J.Sci.Soc.Thailand, 17(1991) 31-49

RESEARCH ARTICLES

CYCLIC CHLORINATED HYDROCARBONS IN BENTHIC INVERTEBRATES FROM THREE COASTAL AREAS IN THAILAND AND MALAYSIA

J. M. EVERAARTS, NASREEN BANO*, C. SWENNEN AND M. T. J. HILLEBRAND

Netherlands Institute for Sea Research, P. O. Box. 59, 1790 AB Den Burg-Texel, the Netherlands.

(Received 22 February 1991)

ABSTRACT

The concentration of individual chlorinated biphenyl congeners (PCBs), cyclic organochlorine pesticides and their persistant metabolites were determined in benthic invertebrate species, representing three phyla, from three estuarine mud-flat areas along the Malay Peninsula: Ao Ban Don and Pattani Bay (Thailand) and Jeram (Malaysia).

Organisms from Pattani Bay (Campus PSU, Laem Nok and Ban Da To), contained the highest PCB concentrations, particularly in bivalves (Glauconome virens *and* Potamocorbula fasciata) *and shrimp* (Metapenaeus lysianassa).

Bivalve molluscs showed significant interspecific differences in their Σ PCB concentrations, independant of the number of individual CB-congeners taken into account for the calculation of Σ PCB.

In all species studied, the concentrations of the organochlorine pesticides dieldrin, p,p'-DDT and its metabolites p,p'-DDE and p,p'-DDD (10 to 250 ng.g^{-1} PEL) were approximately one order of magnitude higher than those of γ-HCH, penta- and hexachlorobenzene (1 to 15 ng.g^{-1} PEL). The compounds α-HCH, endrin and p,p'-DDD were generally below detection limit.

Interspecific differences in concentration levels were found, with crab showing the highest accumulation of especially dieldrin and p,p'-DDE.

Differences in contamination of the coastal areas monitored in terms of lipid-based whole-body concentrations of the organisms could be described for dieldrin and p,p'-DDE, irrespective of the species sampled. Organisms from Ao Ban Don and particularly Jeram showed very high concentrations of dieldrin. Organisms from three sampling sites in Pattani Bay, together with the coastal area of Jeram showed high p,p'-DDE concentrations, compared to organisms from Ao Ban Don.

* Present address : National Institute of Oceanography, 371 K, Block C, P.E.C.H.S., Karachi, Pakistan.

INTRODUCTION

Cyclic chlorinated hydrocarbons are widely applied for industrial and agricultural purposes. Most cyclic organochlorines have been-or are still-used as pesticides: hexachlorobenzene (HCB), p,p'-DDT and its metabolites DDE and DDD, the group of cyclodienes (eg. dieldrin, endrin) and the isomers of hexachlorohexane, such as α-and γ-HCH (lindane). Polychlorinated biphenyls, another group of cyclic organochlorines industrially synthesized, are also ubiquitous contaminants of the environment. PCBs, used for example as dielectric fluid in transformers, hydraulic fluids and additives to paint, have been synthesised in the form of several technical mixtures with different degrees of overall chlorination. They occur as complex mixtures of many of the 209 theoretically possible congeners. However, not all CB-congeners are found in environmental samples and not all of them elute as unambiguous single peaks from a capillary column.[1] Identification and quantification of the individual CB-congeners therefore is essential for tracing the environmental fate of PCBs. The composition of environmental mixtures differs among sample type. Large differences exist between the relative contribution of individual CB-congeners in various environmental compartments, water, suspended matter, sediment and biota, as well as between different animal species.[2-5]

PCBs and the organochlorine pesticides mentioned are highly hydrophobic, extremely lipophilic and resistant to environmental break down, causing high bioaccumulation in apolar animal lipids. Therefore, and because of their prejudicial influence on physiological and biochemical processes in organisms,[6-9] they have long-term deleterious effects on the marine environment.

Benthic invertebrates generally inhabit a certain part of the bottom compartment. These organisms reflect the condition of their specific optimal, environment since they integrate environmental conditions over a leng period, depending for example on their physiological status and the mechanism of food uptake. Benthic organisms can take up cyclic organochlorines from all environmental compartments, water, suspended matter, sediment and food.[10-13] Elimation can occur via equilibrium partitioning of the compounds between tissue and the ambient seawater and fecal excretion[14-16] and biotransformation.[5, 17]

Very little is known about the residue levels of PCBs and cyclic organochlorine pesticides in the various environmental compartments of tropical coastal areas in general and the Malay Peninsula in particular. In some Thai coastal and inland waters, certain organochlorines were present in shellfish and fish, but residue values were extremely low,[18] with the exception of the Inner Gulf area. Here higher concentrations of DDT and its metabolites (DDE and DDD) were found in the green mussel *(Perna viridis).* Pesticides, especially DDT and its metabolites were detectable in sediments, bivalve molluscs (mussels) and fish (mullets) from river mouths (Mae Klong, Ta Chin, Chao Phraya and Ban Pakong) in the upper Gulf of Thailand, whereas PCBs were only found in some samples of mussels and mullets.[19] However, the concentration levels were low. These results were confirmed in a later study on the detection of contaminants in shellfish and fish from the west coast of the Malay Peninsula, in the northern stretch of the Straits of Malacca.[20]

The present study deals with the accumulation of both polychlorinated biphenyls and pesticides in epibenthic (shrimp and crab) and endobenthic (worms and bivalves) invertebrates from three intertidal mud-flats along the coast of the Malay Peninsula (Thailand and Malaysia). The study was carried in order to distinguish bioavailability for organisms in different areas and to establish possible interspecific differences in uptake of organic micro-contaminants. Besides the study can be considered as a description of background levels of lipid-based cyclic halogenated hydrocarbons in macrobenthic species from coastal regions of the Malay Peninsula.

MATERIALS AND METHODS

All organisms were collected in October and November 1985, from the intertidal mud-flats of three coastal areas of the Malay Peninsula. Sampling sites were Ban Changoe (Ao Ban Don or Bay of Surat Thani), Campus of Prince of Songkla University (PSU) Laem Nok and Ban Da To (Pattani Bay), both in Thailand and Jeram (Malaysia) (Fig. 1). The macrobenthic species collected, representing three phyla of invertebrates, the number of specimens in each sample, the mean dry weight of these animals, their lipid contents expressed as a percentage of the dry weight of the pooled organisms and the absolute amounts of lipid extracted for organochlorine analysis, are given in Table 1. The infaunal invertebrates, worms and bivalve molluscs, were collected by sieving from sediment obtained with a sediment corer. The epibenthic species of shrimp and crab were sampled with a small hand-net; one sample of sessile green mussels *(Perna viridis)* was collected by hand.

The samples of the invertebrates were dried at 60-70°C and prepared for sending to the Netherlands Institute for Sea Research. The samples were homogenized with 5 g anhydrous sodium sulphate (Na_2SO_4) and subsequently Soxhlet extracted for 8 h with 150 ml pentane. Each series of ten samples was accompanied by a blank sample of pure Na_2SO_4 to detect any peak due to contamination of the samples during the entire procedure. Further analytical procedures and conditions during capillary GC-ECD analysis were described earlier.[21,22] The methods for sample extraction, clean-up, fractional separation of PCBs from most pesticides, and the analysis by means of capillary gas chromatography with electron capture detection (GC-ECD), are described comprehensively.[12,23-25]

The analyses of the samples were performed using a temperature programmed gas-chromatograph (Hewlett-Packard 5880a) equipped with a capillary fused silica SE-54 column and a ^{63}Ni-electron capture detector.[21] For the identification and quantification of the various chlorinated biphenyl congeners (CBs) and the pesticides in the samples, synthetic mixtures of 66 individual CBs plus penta- (QCB) and hexachlorobenzene (HCB) and 12 pesticides, respectively, were applied as external standard. These standard mixtures were injected every 10th injection for calibration of the retention time and the response factor of each compound. The response factor of each single peak in the standard mixture, representing either a CB-congener or a pesticide should not differ more than 10% between successive standards. A peak in a chromatogram of an environmental sample was only

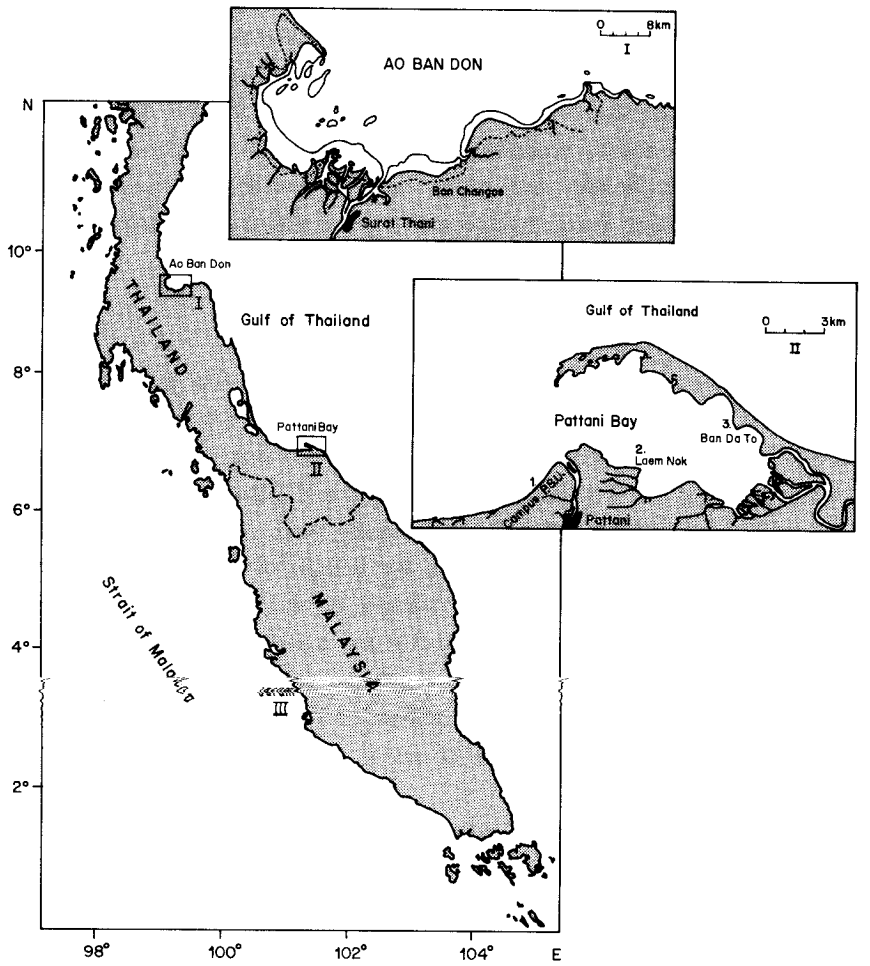

Fig. 1. Sampling locations in Thailand and Malaysia:

I. Ao Ban Don, mud-flats near Ban Changoe,

II. Pattani Bay, intertidal zones near Pattani river mouth at Campus PSU (1), at Laem Nok (2) and Ban Da To (3),

III. Jeram, coastal intertidal mud-flats.

TABLE 1. Species sampled for the analysis of cyclic organochlorines and their sampling sites. Numbers of individuals (N) homogenized, mean dry weight (DW) of these animals (in mg), the pentane extractable lipid (PEL) as a % of the dry weight of N individuals and the amounts of lipid extracted (in mg) for analysis.

Phylum/ Class/ Suborder	Species	Sampling site	N	DW per ind. (mg)	% PEL of DW	Lipids mg used for anal
Annelida/ Polychaeta	*Dendronereis* spp.	Ban Changoe	20	78.7	4.42	69.6
		Ban Da To	20	153.1	9.37	57.4
		Jeram	20	43.8	5.94	52.0
Arthropoda/ Crustacea Natantia	*Palaemon semmelinkii* (De Man)/ *Metapenaeus lysianassa* (De Man) *Exopalaemon styliferus* (H. Milne Edwards)	Ban Changoe	20	414.8	2.71	75.0
		Laem Nok	30	130.2	3.98	77.7
		Jeram	30	112.1	4.20	70.7
Arthropoda/ Crustacea/ Brachyura	*Metaplax longipes* (Stimpson)	Ban Changoe	10	455.3	1.70	77.3
	Uca dussumiera spinata (Crane)	Campus PSU	10	1304.8	5.29	69.1
	Dotilla wichmanni (De Man)	Ban Da to	30	36.6	3.89	42.7
	Uca rosea (Tweedie)	Jeram	10	900.2	2.87	64.6
Molusca/ Bivalvia	*Glauconome virens* (L.)	Campus PSU	10	55.9	3.51	19.6
		Laem Nok	20	86.4	6.85	59.2
	Perna viridis (L.)	Campus PSU	10	300.4	7.27	54.6
	Potamocorbula fasciata (Reeve)	Ban Da To	50	21.4	3.07	32.8
	Anadara granosa (L.)	Jeram	10	653.2	3.37	55.0

assigned to a compound in the standard mixture when its retention time did not differ more than 0.025 min from that compound in the standard.

RESULTS AND DISCUSSION

Polychlorinated biphenyls

The summed concentration of the PCB congeners taken into consideration in the present study encompasses 28 congeners, occurring in the chromatograms of most samples. Examples of chromatograms of the first silica fraction, containing the individual CB-congeners plus pentachlorobenzene (QCB), hexachlorobenzene (HCB) and p,p'-DDE are shown in Figure 2 (a and b). The CB-congeners identified are numbered according IUPAC rules.[26] Co-eluting groups of congeners are given between brackets. Congeners identified and listed in order of elution from the GC-column were the triCBs 31, 28, (20, 33, 53), the tetraCBs 52, 49, (75, 47, 48), 44, 70, the mixed tetra-pentaCBs (93, 66, 95), the tetraCBs (60, 56), the pentaCBs 84, 101, the hexaCBs (153, 132), 138, the heptaCBs 187, 183, 172, 180, 170 and the octaCB 194. The Σ^{28} CB concentration varied between 108 and 104 $ng.g^{-1}$ PEL in shrimp from Ban Changoe and Jeram, resp. and was significantly higher (172 $ng.g^{-1}$ PEL) in specimens from Laem Nok (Fig. 3). On the contrary, in crabs the highest concentrations were found in individuals from Ban Changoe and Ban Da To (120 and 116 $ng.g^{-1}$ PEL, resp.). Relatively low concentrations of 57 and 38 $ng.g^{-1}$ PEL were found in crab from the near-shore coastal area of Campus PSU (Pattani Bay) and Jeram, respectively. The concentration in the polychaete *Dendronereis* spp. did not differ between all sampling sites and varied between 106 and 111 $ng.g^{-1}$ PEL. In bivalve molluscs from Pattani Bay, the Σ^{28} CB concentration varied substantially between species belonging to the same animal class or phylum: high concentrations were measured in *Glauconome virens* from Campus PSU and in the small bivalve species *Potamocorbula fasciata* from Ban Da To (298 and 169 $ng.g^{-1}$ PEL, resp.). In *G. virens* from Laem Nok, however, the Σ^{28} CB concentration was found to be much lower (85 $ng.g^{-1}$ PEL) than in specimens from last mentioned species from Campus PSU and in the edible species *Perna Viridis* (the green mussel; data not shown in Figures) from Campus PSU and *Anadara granosa* (the bloody cockle) from Jeram (46 and 31 $ng.g^{-1}$ PEL, resp.; Fig. 3). Since PCBs have been synthesized in the form of technical mixtures they will always be present in certain patterns in environmental samples. A comparison of the PCBs present in a certain environmental compartment or organisms may be done either on the basis of the sum-concentration of a number or all congeners identified, or the concentration of single congeners. Figure 4 summarizes all quantified peaks of CBs from a number of chromatograms. It is seen that some peaks consist of a number of co-eluting congeners. To use certain congeners for monitoring purposes their environmental occurrence should be well established, they should represent different levels of overall chlorination of the molecule and their peaks should be well separated and absent in the blank chromatograms.

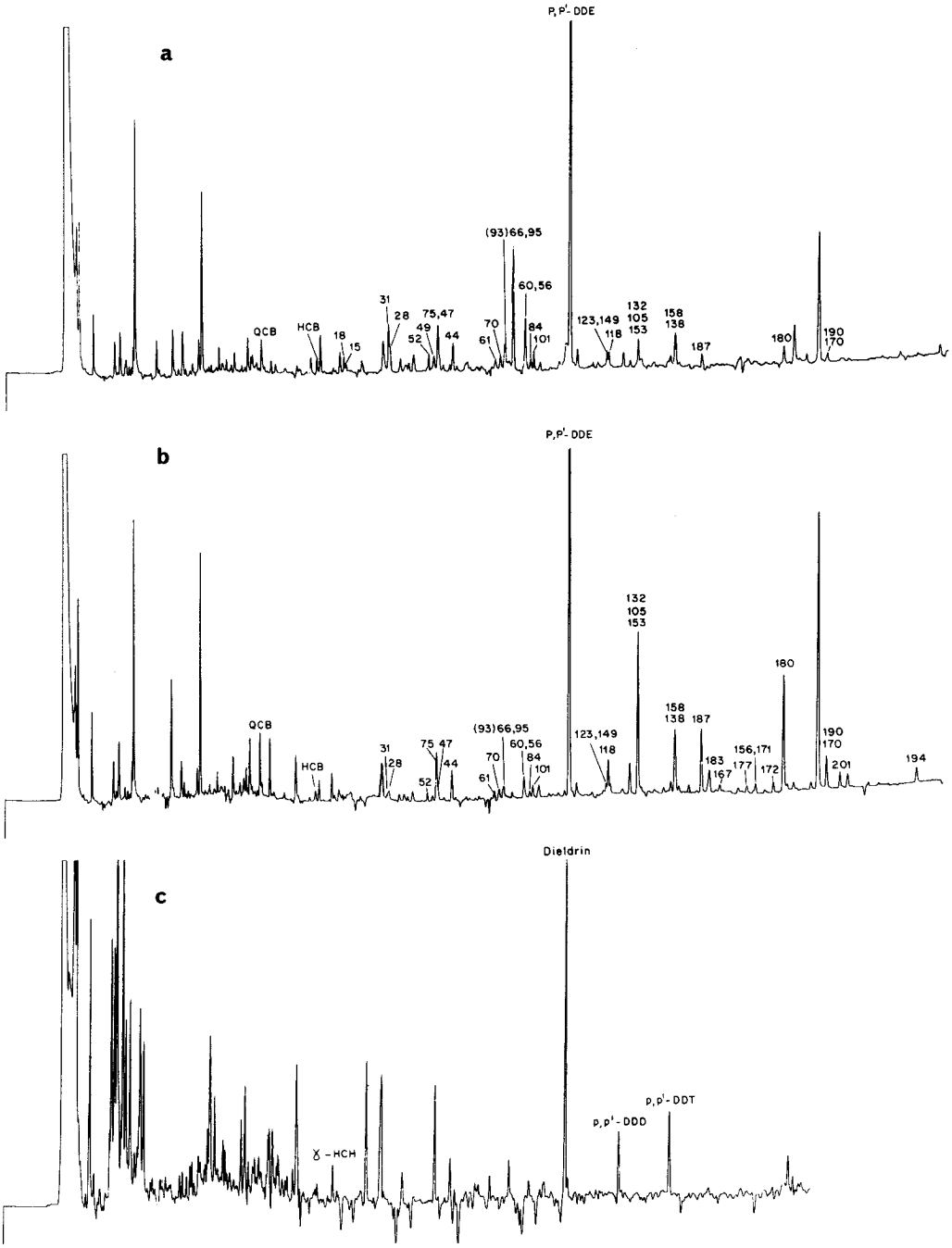

Fig. 2. Chromatograms of samples after capillary GC-ECD of the first (a and b) and second (c) silica fraction. (a) and (c) the crab species *Metaplax longipes* from Ban Changoe (Ao Ban Don) and (b) the shrimp species *Metapenaeus lysianassa* from Laem Nok (Pattani Bay). Some peaks in the chromatogram are assigned to a single CB-congener (a,b), whereas 2 or more other congeners also contribute but to a minor extent to the peak in the chromatogram. The congeners with highest weight percent distribution in the technical mixtures[1] are given in the figure.

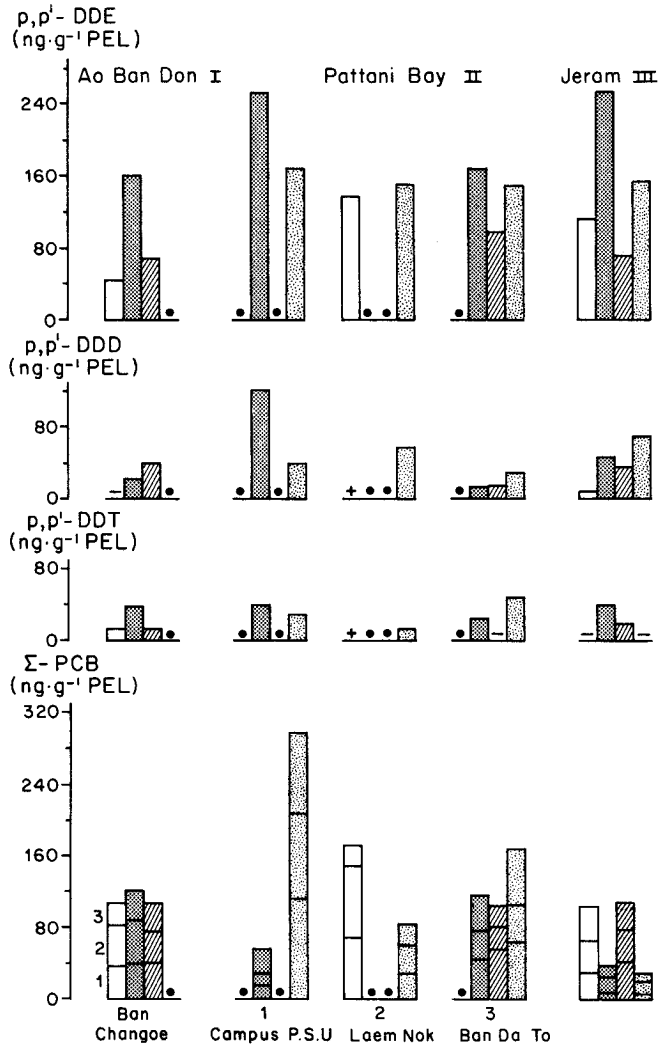

Fig. 3. The concentration (ng.g^{-1} PEL) of the pesticide p,p'DDT and two of its metabolites (p,pDDE and p,p'DDD) and polychlorinated biphenyls (Σ PCB) in benthic invertebrates from three coastal areas of the Malay Peninsula. Organochlorines were analysed in four groups of invertebrate species: shrimp ( ), crab ( ), polychaete worms ( ) and bivalve molluscs ( ). The Σ PCB concentration is based on the sum concentration of either 10 (level 1), 16 (level 2) or 28 (level 3) individual CB-congeners.
o indicates that no samples were available;
+ refers to an identified but not quantified compound
– indicates a not detectable compound.

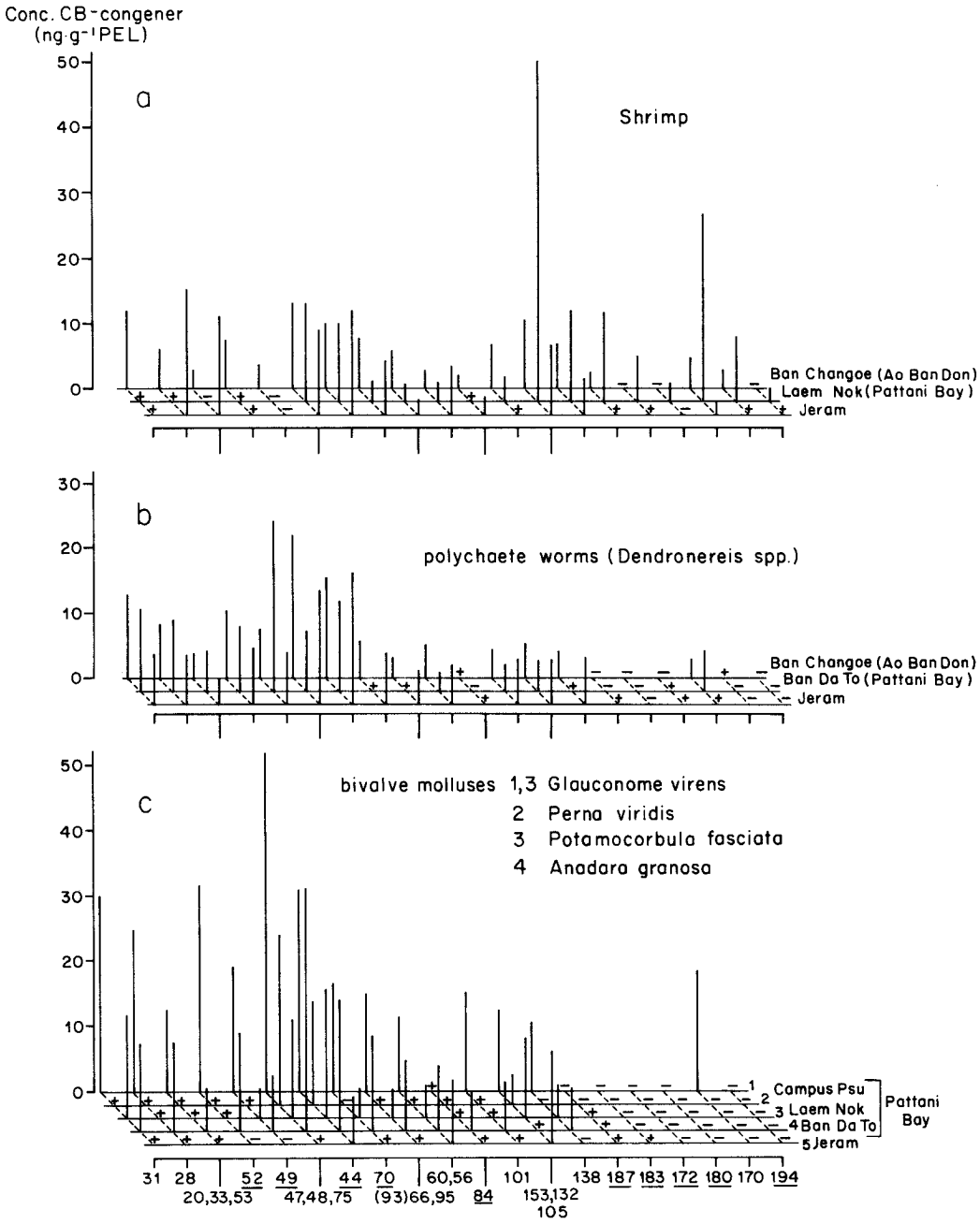

Fig. 4. PCB patterns in benthic invertebrates from various sampling sites along the coast of the Malay Peninsula. Concentrations ($ng.g^{-1}$ PEL) in each histogram refer to 28 CB-congeners identified and quantified in the chromatograms of samples from shrimp (a), polychaete worms (b) and bivalve molluscs (c) from various sampling sites.

\+ indicates an identified but not quantified congener

– indicates a not detectable congener.

Congeners fulfilling these criteria are 52, 49, 44, 70, 84, 187, 183, 172, 180 and 194. Other co-eluting congeners are not suitable for monitoring purposes: they are either not well separated (eg. CBs (20, 33, 53), (47, 48, 75) and ([93], 66, 95, of which CB-93 even does not occur in environmental samples[1] or the separation is questionable (eg. CBs (31, 28) and (60, 56). Some peaks consist of two or three co-eluting congeners, however, with only one major congener[1] (eg. (132, 153, 105), (160, 138, 158) and (170, 190), with CBs 153, 138 and 170 as the major congeners, respectively). In the present study, the sum-concentration of latest mentioned group congeners plus the well separated congeners (Σ^{16} CB; level 2 in Fig. 3) as well as the sum-concentration of the strictly well-separated congeners (eluting as single peaks applying capillary GC-ECD with a SE-54 column;[1] Σ^{10} CB; level 1 in Fig. 3) has been calculated to establish whether interspecific and/or geographic differences in the concentrations of Σ PCB in the benthic biota could be explained on the basis of the selection of congeners taken into account. However, such differences were apparently independent of the choice of CB-congeners. On the contrary, the PCB patterns (i.e. the relative contribution of each congener to Σ CB) were different for the various animal groups but generally highly similar for the different geographical regions (Fig. 4). The differences between the PCB patterns may reflect possibly the differences in route of uptake and different capacities of organisms belonging to different animal classes or phyla to metabolize CB-congeners.

Pesticides

Of the pesticides analysed, γ-HCH, dieldrin and the members of the DDT-family, p,p'DDT, p,p'DDE and p,p'DDD, could be identified and quantified in all samples. An example of a chromatogram of the second silica fraction, containing the more polar pesticides is shown in Fig. 2c. The compounds mentioned above, except p,p'DDE, could be identified and quantified quite obviously; p,p'DDE appearing in the chromatogram of the first silica fraction together with the individual PCBs was quantified on the basis of the external pesticide standard. In a restricted number of samples (eg. crustaceans from Ban Changoe, Laem Nok and Jeram), both α-HCH and endrin could be identified.

Since DDT rapidly metabolizes into DDE, the presence of DDE in environmental samples indicates recent use of DDT. Of the members of the DDT family, p,p'DDE was present in highest concentrations in the samples. The concentrations of p,p'DDE varied between species and was always higher than the concentration of p,p'DDD and p,p'DDT within each species (Fig. 3). Interspecific comparison showed highest concentrations in crab species: 160 to 250 $ng.g^{-1}$ PEL, with the lowest levels in crab from Ban Changoe (Ao Ban Don) and Ban Da To (Pattani Bay), highest levels in crab from the near-shore areas of Campus PSU (Pattani Bay) and Jeram (Malaysia). Considerably lower concentrations were found in shrimp, being 44, 140 and 112 $ng.g^{-1}$ PEL in specimens from Ban Changoe, Laem Nok and Jeram, respectively. In the polychaete worm *Dendronereis* spp. obtained from the same sampling sites the concentrations were 69, 97 and 71 $ng.g^{-1}$ PEL respectively. Intermediate concentrations were measured in bivalve molluscs varying between 150 and 170 $ng.g^{-1}$ PEl without differences between sampling sites.

The distribution pattern of p,p'DDD in the various species resembles very much that of p,p'DDE, except the concentration level (10 to 70 $ng.g^{-1}$ PEL). Only in crab from the Campus PSU coastal area a relatively high concentration of 125 $ng.g^{-1}$ PEL was found. In shrimp the concentration of p,p'DDD was either very low (7 $ng.g^{-1}$ PEL, Jeram), identified but not quantified (Laem Nok) or even below detection limit (Ban Changoe).

Without showing significant differences between species and geographical areas, the concentration of p,p'DDT varies between 10 and 50 $ng.g^{-1}$ PEL, thereby contributing to a minor extent to the concentration of Σ DDT. In a number of samples p,p'DDT was below the detection limit. These data on the distribution of DDT and its metabolites DDD and DDE thus suggest that generally one representative of the DDT family may be considered to reflect environmental contamination in terms of concentration levels in biota: p,p'DDE. On the basis of the present data it can be concluded that there is a different geographical distribution of p,p'DDE with the lowest concentrations in benthic biota from Ao Ban Don compared to Pattani Bay and Jeram coastal area.

Other cyclic chlorinated pesticides, such as γ-HCH, penta- and hexachlorobenzene, did not demonstrate any significant differences in geographical distribution, even though there were some interspecific differences in concentration levels (Fig. 5). With respect to penta- and hexachlorobenzene it has to be noticed that the mainly low concentrations reported here are not reflecting the actual levels. Due to the procedure of drying of the samples at 60-70°C during sample preparation, probably a considerable amount of the volatile compounds was lost.

The concentrations of dieldrin were found to be different in benthic biota from the three estuarine areas (Fig. 5). The concentrations of dieldrin were surprisingly low in organisms from Pattani Bay, irrespective of the species concerned and found to be 10, 12-22 and about 5 $ng.g^{-1}$ PEL, in shrimp, crab and bivalves, respectively. Comparatively, very high concentrations were found in organisms from the coastal area of Jeram and intermediate levels were established in benthic biota from Ao Ban Don (Fig. 5). Interspecific concentration differences were quite obvious.

Many data on organochlorine residues in biota are incomparable and lead to dissimilar conclusions between different publications. This also counts for the data on residues in biota from river mouths in Thailand and coastal areas of the Malay Peninsula.[18-20] The fact that concentrations of organochlorines are expressed on a wet weight as well as on a pentane extractable lipid (PEL) basis, is likely to be an important reason for differences observed. It is recommended to express the concentration of these lipophilic contaminants on an extractable lipid basis. Organochlorines show highest affinity for lipids and thus the lipid content and lipid composition of the tissues determine the organochlorine concentration in organisms.[27-29] Another reason for incomparable data, especially with respect to PCBs, is the heterogenous methodology for quantification. Which individual congeners were involved in the calculations of Σ PCB is often unknown, or concentrations were even calculated on the basis of the technical mixtures equivalents. In this respect the present data can be considered to describe the levels of contamination in benthic invertebrate species in a way to be applied for monitoring to asses environmental quality.

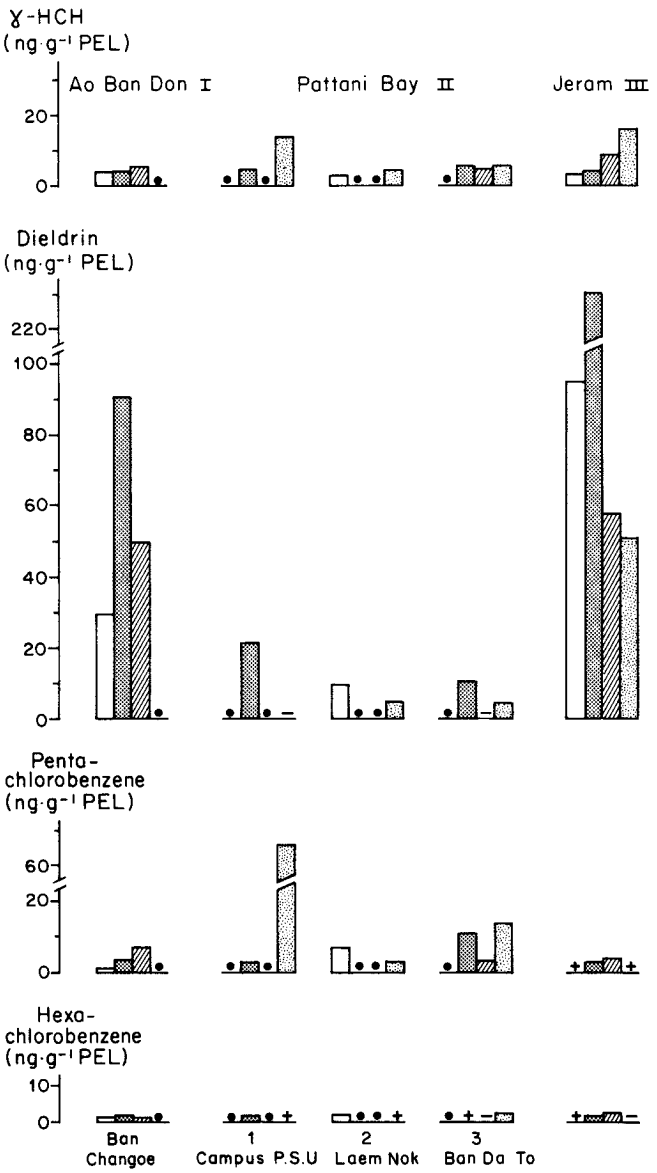

Fig. 5. The concentration (ng.g.$^{-1}$ PEL) of some cyclic organochlorine pesticides in benthic invertebrates from three coastal areas of the Malay Peninsula. Pesticides were analysed in four groups of invertebrate species: shrimp ( ), crab ( ), polychaete worms ( ) and bivalve molluscs ( ).

o indicates that no samples were obtained;

+ refers to a identified but not quantified compound;

– indicates a not detectable compound.

Comparison of the present data with concentrations of PCBs (Table 2) and some pesticides (Table 3) measured in corresponding benthic invertebrate species from marine environments in other regions of Southeast Asia leads to the following conclusions. In the epibenthic species studied, the concentration of total PCB is one to two orders of magnitude lower than in the corresponding species from the upper Gulf of Thailand (e.g. the Rayong area) and the coastal waters of Perak and Penang (Malaysia) as measured in earlier studies[18, 20] (Table 2). The concentration of total PCB in mussels from four river mouths in the Upper Gulf of Thailand (Mae Klong, Ta Chin, Chao Phraya and Ban Pakong) ranged from 0.002 to 0.043 $\mu g.g,^{-1}$ with an exceptionally high concentration of 0.11 $\mu g.g^{-1}$ in mussels from the Mae Klong.[19] These concentrations were expressed on wet weight basis. Assuming a mean lipid percentage of about 1.5% of the wet weight of *Perna,* these concentrations correspond to lipid based concentrations of 0.13 to 2.9 $\mu g.g,^{-1}$ with a maximum of 7.3 $\mu g.g^{-1}$ in specimens of the Mae Klong. These concentration levels are of the same order of magnitude as those described in other studies[18, 20] and are 10 to 100 times higher than indicated by the results of the present study. The concentrations of PCBs in epibenthic macro invertebrates from an other tropical marine environment, the Java Sea and the coastal area of East Java (Strait Madura),[31] agree with the present data (Table 2). A comparison of Σ PCB and the CB-congeners 52 and 180, shows a 10 to 100 times higher concentration in benthic invertebrate species from the North Sea and the Dutch Wadden Sea, a coastal shelf sea and a tidal mud-flat area respectively, from moderate climatological latitude and adjacent to highly industrialized countries of north-west Europe.[4, 12, 21, 32]

With respect to the cyclic chlorinated pesticides γ-HCH, dieldrin and p,p'DDE (Table 3), the following comments can be made. In the organisms from the three coastal areas of Thailand and Malaysia,[30] the concentration of γ-HCH was one order of magnitude lower, whereas dieldrin and p,p'DDE concentrations were in the same order of magnitude, compared to organisms from the estuarine and coastal area of the highly industrialized north-west Europe (the Netherlands) and the North Sea.[12, 32] The ranges of the compounds in the present study are (again) one to two orders of magnitude lower than the ranges reported earlier for estuarine and coastal waters of Thailand and Malaysia[18-20] (Table 3). The concentrations of γ-HCH and p,p'DDE in shrimp, crab and bivalves from Strait Madura (Indonesia)[31] are more than an order of magnitude higher than in the present study. On the contrary, dieldrin could not be quantified in the organisms from Indonesian waters,[31] whereas in organisms from Thai and Malay estuarine areas dieldrin was found in considerable concentrations.

When compared to the same type of animals from temperate latitudes, the concentrations of cyclic chlorinated hydrocarbons tend to be considerably lower. This is in contrast with the concentration levels of certain heavy metals, such as cadmium and lead, in corresponding benthic invertebrates from the different climatological regions considered.[33]

TABLE 2. The concentration ($\mu g.g^{-1}$ pentane extractable lipid, PEL) of two polychlorinated biphenyl congeners (CB-52 and CB-180) and the summed concentration of PCB in benthic invertebrates from marine environments of different geographical regions: the Malay Peninsula (refs. 18,20,30), Java Sea (*) and coastal waters around East Java (ref. 31), the Dutch Wadden Sea (ref. 32) and the Scheldt estuary (ref. 4), the Netherlands, and the North Sea (refs. 12,21).

Ref.:	Species:	CB-52	CB-180	Σ PCB
18.	shrimp:			
	Penaeus spp.	---	---	1.0-10
	bivalve molluscs:			
	Perna viridis	---	---	0.65
	Anadara granosa	---	---	2.0
20.	bivalves molluscs:			
	Anadara granosa	---	---	1.3-3.2
30.	shrimp	nd-0.008	0.004-0.03	0.05-0.17
	crab	nd-0.01	nd-0.004	0.04-0.12
	polychaete worms	0.008-0.01	nd-0.006	0.10-0.12
	bivalve molluscs	nd-0.03	nd	0.03-0.30 (Σ^{28}PCB)
31.	shrimp	* 0.02-0.17	0.004-0.02	< 0.05-0.50
		nd-0.03	nd-0.11	< 0.05-0.30
		* nd-0.09	nd-0.02	< 0.05-0.30
		nd-0.09	nd-0.36	< 0.05-1.0
	bivalve molluscs	* 0.01	0.01	< 0.05-0.06
		nd	nd	< 0.05 (Σ^{8} PCB)
32.	shrimp:			
	Crangon crangon	0.04-0.11	0.26-0.32	---
	polychaete worms:			
	Arenicola marina	0.04-0.12	0.07-0.32	---
	bivalve molluscs:			
	Macoma balthica	0.03-0.12	0.07-0.19	---
4.	bivalve molluscs:			
	Mytilus edulis	0.10-0.90	0.03-1.2	---
12.	polychaete worms:			
	Nephtys spp.	---	---	0.05-13 (Σ^{35}PCB)

TABLE 2. (Cont'd)

Ref.:	Species:	CB-52	CB-180	Σ PCB
21.	shrimp:			
	Crangon allmanni	0.02-0.04	0.02-0.07	0.34-1.15
	Crangon crangon	0.05-0.17	0.08-0.33	0.98-3.0
	polychaete worms:			
	Nephtys hombergii	nd-0.16	nd-0.60	0.11-2.4 (Σ^{35}PCB)

TABLE 3. The concentration ($\mu g.g^{-1}$ pentane extractable lipid, PEL) of some cyclic chlorinated pesticides in benthic invertebrates from marine environments of different geographical regions: Malay Peninsula (refs. 18,20,30), Java Sea (*) and coastal waters around East Java (ref. 31), the Dutch Wadden Sea (ref. 32) and North Sea (ref. 12), the Netherlands.

Ref.:	Species	γ-HCH	Dieldrin	p,p'-DDE
	shrimp:			
	Penaeus spp.	0.30-1.5	0.99-6.2	0.80-8.5
	bivalve molluscs:			
	Perna viridis	0.06	0.65	0.84
	Anadara granosa	0.26	0.58	0.91
20.	bivalve molluscs:			
	Anadara granosa	0.14-0.50	0.10-0.32	0.48-2.66
30.	shrimp	0.002-0.004	0.009-0.10	0.04-0.14
	crab	0.003-0.006	0.01-0.23	0.16-0.25
	polychaete worms	0.004-0.008	0.50-0.58	0.07-0.10
	bivalve molluscs	0.004-0.02	0.004-0.05	0.15-0.17
31.	shrimp	* 0.02-0.05	nd	0.03-0.30
		nd-0.03	nd	0.30-5.1
	crab	* 0.02-0.20	nd	0.10-0.70
		nd-0.03	nd	0.50-3.9
	bivalve molluscs	* 0.03	nd	0.01-0.02
		nd	nd	0.01-2.0
32.	shrimp:			
	Crangon crangon	nd-0.03	nd-0.07	0.10-0.31
	polychaete worms:			
	Arenicola marina	0.02-0.09	0.09-0.20	0.60-0.16
	bivalve molluscs:			
	Macoma balthica	0.04-0.27	0.10-0.40	0.09-0.35
12.	polychaete worms:			
	Nephtys spp.	nd-0.16	nd-0.20	---

CONCLUSION

The data clearly show that the concentration levels of the cyclic chlorinated hydrocarbons can be considered to approach baseline levels, except for dieldrin. Theoretically, the baseline level of an anthropogenic contaminant is zero. In spite of these low background levels of certain organochlorine contaminants, both interspecific and interregional differences in uptake were established for specific species. It could not be established how far the presence of these organochlorines and their concentration levels in the benthic biota have any ecological implications. One consequence might be an increased risk of bioaccumulation in birds, since biomagnification is likely to occur from invertebrates to birds. However, it is quite obvious that locally occurring, relatively high concentrations of certain organochlorines in benthic organisms indicate both extensive use of the compound in the area and contaminated runoff from upstream agricultural regions. Examples were the relatively high concentrations of γ-HCH, p,p'DDE and Σ PCB in bivalve molluscs from Campus PSU (Pattani Bay), the relatively high concentrations of γHCH and p,p'DDE in bivalve molluscs and crab, respectively, from Jeram. High dieldrin levels in all species reflect the extensive use of this pesticide in the agricultural regions around Ao Ban Don and Jeram.

With respect to human health it can be concluded that the concentrations of any of the PCBs and pesticides measured, both in shrimp, crab and bivalve molluscs, do not yet approximate to the maximum admissible concentration (MAC). For example in fish, the MAC-value for dieldrin and Σ DDT is 0.5 and 2-3.5 $\mu g.g^{-1}$ on lipid basis (PEL), respectively, according to German standards and 0.05 and 0.5 $\mu g.g^{-1}$ Wet Weight, respectively, according to Dutch standards. The MAC-value for the CB-congeners 52 and 180 is 0.04-0.2 and 0.12-0.6 $\mu g.g^{-1}$ weight, respectively, in fish according to the Dutch standards for acceptable (daily) intake, which are based on WHO standards and take into account the general consumption pattern.

ACKNOWLEDGEMENTS

Many thanks are due to Mr. Y. Hansopa (Surat Brackish Water Fisheries Station at Ban Changoe), Mr. N. Ruttanadakul and Mr. S. Ardseungnurn (Faculty of Science and Technology, Prince of Songkla University of Pattani) and Prof. A. Sasekumar (Department of Zoology, University of Malaya at Kuala Lumpur) for allowing to use laboratory facilities to prepare the samples. INTERWADER (the East Asia/Pacific Shorebird Programme) provided assistance and part-funding for the collection of samples. Thanks are due to Prof. P.A.W.J. de Wilde and Dr. J.P. Boon for critical reading and valuable advice to improve the manuscript.

REFERENCES

1. Schultz, D. E., Petrick, G. and Duinker, J. C. (1989). Complete characterization of polychlorinated biphenyl congeners in commercial Arochlor and Clophen mixtures by multidimensional gas chromatography-electron capture detection. *Environ. Sci. Technol.* **23,** 852-859.
2. Duinker, J. C. and Hillebrand, M. T. J. (1983). Composition of PCB mixtures in biotic and abiotic marine compartments (Dutch Wadden Sea). *Bull. Env. Contam. Toxicol.* **31,** 25-32.
3. Duinker, J. C. and Boon. J. P. (1986). PCB congeners in the marine environment-a review. In *Organic Micropollutants in the Aquatic Environment,* pp. 187-205, eds. A. Bjorseth and G. Angeletti, D. Reidel Publishing Company, Dordrecht, The Netherlands.
4. Duursma, E. K., Nieuwenhuize, J. and J. M. van Liere (1989). Polychlorinated biphenyl equilibria in an estuarine system. *The Science of the Total Environment* **79,** 141-155.
5. Boon, J. P., Eijgenraam, F. and Everaarts, J. M. (1989). A structure-activity relationship (SAR) approach towards metabolism of PCBs in marine animals from different trophic levels. *Marine Environ. Res.* **27,** 159-176.
6. Moore, J. W. and Rammamoorthy, S. (1984). Organic chemicals in natural waters. Applied monitoring and impact assessment. Chap. 6: Chlorinated pesticides (pp. 88-114) and Chap. 9: Polychlorinated biphenyls (pp. 168-191), Springer-Verlag, New York.
7. Waid, J. S. (Ed.). (1986). PCBs and the Environment. CRC Press, Inc., Florida.
8. Holden, A. V. (1988). Pesticides. In *Environmental Protection of the North Sea,* pp. 66-84, ed. P. J. Newman and A. R. Agg, Heinemann Professional Publ., Oxford.
9. Reijnders, P. (1988). Environmental impact of PCBs in the marine environment. In *Environmental Protection of the North Sea,* pp. 85-98, ed. P. J. Newman and A. R. Agg, Heinemann Professional Publ., Oxford.
10. McLeese, D. W., Metcalfe, C. D. and Pezack, D. S. (1980). Bioaccumulation of chlorobiphenyls and endrin from food by lobsters *(Homarus americanus). Bull. Env. Contam. Toxicol.* **25,** 161-168.
11. Marinucci, A. C. and Bartha, R. (1982). Accumulation of the polychlorinated biphenyl Arochlor 1242 from contaminated sediment and water by the saltmarsh detrivore, *Uca pugnax. Bull. Env. Contam. Toxicol.* **29,** 326.
12. Boon, J. P., van Zantvoort, M. B., Govaert, M. J. M. A. and Duinker, J. C. (1985). Organochlorines in benthic polychaetes *(Nephtys* spp.) and sediments from the Southern North Sea. Identification of individual PCB components. *Neth. J. Sea Res.* **19,** 93-109.
13. Ernst, W., Boon, J. P. and Weber, K. (1988). Occurrence and fate of organic micropollutants in the North Sea. In *Pollution of the North Sea. An Assessment,* pp. 284-299, ed. W. Salomoms, B. L. Bayne, E. K. Duursma and U. Forstner, Springer Verlag Berlin.
14. Goerke, H. and Ernst, W. (1977). Rate of ^{14}C-labelled di-, tri-, and pentachlorobiphenyl in the marine annelid *Nereis virens.* I. Accumulation and elimination after oral administration. *Chemosphere* **9,** 551-558.
15. Calambokidis, J., Mowrer, J., Beug, M. and Herman, S. G. (1979). Selective retention of polychlorinated biphenyl components in the mussel. *Arch. Environm. Contam. Toxicol.* **8,** 299-308.
16. Goerke, H. and Ernst, W. (1980). Accumulation and elimination of ^{14}C-HCH (lindane) in *Nereis virens (Polychaete)* with consideration of metabolism. *Helgolander wiss. Meeresunters.* **33,** 313-326.
17. Everaarts, J. M., Buck, A. de, Hillebrand, M. T. J. and Boon, J. P. (1990). Residues of chlorinated biphenyl congeners and pesticides in brain and liver of the oystercatcher *(Haematopus ostralegis)* in relation to age, sex and biotransformation. *The Science of the Total Environment* **100,** 483-499.
18. Huschenbeth, E. and Harms, U. (1975). On the accumulation of organochlorine pesticides, PCB and certain heavy metals in fish and shellfish from Thai coastal and inland waters. *Arch. Fisch Wiss.* **26,** 109-122.
19. Menasveta, P. and Cheevaparanapiwat, V. (1981). Heavy metals, organochlorine pesticides and PCBs in green mussels, mullets and sediments of river mouths in Thailand. *Mar. Poll. Bull.* **12,** 19-25.
20. Jothy, A. A., Huschenbeth, E. and Harms, U. (1983). On the detection of heavy metals, organochlorine pesticides and polychlorinated biphenyls in fish and shellfish from the coastal waters of Peninsular Malaysia. *Arch. Fisch Wiss.* **33,** 161-206.

21. Everaarts, J. M. and Fischer, C. V. (1989). Micro contaminants in surface sediments and macrobenthic invertebrates of the North Sea. Inst. Sea Res., NIOZ-Rappoprt 1989-6, 1-44.
22. Everaarts, J. M., Otter, E. and Fischer, C. V. (1990). Cadmium and polychlorinated biphenyls: different distribution pattern in North Sea benthic biota. *Neth. J. Sea Res.* **26,** 75-82.
23. Holden, A. V. and Marsden, K. (1969). Single stage clean-up of animal tissue abstract for organal chlorine residue analysis. *J. Chromat.* **44,** 481-492.
24. Duinker, J. C. and Hillebrand, M. T. J. (1978). Minimizing blank values in chlorinated hydrocarbon analysis. *J. Chromat.* **150,** 195-199.
25. Duinker, J. C. and Hillebrand, M. T. J. (1983). Characterization of PCB components in Clophen formulations by capillary GC-MS and GC-ECD techniques. *Environ. Sci. Technol.* **17,** 449-456.
26. Ballschmiter, K. and Zell, M. (1980). Analysis of polychlorinated biphenyls (PCB) by capillary gas chromatography. Composition of technical Arochlor and Clophen-PCB mixtures. *Z. Analyt. Chem.* **302,** 20-31.
27. Hansen, D. J., Parrish, P. R. and Forester, J. (1974). Arochlor 1016: Toxicity to and uptake by estuarine animals. *Environm. Res.* **7,** 363-373.
28. Bruggeman, W. A., Martron, L. B. J. M., Kooiman, D. and Hutzinger, O. (1982). Accumulation and elimination of di-, tri-, and tetrachlorobiphenyls by goldfish after dietary and aqueous exposure. *Chemosphere* **10,** 811-832.
29. Boon, J. P., Oudejans R. C. H. M. and Duinker, J. C. (1984). Kinetics of individual polychlorinated biphenyl (PCB) components in juvenile sole *(Solea solea)* in relation to their concentration in food and to lipid metabolism. *Comp. Biochem. Physiol.* **79,** 131-142.
30. Present study.
31. Boon, J. P., Everaarts, J. M., Kastoro, W. W., Razak, H., Sumanta, I., Sumarno, Nelissen, P. H., Stefels, J. and Hillebrand, M. T. J. (1989). Cyclic organochlorines in epibenthic organisms from coastal waters around East Java. *Neth. J. Sea Res.* **23,** 427-439.
32. Duinker, J. C., Hillebrand, M. T. J. and Boon, J. P. (1983). Organochlorines in benthic invertebrates and sediments from the Dutch Wadden Sea; identification of individual PCB components. *Neth. J. Sea Res.* **17,** 19-38.
33. Everaarts, J. M. and Swennen, C. (1987). Heavy metals (Zn, Cu, Cd, Pb) in some benthic invertebrate species and in sediment from three coastal areas in Thailand and Malaysia. *J. Sci. Soc. Thailand* **13,** 189-203.

บทคัดย่อ

งานวิจัยเรื่องนี้ได้ทำการวัดหาปริมาณยาฆ่าแมลงกลุ่ม chlorinated biphenyl (PCBs), cyclic organochlorine และเมตาบอไลท์ของสารเหล่านี้ในสัตว์ที่ไม่มีกระดูกสันหลังที่อาศัยอยู่บนพื้นน้ำแถบโคลนแลนตามแนวชายฝั่งทะเลของแหลมมาเลย์ บริเวณอ่าวบ้านดอน อ่าวปัตตานี และเจแรม (มาเลเซีย) พบว่าสัตว์น้ำจากอ่าวปัตตานี (บริเวณมหาวิทยาลัยสงขลานครินทร์ วิทยาเขตปัตตานี, แหลมนก และบ้านคาโต๊ะ) มีปริมาณสาร PCB สูงที่สุด โดยเฉพาะในหอยสองฝา *(Gluconome virens* และ *Potamocorbula fasciata)* และในกุ้ง *(Metapenaeus lysianassa)* ในสัตว์ทุกกลุ่มที่ทำการศึกษาพบว่า ปริมาณของยาฆ่าแมลงประเภท organochlorine dieldrin, p, p′-DDT และเมตาบอไลท์คือ p,p′-DDE และ p,p′-DDD มีปริมาณ 10-250 $ng.g^{-1}$ PEL ซึ่งจะเป็นประมาณสิบเท่าของยาฆ่าแมลงประเภท γ-HCH, penta- และ hexachlorobenzene (1-15 $ng.g^{-1}$ PEL) ส่วนพวก α-HCH, endrin และ p,p′-DDD มีปริมาณต่ำกว่าระดับที่จะตรวจหาได้ นอกจากนี้ยังได้พบว่ามีการสะสมของสารพวก dieldrin และ p,p′-DDE ในพวกปูอีกด้วย

เมื่อได้ทำการติดตามการปนเปื้อนของชายทะเลแถบนี้โดยวัดปริมาณสารปนเปื้อนต่อปริมาณลิปิดทั้งตัวของสัตว์ พบว่ามีความแตกต่างในปริมาณของดีลดรินและ p,p′-DDE ในสัตว์ทุกชนิดที่ทำการศึกษา สัตว์ที่อาศัยในแถบอ่าวปัตตานีทั้ง 3 บริเวณที่ทำการสุ่มตัวอย่าง และบริเวณแนวชายฝั่งของเจแรม จะมีประมาณ p,p′-DDE สูงกว่าพวกที่อาศัยอยู่ในอ่าวบ้านดอน