http://www.pjbs.org

PJBS

ISSN 1028-8880

Pakistan Journal of Biological Sciences

ANSInet
Asian Network for Scientific Information
308 Lasani Town, Sargodha Road, Faisalabad - Pakistan

Pakistan Journal of Biological Sciences 10 (11): 1926-1929, 2007
ISSN 1028-8880

Organophosphate Pesticide Concentrations in Coral Tissues of Indonesian Coastal Waters

[1,2]Agus Sabdono, [3]Suil Kang, [3]Hor-Gil Hur, [4]Hans-Peter Grossart,
[5]Meinhard Simon and [1,2]Ocky Karna Radjasa
[1]Department of Marine Science, Diponegoro University, Semarang-50275, Central Java, Indonesia
[2]Center for Tropical Coastal and Marine Studies, Diponegoro University, Widya Puraya, Semarang-50275, Central Java, Indonesia
[3]International Environment Research Center, GIST, Gwangju, Korea
[4]Deptartment of Limnology of Stratified Lakes, Leibniz-Institute of Freshwater Ecology and Inland Fisheries, Neuglobsow, Germany
[5]Institute for Chemistry and Biology of Marine Environment (ICBM), University of Oldenburg, Oldenburg, Germany

Abstract: In this study we evaluated the persistence of diazinon, chlorpyrifos, profenofos, parathion, malathion and ethion in dead coral tissues of Indonesian coastal waters (Java, Bali, Sulawesi and Komodo). Comparison of the residue levels in coral tissues showed that the highest presence of organophosphate concentrations was detected in a coral sample collected from Java coastal waters. While medium amounts of a contaminant diazinon can still lead to detectable in Bali and Sulawesi coastal waters. Prominent contamination of organophosphate was not found in a sample collected from Komodo. Neither parathion nor malathion were detected in any of the samples. This result implies that the geographical variations of organophosphate compounds are determined by the possible usage of these chemicals around coastal waters at the present or in the past. There is need for further work to identify sources and fate of pesticide contaminants, as well as to improve monitoring of pesticide use.

Key words : Organophosphate, coral tissues, GC-MS

INTRODUCTION

Indonesia is the world's largest archipelagic country with approximately 17,508 islands containing valuable coastal and marine resources such as coral reefs. About 85,707 km^2 or 14% of total corals in the world extending all the way in the Indonesian sea (Tomascik *et al*., 1997). Coral reefs are some of the most productive ecosystems on earth and are certainly the most productive and species-rich environments in the oceans (Veron, 1986). It has commonly been known that in developing countries, reefs near coastal areas, are under serious stress from coral mining, cyanide, blasting and land pollution in particular agricultural runoff as the results of the application of pesticides to control the pests and weeds. The use of pesticides, herbicides and fungicides in Indonesia began when the government launched plantation rehabilitation programme in the 1960's. Consequently, large-scale application of these toxic materials in agriculture areas can contribute to the presence of those compounds in surface and ground water, lakes, estuary and ultimately in the coastal areas.

Organophosphates are being increasingly used to substitute for the organochlorines due to their rapid breakdown into environmentally safe products. Most of this compounds have far more immediate toxicity than DDT and other related products (Wolterding, 1981) and their entry into the sea, might be, poses many challenges to the existing coral reefs and even to live in this vicinity in general. There are more than thirty different active compounds of organophosphate pesticides on the market today and they each cause acute and sub-acute toxicity (Table 1). However, there is a lack of information available on those pesticide effects to the coral reefs. In the tropical areas, studies on pesticide occurrence in environmental samples are rare and focus mainly on organochlorine pesticides (Caldas *et al*., 1999; Botello *et al*., 2000), which have been banned from use in most countries during the last two decades. Glynn *et al.* (1984) reported that herbicides 2,4-D and 2,4,5-T can have a deleterious effect

Corresponding Author: Agus Sabdono, Department of Marine Science, Diponegoro University, Semarang-50275, Central Java, Indonesia

Table 1: Organophosphate most commonly used in intensive agriculture in Indonesia

Trade name	Active compounds	Pesticide
Kasumiron	Fosdifen	Fungicide
Rizolex	Methyl tolcoflos	Fungicide
Alugan	Pyrazolos	Fungicide
Aliette	Aluminium focethyl	Fungicide
Basta	Amonium glufosinat	Herbicide
Arozin	Anylophos	Herbicide
Polaris	Ethylen diamine glyphosat	Herbicide
Roundup	Mono ammonium glyphosat	Herbicide
Touchdown	Sulfosat	Herbicide
Komando	IPA glyphosat	Herbicide
Amcotene	Asefat	Insecticide
Merothion	Ethion	Insecticide
Kanon	Dimetoat	Insecticide
Agrothion	Phenythrotion	Insecticide
Dharmasan	Fentoat	Insecticide
Anthic	Phormothion	Insecticide
Zolone	Fosalon	Insecticide
Monitor	Metamidofos	Insecticide
Dyvon	Trichlorfon	Insecticide
Profile	Profenofos	Insecticide
Voltage	Pyrachlofos	Insecticide
Tokuthion	Protiofios	Insecticide
Mestakwin	Kuinaflos	Insecticide
SNIP	Azametifos	Insecticide
Neocido	Diazinon	Insecticide
Minawet	Pyrimifos methyl	Insecticide
Supracide	Metidation	Insecticide
Karphos	Isoksation	Insecticide
Dursban	Chlorpyrifos	Insecticide
Silosan	Methyl pyrimifos	Insecticide
Rugby	Methyl pyrimifos	Nematicide
Nemacur	Fenamifos	Nematicide
Rhocap	Ethrophos	Nematicide

on corals, at relatively low concentrations and for short term. Jeffers *et al*. (1997) showed that herbicide 2, 4-D is known to have lethal effects on corals such as the *Montastrea annulais* species. Contact with this herbicide has caused 100% mortality of the coral within 24 h of exposure. Furthermore, the most abundant coral species, *Pocillopora damicornis*, had the highest mortality due to mecoprop herbicidal exposure (Cruz *et al*., 1997). No reports was found on the study of organophosphate pesticides on coral reefs. The purpose of this study was to detect the presence of organophosphate residues in coral tissues of Indonesian coastal waters.

MATERIALS AND METHODS

Sample collection: Sampling sites were located on Java, Bali, Sulawesi and Komodo islands. Figure 1 shows the sampling sites. Specimens of the dead corals were collected randomly between May and June 2006 by scuba diving at depths of 2 to 3 m, broken away with chisel and hammer and placed in plastic bag submerged in sea water. Upon collection coral fragments were put into sterile plastic bags (Whirl-Pak, Nasco, USA) and immediately brought to our laboratory with dry-ice. In laboratory, corals were dried in room temperature, ground and sieved. Fraction of particles less than 2 mm size was used for chemical analysis. Oceanographic parameters such as temperature, salinity, visibility, current speed, pH and dissolved oxygen concentration. Coral condition were also measured by using Line Intercept Transect (LIT) technique to assess the sessile benthic community of coral reefs (UNEP/AIMS, 1993).

Sample analysis: Approximately 10 g of air-dried coral samples were placed in a conical flask and 100 mL ethyl-acetate was added. The tissue was shaked gently

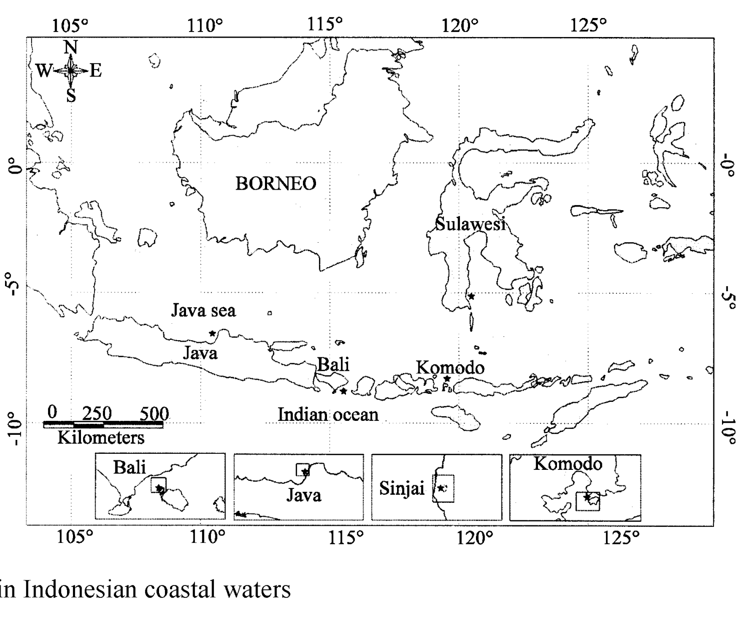

Fig. 1: Sampling sites in Indonesian coastal waters

for 2 h. The ethyl-acetate digest was washed with acid water to remove the acetone and decanted. The extracts were combined and dried over 1 g of acidified anhydrous sodium sulfate. Then the extracts were transferred to evaporator tube and concentrated in water bath. The concentrated extracts were removed from the water bath and allowed to cool. The samples were then analyzed by gas chromatography.

After extractions, the samples were then analyzed by gas chromatograph Model Hitachi 163, FPD (Flame Photometer Detector) and nitrogen High Pure (HP) was used as the carrier gas. A 1 m glass column (3 mm ID) packed with 10% Silikon DC200 on 80-100 mesh Supelcon was used. Gasflow at 50 mL min^{-1}, column temperature at 200°C, detector temperature at 230°C and the injector temperature at 230°C were maintained.

RESULTS

Organophosphate pesticides used in Indonesia: The most commonly used pesticides in Indonesia were organophosphates, carbamates, phenoxy, triazine, bipyridilium and pyrethroids, in that order, with very few organochlorines (Table 1). There are more than 550 pesticides that were registered and permitted to be sold freely on the market today (Indonesian Pesticide Commission, 1999).

Oceanographic and coral conditions: The oceanographic conditions among four sampling sites are still good for coral growth and development. However, the corals are in poor condition, except for Komodo Island (Table 2). Coral condition could be classified into four categories: excellent (76-100% coral cover), good (51-75% coral cover), fair (25-50% coral cover and poor condition (0-25% coral covers) (Gomez and Yap, 1988).

Recovered pesticide residues: Four selected organophosphates, diazinon, chlorpyrifos, profenofos and ethion were detected in dead coral tissues in varying concentrations and frequencies of occurrence. None of the pesticide residues were detected in coral samples from Komodo coastal waters. Two other target compounds in this study, parathion and malathion, were below the limit of detection (Table 3).

Table 2: Oceanography parameters of sampling sites

Oceanography parameter	Sampling site Java	Bali	Sulawesi	Komodo
Temperature (°C)	27.33±0.57	25.66±0.57	26.00±0.00	27.00±0.00
Salinity (‰)	35.66±0.57	34.66±0.57	35.00±0.00	36.00±0.00
Visibility (m)	3.33±0.57	15.33±1.52	5.00±1.00	∞
Current (m/sec)	0.53±0.57	1.20±0.10	0.34±0.10	0.00±0.10
pH	8.33±0.57	8.00±0.00	8.00±0.57	8.00±0.00
DO (mg L^{-1})	4.66±0.00	7.66±0.57	7.00±0.00	8.00±0.00
Coral covers (%)	11.45±1.71	29.67±2.52	21.67±3.55	64.81±7.26

Table 3: Range , frequency of occurrence and mean±standard deviation of organophosphate pesticide residue levels (μg kg^{-1}) in corals from Indonesian coastal waters[a]

Organophosphorus	Sampling site Java	Bali	Sulawesi	Komodo
Diazinon	37.93-40.24 4/4 39.43±1.06	12.71-13.39 2/4 13.05±0.48	20.44-24.10 3/4 22.17±2.73	BD
Chlorpyrifos	41.22-44.87 4/4 42.88±1.61	24.76 1/4 24.76	21.54-23.25 2/4 22.39±1.21	BD
Profenofos	11.21-23.35 3/4 17.35±6.07	BD	12.31-14.10 2/4 13.20±1.67	BD
Parathion	BD	BD	BD	BD
Malathion	BD	BD	BD	BD
Ethion	12.23-13.11 3/4 12.63±0.44	13.22 1/4 13.22	BD	BD

[a]10 μg kg^{-1} = lowest working concentration (below which residues could not be quantified).[b]Residue levels given on wet weight basis. Mean was calculated for positive samples. [c]Total samples = 4; BD, = below detection

DISCUSSION

Organophosphate compounds are among the most widely used pesticides. There are about 33 active compounds used as organophosphate pesticides (Table 1). Contamination of coastal waters by these compounds is of concern because of potential toxicity to marine organisms, especially to those at the coral ecosystem. In this study we evaluated the presence of diazinon, chlorpyrifos, profenofos, malathion, parathion and ethion in coral tissues from four different islands in the Indonesian coastal waters. Chlorpyrifos had the highest concentration of any pesticide detected in dead coral tissues. Diazinon was detected at concentration averaging similar to chlorpyrifos (Table 3). Concentration of these two organophosphorus pesticides, diazinon and chlorpyrifos, were also detected in Bali and Sulawesi , but at lower concentrations. Bondarenko *et al*. (2004) reported that the persistence of diazinon and chlorpyrifos was much longer than that of malathion or carbaryl and was further prolonged in seawater. Moreover, microbial degradation contributed significantly to the dissipation of diazinon and chlorpyrifos in freshwater, but was inhibited in seawater, leading to increased persistence (Bondarenko *et al*., 2004). Two other pesticides were also found in this study: profenofos and ethion. Both of them were detected in Java. Two other target compounds in this study, parathion and malathion, were below the limit of detection. This is probably because of their relatively short half-lives, whereby they do not remain active in the environment for long (Lalah and Wandiga, 1996). In addition, degradation of malathion and carbaryl was rapid and primarily abiotic (Bondarenko *et al.*, 2004) . Prominent contaminations of organophosphates were not found in a sample collected from Komodo and not surprisingly, this sampling site was assumed to be a pristine area. However, it does not mean that lack of organophosphate residues in samples does not necessarily indicate lack of impact of organophosphate compounds on the environment. They may still impact on the aquatic system in the short term, before they break down to non-toxic products. This result implies that the geographical variations of organophosphate are determined by the possible usage of these chemicals around coastal waters at the present or in the past. However we couldn't attributed that organophosphate played a role in the Indonesian coral death. Further research is needed in order to ascertain the exact manner by which the organophosphate affects the coral to be able to fully understand the observations in this study.

ACKNOWLEDGMENTS

This study was part of collaborative project with Institute for Chemistry and Biology of Marine environment (ICBM) Oldenburg, Germany funded by DAAD. This research was supported by and International Environment Research Center, UNU-GIST, Gwangju, Korea.

REFERENCES

Botello, A.V., L. Ruede-Quintana, G. Diaz-Gonza´ lez and A. Toledo, 2000. Persistent Organochlorine Pesticides (POPs) in coastal lagoons of the subtropical Mexican Pacific. Bull. Environ. Contam. Toxicol., 64: 390-397.

Bondarenko, S., J. Gan, D.L. Haver and J.N. Kabashima, 2004. Persistence of selected organophosphate and carbamate insecticides in water from a coastal watershed. Environ. Toxicol. Chem., 23: 2649-2654.

Caldas, E.D., R. Coelho, L.C. Souza and S.C. Silva, 1999. Organochlorine pesticides in water, sediment and fish of Paranoa´ Lake of Brasilia. Brazil. Bull. Environ. Contam. Toxicol., 62: 199-206.

Cruz, C.L., E.D. La and R. Clemens, 1997. Ecotoxicology and pesticides in tropical aquatic ecosystems of central America. Environ. Toxicol. Chem., 16: 41-51.

Glynn, P.W., L.S. Howard, E. Corcoran and A.D. Freay, 1984. Occurrence and toxicity of herbicides in reef building corals. Marine Poll. Bull., 15: 370-374.

Gomez, E.D. and H.T. Yap, 1988. Monitoring Reef Condition. In: Coral Reef Management Handbook. 2nd Edn., Kenchington R.A. and B.E.T. Hudson (Eds.). UNESCO Regional Office for Science and Technol. South East Asia. Jakarta, pp: 186.

Indonesian Pesticide Commission, 1999. Pesticide for Agriculture and Forestry. Koperasi Daya Guna, pp: 3-134.

Jeffers, H.W., D. Russel, J.R. Lacher, Kendall and J. Ronald, 1997. Agrochemical use on banana plantations in latin America: Perspectives oh Ecological Risk. Environ. Toxicol. Chem., 16: 91-99.

Lalah, J.O. and S.O. Wandiga, 1996. The persistence and fate of malathion residues in stored beans (*Phaseolus vulgaris*) and maize (*Zea mays*). Pestic. Sci., 46: 215-220.

Tomascik, T., A.J. Mah, A. Nontji and M. K. Moosa, 1997. The Ecology of the Indonesian Seas. Periplus, Hong Kong.

UNEP/AIMS, 1993. Monitoring coral reefs for global change. Reference Methods for Marine Pollution Studies No.61. United Nations Environment Programme.

Veron, J.E.N., 1986. Corals of Australia and the Indo-Pacific. Angus and Robertson Publisher.

Wolterding, M., 1981. The Poisoning of Central America. Sierra Sept/Oct 63-66.