33	0.26
Fluorene	FI	0.22	nd	nd	nd	Nd	nd
Phenanthrene	Phe	0.34	nd	0.27	nd	0.33	0.27
Anthracene	Ant	0.93	2.53	2.17	2.12	2.1	2.01
Fluoranthene	Flu	5.83	4.49	0.72	3.65	6.61	4.44
Pyrene	Pyr	9.87	4.95	0.86	3.42	4.88	4.53
Benzo(a) Anthracene	BaA	17.49	12.25	3.00	9.25	11.78	12.95
Chrysene	Chr	42.71	19.33	11.46	13.36	19.2	20.61
Benzo(b)Fluoranthene	BbF	32.05	7.04	14.81	6.29	8.23	9.6
Benzo(a) Pyrene	BaP	18.58	11.73	28.49	12.44	15.05	16.86
Indeno(123-cd) Pyrene	DBahA	46.6	12.48	23.38	11.16	11.02	11.85
Dibenzo(ah)Anthracene	InP	23.66	13.73	32.34	16.57	18.37	21.90
Benzo(ghi) Pyrylene	BghiP	14.79	4.06	9.46	2.77	2.37	5.57
Total PAHs		213.70	92.92	127.55	81.60	100.51	111.11
PAHs Compound		St 7	St 8	St 9	St 10	St 12	St 13
PAHs Compound	Naph	St 7 0.26	St 8 0.49	St 9 0.52	St 10	St 12	St 13 1.19
PAHs Compound Naphthalene Acenaphthylene	Naph AceThy	St 7 0.26 nd	St 8 0.49 nd	St 9 0.52 nd	St 10 1.09 0.28	St 12 1.10 0.22	St 13 1.19 0.29
PAHs Compound Naphthalene Acenaphthylene Acenaphthene	Naph AceThy Ace	St 7 0.26 nd 0.32	St 8 0.49 nd 0.25	St 9 0.52 nd 0.30	St 10 1.09 0.28 0.26	St 12 1.10 0.22 0.26	St 13 1.19 0.29 0.32
PAHs Compound Naphthalene Acenaphthylene Acenaphthene Fluorene	Naph AceThy Ace Fl	St 7 0.26 nd 0.32 nd	St 8 0.49 nd 0.25 nd	St 9 0.52 nd 0.30 nd	St 10 1.09 0.28 0.26 0.39	St 12 1.10 0.22 0.26 0.33	St 13 1.19 0.29 0.32 0.50
PAHs Compound Naphthalene Acenaphthylene Acenaphthene Fluorene Phenanthrene	Naph AceThy Ace Fl Phe	St 7 0.26 nd 0.32 nd 0.32	St 8 0.49 nd 0.25 nd nd	St 9 0.52 nd 0.30 nd nd	St 10 1.09 0.28 0.26 0.39 0.59	St 12 1.10 0.22 0.26 0.33 0.42	St 13 1.19 0.29 0.32 0.50 0.64
PAHs Compound Naphthalene Acenaphthylene Acenaphthene Fluorene Phenanthrene Anthracene	Naph AceThy Ace Fl Phe Ant	St 7 0.26 nd 0.32 nd 0.32 2.23	St 8 0.49 nd 0.25 nd nd 2	St 9 0.52 nd 0.30 nd nd 2.81	St 10 1.09 0.28 0.26 0.39 0.59 2.84	St 12 1.10 0.22 0.26 0.33 0.42 2.77	St 13 1.19 0.29 0.32 0.50 0.64 3.35
PAHs Compound Naphthalene Acenaphthylene Acenaphthene Fluorene Phenanthrene Anthracene Fluoranthene	Naph AceThy Ace Fl Phe Ant Flu	St 7 0.26 nd 0.32 nd 0.32 2.23 5.67	St 8 0.49 nd 0.25 nd nd 2 5.64	St 9 0.52 nd 0.30 nd nd 2.81 3.19	St 10 1.09 0.28 0.26 0.39 0.59 2.84 3.78	St 12 1.10 0.22 0.26 0.33 0.42 2.77 6.00	St 13 1.19 0.29 0.32 0.50 0.64 3.35 4.30
PAHs Compound Naphthalene Acenaphthylene Acenaphthene Fluorene Phenanthrene Anthracene Fluoranthene Pyrene	Naph AceThy Ace Fl Phe Ant Flu Pyr	St 7 0.26 nd 0.32 nd 0.32 2.23 5.67 5.38	St 8 0.49 nd 0.25 nd nd 2 5.64 4.05	St 9 0.52 nd 0.30 nd nd 2.81 3.19 3.44	St 10 1.09 0.28 0.26 0.39 0.59 2.84 3.78 3.27	St 12 1.10 0.22 0.26 0.33 0.42 2.77 6.00 4.32	St 13 1.19 0.29 0.32 0.50 0.64 3.35 4.30 3.71
PAHs Compound Naphthalene Acenaphthylene Acenaphthene Fluorene Phenanthrene Anthracene Fluoranthene Pyrene Benzo(a) Anthracene	Naph AceThy Ace Fl Phe Ant Flu Pyr BaA	St 7 0.26 nd 0.32 nd 0.32 2.23 5.67 5.38 15.61	St 8 0.49 nd 0.25 nd nd 2 5.64 4.05 9.13	St 9 0.52 nd 0.30 nd nd 2.81 3.19 3.44 10.93	St 10 1.09 0.28 0.26 0.39 0.59 2.84 3.78 3.27 8.49	St 12 1.10 0.22 0.26 0.33 0.42 2.77 6.00 4.32 12.28	St 13 1.19 0.29 0.32 0.50 0.64 3.35 4.30 3.71 9.96
PAHs Compound Naphthalene Acenaphthylene Acenaphthene Fluorene Phenanthrene Anthracene Fluoranthene Pyrene Benzo(a) Anthracene Chrysene	Naph AceThy Ace Fl Phe Ant Flu Pyr BaA Chr	St 7 0.26 nd 0.32 nd 0.32 2.23 5.67 5.38 15.61 25.78	St 8 0.49 nd 0.25 nd nd 2 5.64 4.05 9.13 10.73	St 9 0.52 nd 0.30 nd nd 2.81 3.19 3.44 10.93 14.72	St 10 1.09 0.28 0.26 0.39 0.59 2.84 3.78 3.27 8.49 9.54	St 12 1.10 0.22 0.26 0.33 0.42 2.77 6.00 4.32 12.28 17.55	St 13 1.19 0.29 0.32 0.50 0.64 3.35 4.30 3.71 9.96 14.52
PAHs Compound Naphthalene Acenaphthylene Acenaphthene Fluorene Phenanthrene Anthracene Fluoranthene Pyrene Benzo(a) Anthracene Chrysene Benzo(b)Fluoranthene	Naph AceThy Ace Fl Phe Ant Flu Pyr BaA Chr BbF	St 7 0.26 nd 0.32 nd 0.32 2.23 5.67 5.38 15.61 25.78 12.88	St 8 0.49 nd 0.25 nd nd 2 5.64 4.05 9.13 10.73 2.79	St 9 0.52 nd 0.30 nd nd 2.81 3.19 3.44 10.93 14.72 5.36	St 10 1.09 0.28 0.26 0.39 0.59 2.84 3.78 3.27 8.49 9.54 3.37	St 12 1.10 0.22 0.26 0.33 0.42 2.77 6.00 4.32 12.28 17.55 5.47	St 13 1.19 0.29 0.32 0.50 0.64 3.35 4.30 3.71 9.96 14.52 3.99
PAHs Compound Naphthalene Acenaphthylene Acenaphthene Fluorene Phenanthrene Anthracene Fluoranthene Pyrene Benzo(a) Anthracene Chrysene Benzo(b)Fluoranthene Benzo(a) Pyrene	Naph AceThy Ace Fl Phe Ant Flu Pyr BaA Chr BbF BaP	St 7 0.26 nd 0.32 nd 0.32 2.23 5.67 5.38 15.61 25.78 12.88 22.03	St 8 0.49 nd 0.25 nd nd 2 5.64 4.05 9.13 10.73 2.79 7.78	St 9 0.52 nd 0.30 nd nd 2.81 3.19 3.44 10.93 14.72 5.36 11.03	St 10 1.09 0.28 0.26 0.39 0.59 2.84 3.78 3.27 8.49 9.54 3.37 8.05	St 12 1.10 0.22 0.26 0.33 0.42 2.77 6.00 4.32 12.28 17.55 5.47 9.28	St 13 1.19 0.29 0.32 0.50 0.64 3.35 4.30 3.71 9.96 14.52 3.99 8.14
PAHs Compound Naphthalene Acenaphthylene Acenaphthene Fluorene Phenanthrene Anthracene Fluoranthene Pyrene Benzo(a) Anthracene Chrysene Benzo(b)Fluoranthene Benzo(a) Pyrene Indeno(123-cd) Pyrene	Naph AceThy Ace Fl Phe Ant Flu Pyr BaA Chr BbF BaP DBahA	St 7 0.26 nd 0.32 nd 0.32 2.23 5.67 5.38 15.61 25.78 12.88 22.03 15.74	St 8 0.49 nd 0.25 nd nd 2 5.64 4.05 9.13 10.73 2.79 7.78 3.82	St 9 0.52 nd 0.30 nd nd 2.81 3.19 3.44 10.93 14.72 5.36 11.03 6.06	St 10 1.09 0.28 0.26 0.39 0.59 2.84 3.78 3.27 8.49 9.54 3.37 8.05 2.84	St 12 1.10 0.22 0.26 0.33 0.42 2.77 6.00 4.32 12.28 17.55 5.47 9.28 6.68	St 13 1.19 0.29 0.32 0.50 0.64 3.35 4.30 3.71 9.96 14.52 3.99 8.14 5.63
PAHs Compound Naphthalene Acenaphthylene Acenaphthene Fluorene Phenanthrene Anthracene Fluoranthene Pyrene Benzo(a) Anthracene Chrysene Benzo(b)Fluoranthene Benzo(a) Pyrene Indeno(123-cd) Pyrene Dibenzo(ah)Anthracene	Naph AceThy Ace Fl Phe Ant Flu Pyr BaA Chr BbF BaP DBahA InP	St 7 0.26 nd 0.32 nd 0.32 2.23 5.67 5.38 15.61 25.78 12.88 22.03 15.74 27.02	St 8 0.49 nd 0.25 nd nd 2 5.64 4.05 9.13 10.73 2.79 7.78 3.82 9.15	St 9 0.52 nd 0.30 nd nd 2.81 3.19 3.44 10.93 14.72 5.36 11.03 6.06 12.19	St 10 1.09 0.28 0.26 0.39 0.59 2.84 3.78 3.27 8.49 9.54 3.37 8.05 2.84 9.68	St 12 1.10 0.22 0.26 0.33 0.42 2.77 6.00 4.32 12.28 17.55 5.47 9.28 6.68 13.67	St 13 1.19 0.29 0.32 0.50 0.64 3.35 4.30 3.71 9.96 14.52 3.99 8.14 5.63 10.83
PAHs Compound Naphthalene Acenaphthylene Acenaphthene Fluorene Phenanthrene Anthracene Fluoranthene Pyrene Benzo(a) Anthracene Chrysene Benzo(a) Pyrene Indeno(123-cd) Pyrene Dibenzo(ah)Anthracene Benzo(ghi) Pyrylene	Naph AceThy Ace Fl Phe Ant Flu Pyr BaA Chr BbF BaP DBahA InP BghiP	St 7 0.26 nd 0.32 nd 0.32 2.23 5.67 5.38 15.61 25.78 12.88 22.03 15.74 27.02 5.18	St 8 0.49 nd 0.25 nd nd 2 5.64 4.05 9.13 10.73 2.79 7.78 3.82 9.15 nd	St 9 0.52 nd 0.30 nd nd 2.81 3.19 3.44 10.93 14.72 5.36 11.03 6.06 12.19 nd	St 10 1.09 0.28 0.26 0.39 0.59 2.84 3.78 3.27 8.49 9.54 3.37 8.05 2.84 9.68 nd	St 12 1.10 0.22 0.26 0.33 0.42 2.77 6.00 4.32 12.28 17.55 5.47 9.28 6.68 13.67 Nd	St 13 1.19 0.29 0.32 0.50 0.64 3.35 4.30 3.71 9.96 14.52 3.99 8.14 5.63 10.83 2.65

Note: nd=not detected

(Flu), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chr), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(123-cd)pyrene (InP), dibenzo(ah)anthracene (DBahA), and benzo(ghi)pyrylene (BghiP). The total concentration of PAHs from 12 research stations for the surface seawater ranged from 54.46 to 213.70  $\mu$ g/l, with an average of 99.75  $\mu$ g/l, respectively (Table 2).

Highest abundance of PAHs compound in seawater was dominated by carcinogenic PAHs. The highest average total abundance of PAHs in the Timor Sea waters were, benzo(b)fluoranthene (BbF=9.323  $\mu$ g/l), benzo(a)anthracene (BaA=11.039  $\mu$ g/l), dibenzo(ah)anthracena (DbahA=13.105  $\mu$ g/l), benzo(a)pyrene (BaP=14.122  $\mu$ g/l), indeno (123-cd)pyrene (InP=17.426  $\mu$ g/l), and chrysene (Chr=18.293  $\mu$ g/l) (Fig. 2).

PAHs in sediment were collected at Stns 12 and 13. Total sediment PAHs concentration ranged from 23.63 to 24.5 mg/kg dw, with the average concentration of 24.06 mg/kg dw. The sediment PAHs were also dominated by carcinogenic PAHs with high molecular weight. Four PAHs compounds were detected at relatively high concentrations such as anthracene (7.19 mg/kg), chrysene (8.11 mg/kg), benzo(a)pyrene (4.85 mg/kg), and indeno(123-cd)pyrena

(12.21 mg/kg) (Fig. 3).

#### Discussion

The Timor Sea region is in a relatively pristine condition, particularly when compared with other parts of Australia and Indonesia (Morrison and Delaney 1996). Total PAHs concentrations in seawater and sediments in the present study were higher than in the study by Burn et al. (2010) in the north coast of Australia (i.e.,  $0-60.5 \,\mu g/l$  in surface seawater and 0.35-3.42 mg/kg in sediments) (Fig. 4). The result provided information that these areas were contaminated with persistent organic pollutants like PAHs besides natural seepage (Burn et al. 2010). This condition was strengthened with sea surface temperature in the Timor Sea between 25-29°C, with an average of 27°C. These temperature conditions are important for marine pollution, since reaction rates increase with temperature, resulting in increased evaporation of organic compounds and enhanced chemical decomposition (Morrison and Delaney 1996).

Total PAHs concentration in the present study was higher than the allowable levels for the total PAHs concentration in "the seawater quality for marine life in Indonesia"



PAHs compound and benzene ring number



Fig. 2. Distribution of individual PAHs concentration in water of the Timor Sea.

Fig. 3. Distribution of total concentration of PAHs in sediments from the Timor Sea.

(the Environment Ministerial Decree No. 54/2004:  $\langle 3 \mu g/l \rangle$ ). Especially at Stns 1 through 7, the total PAHs was higher than 80  $\mu g/l$ . High concentration of and long exposure to this contaminant can cause negative effect to the life of marine biota. As PAHs compounds have long persistent nature and large molecular sizes, they will accumulate in various types of matrix in sediments and marine biota and can influence globally with ability to move away and bind with the air- and sediment particles (Sauer 1998, Connell 2006, Nizzetto et al. 2008).

Comparison was also attempted with other coastal areas including pristine areas and densely-populated areas (Table 3). PAHs concentration in the Atlantic Region is 0.00006-

 $0.0005 \,\mu$ g/l. This region is still clean and differences with the Timor Sea are highly significant. The levels in the Timor Sea are lower than those in Lampung Bay, where overall average is  $110.17 \,\mu$ g/l, which is attributable to many industrial activities that use fuel oil and more marine transportation activity (Munawir 2010). The Rhode Island waters, U.S.A, which also show higher levels than in the Timor Sea, is polluted by oil spills from the North Cape in 1996 (Table 3). The Timor Sea is still far from the source of the oil spill in Montara.

Assessment of ecological toxicity of individual PAHs compound in sediments were compared with Interim Marine Sediment Quality Guidelines (ISQGs) and probable effect levels (PELs) value on Canadian Sediment Quality Guide-



Fig. 4. Comparation of distribution of total concentration of PAHs in seawater from the Timor Sea with average of total PAHs concentration on Burns *et al.* (2010) study.

No	Area	Vear of study	Total concentr	- References		
		Tear of Study	Seawater (µg/l)			Sediment (mg/kg)
1	Timor Sea coastal waters	May, 2010	54.46–213.70 (99.75)	23.63–24.50 (24.06)	Present study	
2	South Atlantic region	2008	0.00006-0.0005	_	Nizzotto at al. (2008)	
3	Biscay bay, France	2000	0.0007–0.001	_	NIZZELLO AL EL. (2008)	
4	Lampung Bay, Indonesia	2008	5.52–411.69 (110.17)	0.20–0.01 (0.32)	Munawir (2008)	
5 Klab	Klabat Dangka Day, Indonasia	March, 2006	0.38–44.49 (7.47)	0.03–0.21 (0.11)	Mupawir (2007)	
	Nabat-Daligka Day, Indonesia	July, 2006	1.33–27.83 (15.2)	1.00–4.79 (1.93)		
6	Sangatta coastal waters, East Kalimantan	gatta coastal waters, East nantan		6.28–8.45	Bazak (1996)	
0	Balikpapan coastal waters, East Kalimantan			0.10-4.32		
7	Rhode Is., USA	1996	115	_	Reddy (1999)	

Table 3. Worldwide concentrations of total PAHs in seawater and sediments

Substance	St 12L (mg/kg)	St 13L (mg/kg)	ISQG (µg/kg)	PEL (µg/kg)			
Low molecular weight PAHs compound							
Acenaphthene	0.08	0.07	0.00671	0.0889			
Acenaphthylene	0.14	0.09	0.00587	0.128			
Anthracene	5.20	1.99	0.0469	0.245			
Fluorene	0.12	0.13	0.0212	0.144			
Naphthalene	0.16	0.10	0.0346	0.391			
Phenanthrene	0.16	0.17	0.0867	0.544			
High molecular weight PAHs compound							
Fluoranthene	0.29	1.85	0.113	1.494			
Pyrene	0.33	1.39	0.153	1.398			
Chrysene	3.24	4.87	0.108	0.846			
Dibenz (a, h) anthracene	0.94	1.70	0.00622	0.135			
Benz(a)anthracene	0.59	3.39	0.0748	0.693			

 Table 4.
 Interim marine sediment quality guidelines (ISQGs) and probable effect levels (PELs; dry weight) (CCME 2001)

lines for the Protection of Aquatic Life (CCME 2001). The concentration of all individual PAHs at Stns 12 and 13 exceeded the ISQG standard. All individual PAHs at Stns 12 and 13 were below the PEL standards except those of Ace, Ant, Chr, and DBahA (Stn 12) and Ant, Flu, Chr, DBahA, and BaA (Stn 13). The results confirmed that sediments at Stns 12 and 13 are contaminated with acutely toxic PAHs and possible risk posed to biota (Table 4).

The identification of PAHs sources is great importance for the regulation of the input of PAHs to waters. Identification of the origin of PAHs to be petrogenic or pyrogenic is relevant to the impact of PAHs accumulation on aquatic life. Petrogenic PAHs with more of small molecular weight compounds may be more available for uptake with biological than pyrogenic PAHs (more of high molecular weight). There are several tools for identification of PAHs sources, such as those applying unique molecular compounds as markers, or diagnostic ratios (Saha et al. 2009). Diagnostic ratio methods based on difference in thermodynamic stability among PAHs species to distinguish natural and anthropogenic sources is exibited by PAHs isomer ratio of the principal mass m/z=178 (Ant/178, Phe/Ant, Ant/(Ant+Phe)), m/z=202(Flu/(Flu+Pyr), Flu/Pyr) and alkyl homologues to distinguish petroleum from combustion; m/z=228 (BaA/228), and m/z=276 (InP/(InP+BghiP)) to corroborate the assignment of combustion sources, 1,7/(2,6+1,7-DMP) to identify wood combustion, and other applied PAHs compounds ratio like BaP/ (BaP+Chr) (Yunker et al. 2002, Nemr et al. 2006).

Based on the PAHs isomer ratio by Yunker et al. (2002), PAHs m/z 178 and m/z 202 are generally used to distinguish between combustion and petroleum sources. An/178 ratios of <0.10 indicate petroleum, those of >0.1 indicate dominance of combustion, and the ratio 0.1 indicates mixture of petrogenic and pyrogenic sources; Phe/Ant ratios of >10 indicate petroleum sources and those of <10 indicate combustion sources; Ant/(Ant+Phe) ratios of <0.1 usually indicate petroleum, while those of >0.1 indicate combustion of diesel oil, shale oil, coal, and some crude oil samples.

Flu/Pyr ratios of <1 indicate petroleum sources, while those of >1 indicate combustion sources; Flu/(Flu+Pyr) ratios of <0.4 imply petroleum (crude oil samples, but for Australian crude oil is >0.4), 0.4–0.5 imply petroleum (vehicle, crude oil, gasoline, diesel, fuel oil, emisions from cars and diesel trucks) combustion, whereas ratios of >0.5 indicate kerosene, grass, wood, coal combustions, and creosote.

PAHs of molecular masses 228 and 276 has been less applied for identification of PAHs sources. However, BaA/228 ratio less than 0.2 indicated petroleum sources, from 0.2 to 0.35 indicate either petroleum or combustion, and >0.35 imply combustion. In P/(In P+BghiP) ratios <0.2 for petroleum, between 0.20 to 0.50 for liquid fossil fuel (vehicle and crude oil) combustion, and ratios >0.50 for grass, wood soot, creosote, and coal combustion. The last ratio is BaP/(BaP+Chr), if less than 0.2 for combustion, between 0.4–0.6 for mixture of petroleum and combustion, and between 0.6–0.9 is for petroleum sources (Yunker et al. 2002, Opuene et al. 2009, Hiller et al. 2010).

Results of diagnostic ratio are shown in Table 5. At Stn 1, petroleum and petroleum combustion sources were suggested from biplot analyses of Ant/178 vs Flu/(Flu+Pyr), BaA/228 vs Flu/(Flu+Pyr), Ant/(Ant+Phe) vs Flu/(Flu+Pyr), and BaP/(BaP+Chr) vs Ant/(Ant+Phe), and the similar analyses of Inp/(Inp+BghiP) vs Flu/(Flu+Pyr), and Inp/(Inp+BghiP) vs Ant/(Ant+Phe) suggested combustion sources (Fig. 5). Based on the result at Stn 1, combustion source of PAHs are likely to be characterized by plotting with Flu/(Flu+Pyr) or Inp/(Inp+BghiP) (Fig. 5).

Stns 2, 3, 9, and 12S exhibited similar results from the biplot analysis and classified into one group. Stns 2 and 9 showed ratios of combustion from petroleum (diesel oil, shale oil, crude oil, fuel oil, emission from car and truck) and organic material (grass, wood, and coal), while Stns 3 and 12 showed ratios of mixture from petroleum and combustion. Station 6 showed a very unique position in the biplot analysis indicating a critical point between combustion of petroleum and organic material, but more likely from combustion of petroleum sources.

The last calculation result of diagnostic ratios for Stns 4, 5, 7, 8, 10, 12, 13, and 13S is as follows. Stns 5, 8, 12, and 13S were in a first group where a source of PAHs compound was more likely from combustion mixture, despite influence from petroleum combustion. Stns 13 and 10, which are distant from coastal area, were in the second group where the source of PAHs was from petroleum combustion with combustion mixture influence. As for Stns 4 and 7, the source of PAHs was similar with Stns 13 and 10 but less influenced by combustion mixture. Generally, our results showed that the source could come from petroleum, combustion petroleum,



**Fig. 5.** Ratio diagnostic cross plot for PAHs concentration in surface seawater and sediments from the Timor Sea waters, (a) Ant/178 vs Flu/(Flu+Pyr), (b) BaA/228 vs Flu/(Flu+Pyr), (c) Inp/(Inp+BghiP) vs Flu/(Flu+Pyr), (d) Ant/(Ant/Phe) vs Flu/(Flu+Pyr), (e) (BaP+Chr) vs Ant/(Ant+Phe), and (f) Inp/(Inp+BghiP) vs Ant/(Ant+Phe).

and combustion mixture organic material. However, the main sources of the observed PAHs are considered to be petroleum and petroleum combustion.

PCA analysis was applied to examine the relationship and correlation between individual PAHs to make a component factor variable (Hiller et al. 2010, Nemr et al. 2006, Yunker et al. 2002). The PCA plot of seawater PAHs (Fig. 6a) resulted in the three dimension plot with the first component as petrogenic factor correlated with acenaphtylene, naphthalene, phenanthrene, fluorene, and anthracene, the sec-



Fig. 6. (a) The PCA loading plot of 3D component factor illustrated of distribution individual PAHs in surface seawater, and (b) Plot of factor coordinates of the surface seawater location sampling from Timor Sea.



Fig. 7. HCA histogram analysis of PAHs compound in the coastal waters of the Timor Sea.

ond component as pyrogenic factor correlated with for dibenzo(ah)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, and indeno(123-cd)pyrene, and the last component as mixture of petrogenic and pyrogenic factor corelated with chrysene, pyrene, fluoranthene, acenaphthene, and benzo(a)anthracene. Figure 6b shows corelation between PAHs concentration and station location of surface sea water sampling, where Stn 1 was significantly different from other stations, due to its highest total PAHs concentration. Hierarchical cluster analysis (HCA) of PAHs was performed to classify individual PAHs compound into cluster groups (Nemr et al. 2006). The dendogram (Fig. 7) shows three major groups which agree with the PCA results, corresponded to petrogenic, pyrogenic and mixture of both

sources. These suggest that the PAHs in the Timor Sea waters are contibuted by the 3 major sources, wherein petroleum and petroleum combustion are likely main sources.

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