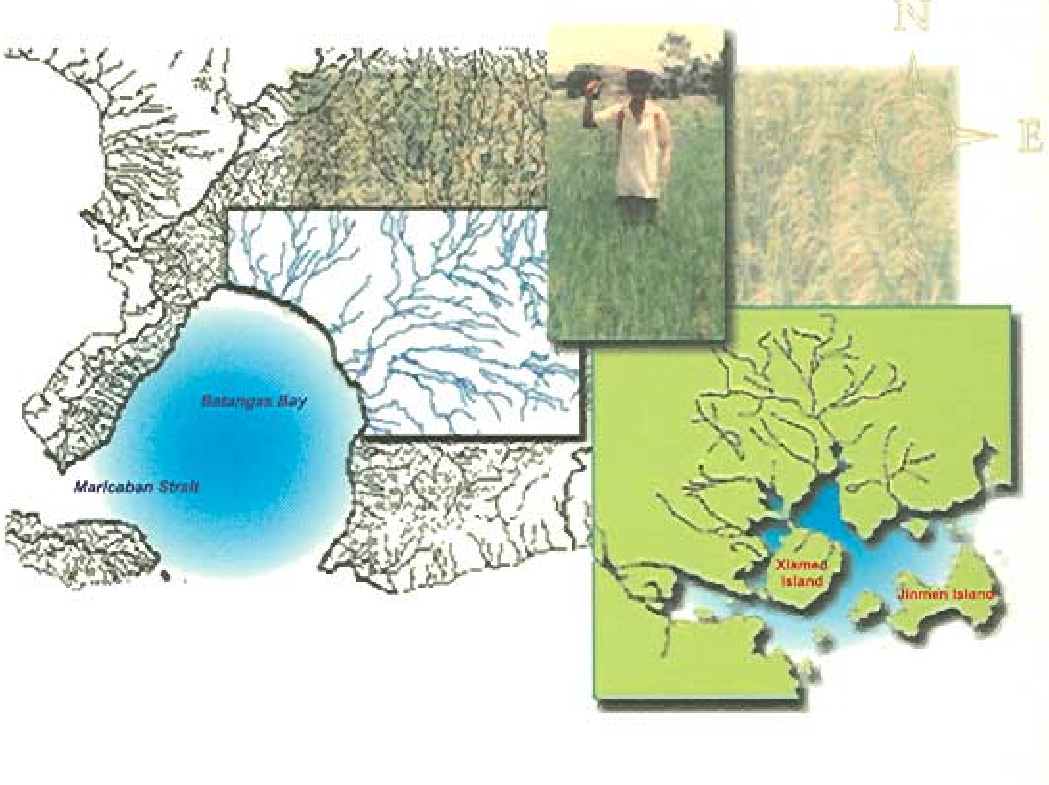
Initial Environmental Risk Assessment of Pesticides

in the Batangas Bay Region, Philippines and the Xiamen Seas, China



Food and Agriculture Organization
of the United Nations
Fisheries Department
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Rome, Italy

GEF/UNDP/IMO
Regional Programme for the Prevention
and Management of Marine Pollution
in the East Asian Seas
Quezon City, Philippines

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PREPARATION OF THIS DOCUMENT

This document was prepared by ***Dr. Davide Calamari***, consultant, under a Memorandum of Agreement between the GEF/UNDP/IMO Regional Programme for the Prevention and Management of Marine Pollution in the East Asian Seas (MPP-EAS) and the Food and Agriculture Organization of the United Nations (FAO).

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MISSION STATEMENT

The primary objective of the Global Environment Facility/United Nations Development Programme/International Maritime Organization Regional Programme for the Prevention and Management of Marine Pollution in the East Asian Seas is to support the efforts of the eleven (11) participating governments in the East Asian region to prevent and manage marine pollution at the national and subregional levels on a long-term and self-reliant basis. The 11 participating countries are: Brunei Darussalam, Cambodia, Democratic People's Republic of Korea, Indonesia, Malaysia, People's Republic of China, Republic of the Philippines, Republic of Korea, Singapore, Thailand and Vietnam. It is the Programme's vision that, through the concerted efforts of stakeholders to collectively address marine pollution arising from both land- and sea-based sources, adverse impacts of marine pollution can be prevented or minimized without compromising desired economic development.

The Programme framework is built upon innovative and effective schemes for marine pollution management, technical assistance in strategic maritime sectors of the region, and the identification and promotion of capability-building and investment opportunities for public agencies and the private sector. Specific Programme strategies are:

- Develop and demonstrate workable models on marine pollution reduction/ prevention and risk management;
- Assist countries in developing the necessary legislation and technical capability to implement international conventions related to marine pollution;
- Strengthen institutional capacity to manage marine and coastal areas;
- Develop a regional network of stations for marine pollution monitoring;
- Promote public awareness on and participation in the prevention and abatement of marine pollution;
- Facilitate standardization and intercalibration of sampling and analytical techniques and environment impact assessment procedures; and
- Promote sustainable financing mechanisms for activities requiring long-term commitments.

The implementation of these strategies and activities will result in appropriate and effective policy, management and technological intervention at local, national and regional levels, contributiong to the ultimate goal of reducing marine pollution in both coastal and international waters, over the longer term.

Dr. Chua Thia-Eng
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of Marine Pollution in the East Asian Seas

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Acronyms

ADI	Admissible daily intake
a.i.	Active ingredient
BCF	Bioconcentration factor
EC	Effective (immobilization) concentration
EQC	Equilibrium criterion
FAO	Food and Agriculture Organization
GUS	Groundwater ubiquity score
ICM	Integrated coastal management
IMO	International Maritime Organization
IWMAP	Integrated waste management assessment and action plan
Kd	Soil absorption
LC	Lethal concentration
LD	Lethal dose
K_{oc}	Ratio of sorbed to solution pesticides in water-soil slurry
K_{ow}	Octanol/water partition coefficient
MPP-EAS	Regional Programme for the Prevention and Management of Marine Pollution in the East Asian Seas
NOEL	No observable effect level
PAGASA	Philippine Atmospheric, Geophysical and Astronomical Services Administration
PAH	Polycyclic aromatic hydrocarbon
PCB	Polychlorinated biphenyl
PEC	Predicted environmental concentration
SoilFug	Soil fugacity
T	Trace
TBTO	Tributyltinoxyde
UN	United Nations

FOREWORD

Pesticide use has played a significant role in increasing agricultural production in the East Asian Region during the past several decades. Although pesticides are considered to be a step towards food sufficiency, the environmental cost of increased pesticide use still raises significant concerns. The main problem is that even with extremely small amounts of pesticides applied on a given area, less than 0.1% of many insecticides actually reach the target organism. The remainder becomes an environmental contaminant.

In view of these concerns, a collaborative project on hazardous waste management was conducted through a Memorandum of Agreement between the GEF/UNDP/IMO Regional Programme for the Prevention and Management of Marine Pollution in the East Asian Seas and the Food and Agriculture Organization of the United Nations (FAO) at the two Regional Programme demonstration sites in Batangas Bay, Philippines and in Xiamen, China. The Regional Programme applies an integrated coastal management (ICM) approach to address marine pollution from both sea- and land-based sources at these two sites. This ICM framework incorporates the implementation of an integrated waste management assessment and action plan (IWMAP). Pesticide appraisal was conducted as part of IWMAP. The main aim of the study is to assist in agricultural waste management at the two sites and to train local professionals in risk assessment.

This report describes the results of the rapid appraisal of environmental risk from pesticide contamination in the two sites. In Batangas Bay, pesticide use under present conditions presented a relatively low risk to the marine environment. There were signs, however, that certain pesticides were appearing in marine waters, and this should be considered a warning. In Xiamen, relatively high pesticide application rates are used on agricultural lands. The report made specific recommendations for preventing and reducing negative impacts on coastal waters, particularly in the vicinity of mariculture activities.

We wish to thank Dr. Davide Calamari for his efforts in strengthening local professionals in pesticide risk assessment through lectures and hands-on training using models; Dr. Huming Yu, Dr. Mario Delos Reyes and Mr. James Paw for technical coordination and guidance in the project implementation and the review of the report; Prof. Zhang Louping, Ms. Ma. Theresa Kalaw and Mr. Fan Zhijie for their technical assistance; Dr. Vidhisha Samarasekara for technical editing; Dr. Leticia Dizon and Ms. Maricel Bigal for copyediting; and Ms. Victoria Grace Aseron and Mr. Jonel Dulay for the layout/graphics of the report.

Special thanks should be extended to the demonstration project offices in both Batangas and Xiamen for their initiative in developing the local capability to undertake this assessment.

The importance of this study is that it can represent a cost-effective method that may be used before engaging in a much expensive monitoring program. The findings could enrich important baseline data useful to the sustainable development of agriculture and industry in Batangas and Xiamen. It is hoped that this document will be of value not only to the countries of the East Asian Region but also to developing countries elsewhere engaged in pesticide use.

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Introduction

Background

The Global Environment Facility/United Nations Development Programme/International Maritime Organization Regional Programme for the Prevention and Management of Marine Pollution in the East Asian Seas (MPP-EAS) established two integrated coastal management (ICM) demonstration projects located in Batangas Bay, Philippines and in Xiamen, China.

Among the various activities in the two sites is to assess the impacts of hazardous wastes, particularly pesticides in the coastal zone. Thus, an initial risk assessment of pesticides was conducted in the two demonstration sites. The study was carried out through the services of the Food and Agriculture Organization of the United Nations (FAO) by hiring a consultant under a memorandum of agreement between IMO and FAO.

This report describes the results of the work conducted in the Batangas Bay Region, Philippines and in the Xiamen Seas, China.

Objectives

The specific objectives of the study are:

- To assess the impact of hazardous wastes generated in the Batangas Bay Region and in the Xiamen Seas from major agricultural activities, in particular pesticide use;
- To evaluate the information available on the different types of pesticides used for agricultural purposes within the management boundaries of the demonstration sites, including the quantity and frequency of application by type of agricultural crop on an annual basis, the level of these pesticides in selected substrate or indicator species and profiles of discharge relating to areas of use/disposal in the coastal waters;
- To delineate specific areas in the demonstration sites that were contaminated with pesticides or potentially at risk for contamination, by type of pesticide;
- To assess the management and regulatory systems in operation at the demonstration sites with respect to pesticide use and management and to recommend appropriate measures, options and strategies to be adopted in order to establish and improve such systems;
- To assess the impacts of pesticide use on water resources (including coastal waters) and on primary resource-based economic activities such as agriculture, fisheries, aquaculture and eventually on coastal tourism and public health; and
- To recommend appropriate measures and actions to be taken to address the impacts arising from the above-mentioned activities.

Risk Assessment

The activities described in this report take into consideration that risk assessment is a process which involves many elements, i.e., hazard identification, effects assessment, exposure assessment and risk characterization (Van Leeuwen and Hermens, 1995). It is also recognized that risk assessment may be performed at differing levels of sophistication ranging from qualitative to precise evaluations including statistical and probabilistic considerations, as required (Calabrese and Baldwin, 1993).

An initial compilation of existing data on toxicological properties of pesticides was made in order to make a risk identification of a substance which has an inherent capacity to cause undesirable effects on the aquatic environment (Calamari et al., 1997). A physico-chemical profile that represents the basis for the understanding of the behavior of the molecule into the environment was defined. The information was utilized for inclusion in the evaluative models that will allow a generic evaluation of the environmental distribution and fate of each chemical in a standard environment (ECETOC, 1992; Cowan et al., 1995). Simulation of the environmental behavior of the pesticides in relation to the load applied into the agricultural area was also completed (DiGuardo et al., 1994a, 1994b; Baldry et al., 1995). Finally, risk assessment was performed comparing exposure and effects assessment.

Sources of Data

Three major sources of data were used in this report. The first included the coastal environmental profiles for the Batangas Bay Region, Philippines (MTE, 1996), and for the Xiamen Seas, China (ITTXDP, 1996). The second consisted of data collected locally from government offices and from local institutions and commercial establishments (e.g., pesticide dealers). Lastly, information was gathered from secondary literature sources (books and articles that are listed in the references).

Physical Features

Geography and Climate

The management area of the Batangas Bay Demonstration Project is located in the southern portion of Batangas Province. The total land area is estimated at 871 km^2, with a total coastline of 470 km and the area of the bay is about 220 km^2. The drainage basin is actually slightly larger than the area contained within the administrative boundaries of the region *(Figure 1)*. During the warmest months (April and May) daily temperatures range from 23 to 34°C with a mean of 29°C. During the coldest months (December and January), temperatures range from 21 to 30°C with a mean of 26°C. The area is characterized by two seasons, one wet and the other dry. The wet season lasts from June to September/October, while the dry season normally is from January to April. The mean annual rainfall is 1.737 m. Daily rainfall data for 1995 and 1996 were used for the computer simulation modelling (*Table 1*). These data were obtained from the Ambulong and Tanauan, Batangas gauging stations of the Philippine Atmospheric, Geophysical and Astronomical Services Administration (PAGASA).

The total land area of Xiamen Municipality is 1,516 km^2, located in the southern coast of Fujian province. Xiamen Island proper has a surface area of 129 km^2. It is surrounded by a complex bay with several islands and different seas, i.e., the West Harbour, Maluan Bay, Tong'an Bay, Jiulongjiang River Estuary, the Southern Seas and the Eastern Seas *(Figure 2)*. *Figure 3* shows the drainage area and the rivers of Xiamen Municipality. It has been assumed that the pesticide loads from the Xiamen drainage basin are directly influencing the Western Seas, Tong'an Bay and the Eastern Seas. In contrast, the Jiulongjiang River because of its high discharge into the open sea, is considered of minor relevance. Furthermore, during periods of marine flood tides, the sea water circulates around Xiamen Island, rather than the fresh water from the Jiulongjiang River. The average annual temperature is 20.9°C; the warmest month is July with an average of 28.4°C; and the coldest period is January/February with an average of 12.6°C. Rainfall is concentrated in spring and summer seasons with an annual average of 1.143 m and a distinct

Figure 1. Map of the Batangas Bay Region.

Table 1. Daily Rainfall (mm) Values in the Batangas Bay Region, 1995-1996.

Days	Jan		Feb		Mar		Apr		May		June		July		Aug		Sep		Oct		Nov		Dec	
	1995	1996	1995	1996	1995	1996	1995	1996	1995	1996	1995	1996	1995	1996	1995	1996	1995	1996	1995	1996	1995	1996	1995	1996
1	0	0	0	0	0	11.5	0	0	0	0	4	0	19.8	0	7	44.9	3.9	0	14	0	5.5	6.6	0	0
2	0	0	2.5	T	0	5	0	1	0	T	75.7	0	21.7	1.3	0	2	0.5	0	0	0	26.1	6.5	0	0
3	0	0	25.7	0	0	1.5	0	1.5	0	0	27.6	0	20.2	7.7	0	3.1	69.9	0	4.2	3.6	277	7	0	3.5
4	0	0	16.2	0	0	T	0	0	0	0	1.5	0	0	0	4	7.1	22.2	64.4	T	0.5	1	4.5	0	1.5
5	0	0	0	0	0	0	0	0	0	0	7	T	0.5	0	0	0	5	12.6	0	0	3.6	14.5	0	0
6	0	0	0	0	0	0	0	0	0	0	0	T	15.8	T	0	0	0	4.8	0	0	0	49	0	0.5
7	0	0	0	0	0	0	0	0	0	0	0	T	14	0	1.5	0	0.5	5	52.2	0	3.1	19.3	0	3
8	0	0	0	0	0	0	0	2	0	0	0	0	0	5	2	0	0	0	37.2	0	0	8.3	0	0
9	7.5	0	0	0	0	0	0	T	0	0	0	0	16	0	6.5	0	0	28.4	1.5	0	0	8	0	0
10	0	0	0	0	0	0	0	T	0	4.8	0	0	3.5	0	0	0	13.6	T	19.3	0.5	0	3.5	0	0
11	0	0	0	0	0	0	0	4	5.1	0	0	1.5	16.2	0	0	T	70.8	12	0	1	0	0	0	0
12	0	0	0	0	0	0	0	0	0	2.5	1.5	3.4	0.5	0	0.5	2	16.9	14.1	0	0	0	0	0	0
13	0	0	0	0	0	0	0	0	0	4	0	1	0.5	0	28.5	3.8	14.9	2.6	0	0	0	0	0	0.2
14	0	0	0	0	0	0	0	T	0.5	0	12.3	T	0	0	1.5	0	7.3	25.1	0	10.5	T	0	0	0
15	0	0	0	0	0	0	0	0	0	T	0	T	0	2	T	2.5	43.2	0	T	0.5	0	T	0	0
16	0	0	0	0	0	0	0	0	7.5	2.5	0	0	0	T	5.5	2.1	6	3	0	0	0	0	0	T
17	0	0	0	0	0	0	T	0	0	1	0	T	0	2.5	0	0	9.5	9.2	0	7	5.5	T	0	9.1
18	0	0	0	0	0	0	0	0	0	3	0	3.2	12	T	4.5	0	5	0	0	0	4	5	0	1.5
19	0	0	0	0	0	0	0	0	0	0	0.5	0	0	29.1	39.1	0.8	29.2	0.2	0	0	1.5	0.5	0	0
20	0	0	0	0	0	0	0	0	1.5	0	0	0	0	5	8.1	3.9	5.5	0.5	0	0	0	10.3	0	0
21	0	0	0	0	0	0	0	0	0	0	0	1	0	3	0	3.8	3	T	0	2	0	1	0	0
22	0	0	0	0.5	0	0	0	0	1	0	0	0	37.7	T	2.5	5.6	0	9.6	0	4	0	20.5	0	0
23	0	0	0	0	0	0	0	57	0	T	0	0	3	55	0	3.2	0	T	8.6	0	0	1.5	0	T
24	0	0	0	0	0	0	0	0	23	0	0	5.5	0	191	16.4	0	0.5	5	3.8	25	0	4.5	0	0
25	0	0	0	0	0	0	0	0	1.5	0	2.5	0	0	197	0.5	0	2	T	0.2	0	1.5	3.5	0	0
26	0	0	0	0	0	0	0	0	11	55	0	0	13.2	8.4	26.4	5.4	4.5	0	0	3.7	T	80.2	0	0
27	0	0	0	0	0	0	0	0	0	T	0	0	2	0	1	12.8	7	0	0	0	8	T	0	1.2
28	0	0	0	0	0	0	0	0	4.5	T	29	4.5	41.1	23.3	41	0	0	0	8.6	2.4	0	21.8	0	0
29	0	0	0	1.5	0	0	0	0	6	0	73	0	2	77.9	75.8	0	18.2	5.5	19	13.4	1	19.5	0	0
30	0	0			0	0	2	0	0	0	8.6	8.5	1	61.2	41.4	1.8	119	0.5	0	17.6	0	0	0	0
31	0	0			0	0			0	0			24.3	10	8.5	0			5	8			0	0

T= Trace

Figure 2. The Xiamen Area.

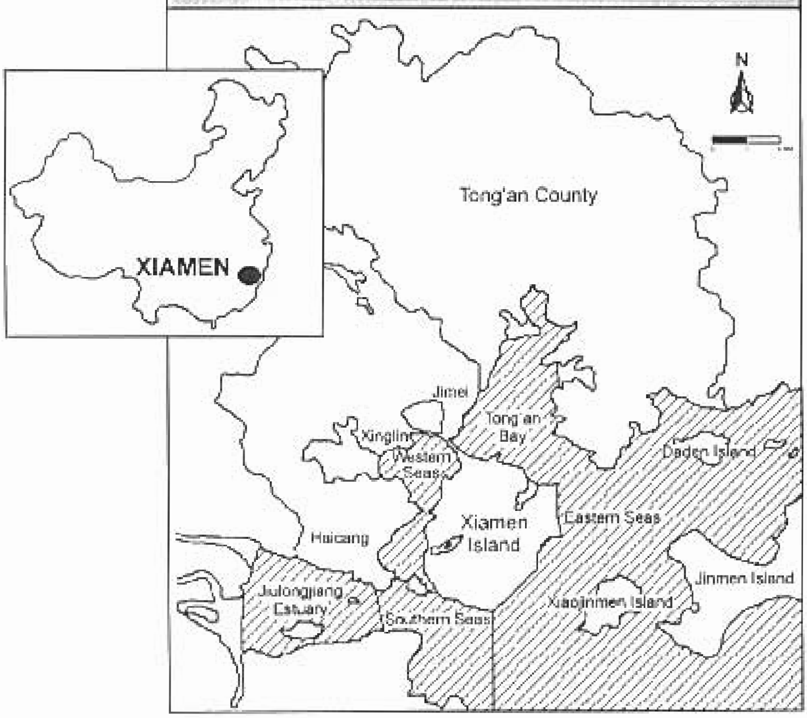
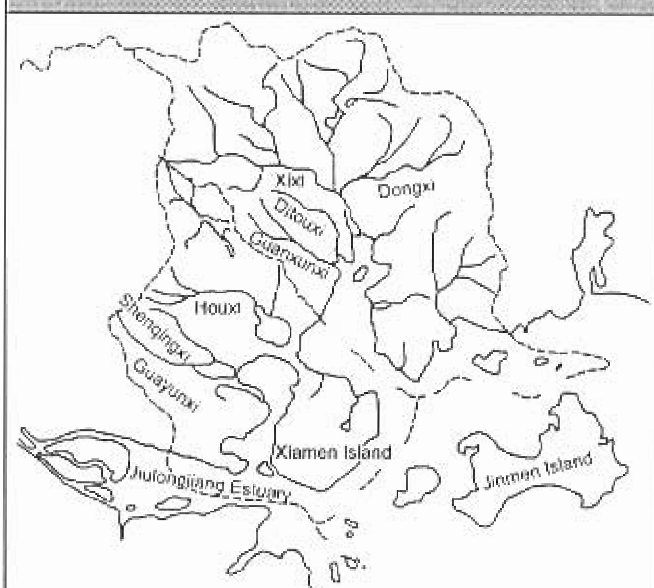


Figure 3. Drainage Basin and Rivers of Xiamen Municipality.



separation between the dry and wet seasons. Annual rainfall distribution, obtained by local meteorological services, is given in *Table 2*.

LAND USE PATTERNS

Figure 4 shows the land use distribution in the Batangas Bay Region, according to seven major categories, clearly illustrating that agricultural land covers less than half of the drainage basin.

In the last year, Xiamen has undergone rapid socioeconomic development, with the construction of a port, a large-scale development of mariculture, industrialization and increased trading. The cultivated soil in the municipality covers approximately 25% of the Xiamen area.

SOIL CHARACTERISTICS

Detailed descriptions of soil characteristics have been reported in the environmental profile documents (ITTXDP, 1996; MTE, 1996). The data necessary for the calculation of the pesticide runoff by means of the SoilFug model (Di Guardo et al., 1994a, 1994b) were obtained from the Department of Agriculture, Batangas Province for the Batangas Bay Region and from various local administrative sources for the Xiamen Seas.

Table 2. Daily Rainfall (mm) Values in the Xiamen Area, 1996.

Days	Jan	Feb	Mar	Apr	May	June	July	Aug	Sep	Oct	Nov	Dec
1	0	0	0.9	9.5	1.7	0.3	T	62.6	22.3	0	0	T
2	0	0	0	9.3	0.2	0	2.8	170.9	0.9	0	0	T
3	0	0	0	11.5	0	0	0	0.4	10.5	0	0	T
4	0	0	0	0.2	0.3	0	T	2.5	0	0	T	0
5	0	0	0	T	12.7	0	0	0	0	0	0	0
6	T	0	0	10.6	8.5	0	0	12.3	0	0	0	0
7	0	0	T	0	0.4	0	0	36.6	T	0	T	0
8	T	T	0	2.3	6.2	0	0	16.1	0	T	0	0
9	0	0	1.4	T	T	0	0.6	3.3	2.1	1.1	1.5	T
10	0	0	11.7	17.5	0	0	0	1.4	0	0	21.2	0
11	0	0	0	T	3.9	0	11.4	0	0	0	7.5	0
12	0	0	4.2	0.6	0	0.1	6.6	0	0	0	T	0
13	0	0	3	3.1	0	1.4	0	0	0	T	0	0
14	0	0	T	T	0	0	0	T	0	0.5	0	0
15	0	0	0	0	0	1.2	0	4.2	0	0	T	0
16	0	T	0.3	0	0	10.3	0	4.2	0	0	0	0
17	0	0	0	0	0	0.1	0	7.8	0	0	0	0
18	T	T	1.7	0	0	T	0	T	0	0	0	0
19	0	14.9	4.5	45.7	0	0	T	0	0	0	T	0
20	0	4.2	4.1	29.2	0	0	0	0	0	0.9	T	0
21	0	1.9	T	0	0	12.2	0	0	0	0.3	0	0
22	0	3	T	T	0	2.8	0	0	T	0	0	0
23	0	3.2	0	0	0	18	0	17.9	21.4	0	T	0
24	0	13.2	0	0	0	10.9	7.7	3.6	T	0	0	0
25	0	1.3	T	0	T	12.5	0	0.2	0.6	0	0	1.5
26	0	21.8	0	0	27.2	0	0	0	0	0.3	0	4
27	T	0	0	0	4.8	0	93.2	0	0	0	0	T
28	0	T	0	0	20.9	0.6	50.4	0	0	0	0	0
29	0		32.2	0	54.2	T	2.8	45.3	0	0	0	0
30	0		52.6	0.7	31	0	0	0	0	0	0	0
31	0		30.3		0.4		T	1.5		0		0

T= trace

Quantification of Pesticide Loads

Agricultural Land Use

The general land use patterns in Batangas Bay basin are shown in *Figure 4*. *Tables 3* and *4* present the patterns of agricultural use in 1985 and 1996, respectively. *Table 4* shows data from the Department of Agriculture in Batangas which reflect the current situation and refer only to the major crops on which pesticides are actually applied. These major crops are rice, corn, mango and vegetables. Sugar, banana, peanuts and fruits use only minimal quantities of pesticide.

The agricultural use in relation to total land use in the various Xiamen Districts is shown in *Table 5*. *Table 6* shows that crops in Xiamen which utilize only minimal quantities of pesticide are rice, peanuts, vegetables and fruits.

Application of Pesticides

In the Batangas Bay basin, herbicides are applied only on rice. Fungicides and insecticides are used on mango and vegetable, while insecticides and acaricides are applied on any crop type. The rate of application reflects the standard use of the products in common agricultural practice. *Table 7* lists the crops, period of application, type of pesticide and application rate in kg active ingredient per hectare in Batangas Bay.

In the Xiamen basin, herbicides are applied only to rice, while fungicides and carbamates are applied on any crop. Organophosphates are applied mainly on rice, and organochlorines on fruits and vegetables. The application rates reflect the standard agrochemical use of the different

Figure 4. Land Use Distribution in the Batangas Bay Region: (1) Agroforestry, (2) Tourism, (3) Protection, (4) Industrial, (5) Vari-crop, (6) Conservation, (7) Rice Production.

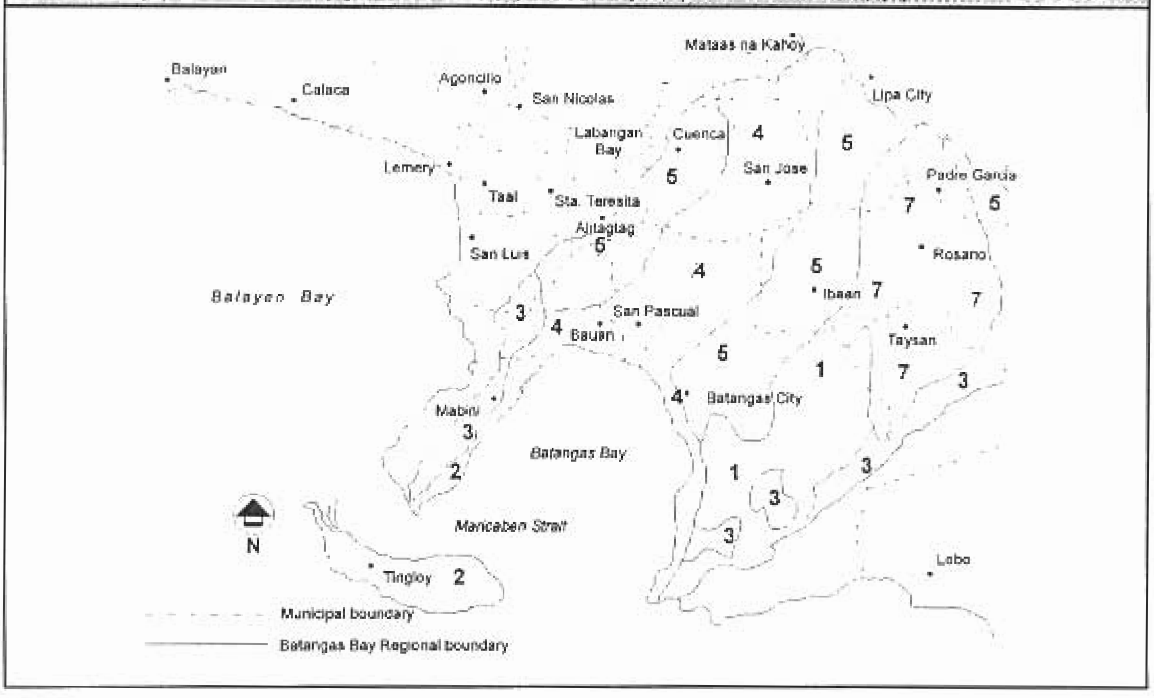


Table 3. Distribution of Area (ha) by Agricultural Land Use, Batangas Bay Region, 1985.										
Municipality/ City	Paddy Rice	Upland Rice Non-Irrigated	Corn	Banana	Sugar-cane	Coconut (Mono-crop)	Coconut (Multi-storey)	Coconut Banana	Coconut Shrubs	TOTAL AREA
A. Coastal										
Batangas City	138	2,215	138	111	6,368	28	28		1,689	10,715
Bauan	345	329	52	26	2,324		250		65	3,400
San Pascual	42	285	67	16	2,505					2,905
Mabini	32	66				194	68		1,697	2,284
Subtotal	**557**	**2,895**	**247**	**153**	**11,197**	**222**	**346**	**0**	**3,451**	**19,304**
B. Interior										
Lipa City		1,712	662	72	4,556	195	8,156			15,353
Cuenca		519	82	7	1,053		832		148	2,641
Ibaan		1,026	134	131	5,965	9				7,265
Padre Garcia	1,150	1,411	660	34	4,264	305	608	146		8,578
Rosario	6,806	1,302	265	93	2,898	114	269	2,349	677	14,773
San Jose		257	62	27	1,591	16	2,373			4,326
Taysan	1,587	2,804		51	989	69			1,177	6,677
Lobo	307	109				2,062			3,332	5,810
Alitaglag		567	92	331	1,118					2,108
Subtotal	**9,850**	**9,707**	**1,957**	**746**	**22,434**	**2,770**	**12,238**	**2,495**	**5,334**	**67,531**
C. Island Municipality										
Tingloy	-	234	-	72	-	-	-	-	1,075	1,381
TOTAL AREA	10,407	12,836	2,204	971	33,631	2,992	12,584	2,495	9,860	88,216

Table 4. Distribution of Area (ha) by Agricultural Land Use, Batangas Bay Region, 1996.						
Municipality/City	Crops					
	Rice			Corn	Mango	Vegetable
	Irrigated	Rainfed	Upland			
A. Coastal						
Batangas City	122	14	1,500	1,150	3,208	2,039
Bauan	96	-	576	50	250	405
San Pascual	33	-	320	50	400	160
Mabini	-	-	34	42	160	24
Subtotal	251	14	2,430	1,292	4,018	2,628
B. Interior						
Cuenca	-	-	220	90	22	18
Ibaan	450	75	187	72	210	45
Padre Garcia	219	223	365	312	65	70
Rosario	1,176	4,515	4,149	82	740	45
San Jose	-	-	1,073	390	166	250
Taysan	125	1,246	954	-	500	45
Lobo	198	-	5	50	137	29
Alitaglag	-	-	148	65	77	18
Subtotal	2,168	6,059	7,101	1,061	1,917	520
C. Island Municipality						
Tingloy	-	-	-	-	50	510
Total	2,418	6,073	9,531	2,353	5,985	3,658

Table 5. Total Land and Cultivated Area (km²) in Xiamen, 1996.

Area	Total Land Area	Cultivated Area
Western Bay Catchment Area		
Western Area of Xiamen Island	47.25	0.00
Xinglin and Haicang Area	184.90	82.23
TOTAL	232.15	82.23
Tong'an Bay Catchment Area		
Northern Area of Xiamen Island	23.01	6.66
Jimei Area	188.79	55.02
Tonggan County	961.42	211.84
TOTAL	1,173.22	273.52
Two Basins Total	1,405.37	355.75
Whole Xiamen	1,516.12	427.23

Table 6. Percentage Distribution of Main Cultivated Crops in Xiamen.

Crops	Western Bay Catchment Area	Tong'an Bay Catchment Area
Rice	29.8	27.9
Peanuts	13.6	11.5
Vegetables	23.2	20.4
Fruits	30.0	34.2

products. *Table 8* shows the pesticides used in Xiamen. Dichlorvos has a very high consumption rate being applied up to 8 times per year at a rate of 2.4 kg/ha. All these data were obtained from the supply company for agricultural manufacture material in Xiamen City.

Pesticides Available from Distributors and Dealers

Table 9 lists the pesticides available commercially in Batangas. Some of the products are sold in limited quantities, while others are in tonnes per year. Generic evaluation was performed on every chemical while more detailed assessments were made only of the few chemicals with the highest consumption rates, namely butachlor, chlorpyrifos, carbaryl and cypermethrin.

Table 7. Application of Pesticides, Batangas Bay Region.

Crop	Application	Pesticide	Kg a.i. per ha
Rice	June - July (1st cropping) Dec - Jan (2nd cropping)	butachlor	0.600
		cyhalofop-butyl	0.084
		2,4-D isobutyl ester	0.312
		fenclorim	0.126
		niclosamide	0.300
	August	chlorpyrifos	0.126
		chlorpirifos	0.088
		+ fenobucarb	0.044
		chlorpyrifos	0.090
		+ cypermethrin	0.009
		cypermethrin	0.012
		lambdacyhalothrin	0.003
		fipronil	0.018
Mango	Nov - Jan Feb - March (1st cropping)	mancozeb	0.720
		chlorpyrifos	0.075
		+ cypermethrin	0.0075
		diazinon	0.288
		carbaryl	0.408
		deltamethrin	0.006
		lambdacyhalothrin	0.003
		imidacloprid	0.030
Corn	Nov - Jan (2nd cropping)	carbofuran	0.023
		deltamethrin	0.006
		lambdacyhalothrin	0.003
Vegetable	Aug - May (1st cropping)	benomyl	0.120
		mancozeb	0.720
		triazophos	0.144
		chlorpyrifos	0.126
		profenofos	0.300
		methamidophos	0.360
		deltamethrin	0.006
		fipronil	0.018

a.i. - active ingredient

The insecticides represent different chemical groups (organophosphates, carbamates, pyrethroids) and the type of target organism to be controlled (insects, mites).

Table 8. Pesticide Consumption in Xiamen.

Pesticides	Quantity (t/year)	% a.i.	Quantity a.i. (t/year)	Application (kg/ha)	Application a.i. (kg/ha)
Fungicides	50				
carbendazim	15	50	7.5	1.5	0.75
copper sulfate	10	96	9.6	0.75-1.125	0.72-1.08
thiophanate-methyl	15	70	10.5	1.5	1.05
others	10				
Herbicides	100				
butachlor	20	60	12.0	1.5-1.85	0.9-1.11
glyphosate	50	10	5	15.0	1.5
glyphosate	10	41	4.1	2.25-6.0	0.9-2.4
others	20				
Insecticides	1,000				
Organochlorines					
dicofol	20	20	4	1.5	0.3
Organophosphates					
dichlorvos	225	80	180	3.0	2.4(8)
dimethoate	85	40	34.0	1.5-3.0	0.6-1.2
methamidophos	105	50	52.5	1.5	0.75
omethoate	40	40	16	1.5-3.0	0.6-1.2
parathion-methyl	40	1.5	0.6	22.5-37.5	0.34-0.56
trichlorfon	10	90	9	3.0	2.7
Carbamates					
carbofuran	215	3	6.5	30-45	0.9-1.35
isoprocarb	20	6	1.2	7.5-15.0	0.45-0.90
others	240				

a.i. = active ingredient

Fungicide = pesticide used to kill or control fungi which cause plant disease (ADB, 1987).

Herbicide = a substance or mixture of substances intended to control unwanted plants, including algae or aquatic weeds (ADB, 1987).

Insecticide = any substance or mixture of substances intended for preventing, killing, repelling or controlling an insect pest (ADB, 1987).

Table 9. List of Pesticides Available from Batangas Distributors and Dealers.

Pesticides	Quantity Sold	Kg a.i. per year
Fungicides		
benomyl	1,260 kg	630
mancozeb	2,400 kg	1,920
Herbicides		
butachlor	4,260 l	2,256
cyhalofop-butyl	602 l	60.2
2,4-D isobutyl ester	1,260 l	504
fenclorim	600 l	180
glyphosate	20 l	-
Insecticides		
Organophosphates		
chlorpyrifos	710 l	186
chlorpyrifos	7,500 l	1,862.5
+ cypermethrin		186.25
chlorpyrifos	2,400 l	504
+ fenobucarb		252
diazinon	6,020 l	2,408
malathion	230 l	-
methamidophos	1,200 l	720
phenthoate	50 l	-
+ fenobucarb		-
profenofos	3,000 l	1,500
triazophos	1,200 l	480
Carbamates		
carbaryl	6,030 kg	5,125.5
carbofuran	16,700 kg	501
fenobucarb	50 l	-
methomyl	40 l	-
Pyrethroids		
cyfluthrin	109 l	-
cypermethrin	2,500 l	123
deltamethrin	4,330 l	108.25
esfenvalerate	40 l	-
fenvalerate	20 l	-
lambdacyhalothrin	2,440 l	61
Others		
fipronil	240 l	12
imidacloprid	3,016 l	301.6
Molluscicide		
niclosamide	3,660 l	915

a.i.= active ingredient

Pesticide Properties and Toxicological Characteristics

Toxicological and Ecotoxicological Characteristics

Lists of chemicals used in the two areas were compiled. Ecotoxicological profiles of these substances and synopses of their physico-chemical properties including persistence levels were gathered from Howard (1991a, 1991b) and Tomlin (1994). *Tables 10* and *11* reveal the ecotoxicological characteristics of pesticides in Batangas Bay and the Xiamen Seas, respectively. Chemicals were characterized as being in lethal concentration (LC) for 50% of the fish, and effective (immobilization) concentration (EC) for 50% of the freshwater brachiopod *Daphnia*. Data on mammalian toxicology such as admissible daily intake (ADI) in mg/kg body weight, lethal dose (LD) for 50% of rats in mg/kg for acute oral toxicity and no observable effect level (NOEL) in mg/kg active ingredient in the diet on long-term tests, have been referred to in order to furnish a wider set of information to the reader and, if necessary, to be utilized for further evaluation.

Physico-chemical Properties

Tables 12 and *13* present the basic physico-chemical properties of the different pesticides found in the Batangas Bay Region and the Xiamen Seas. These give a basic understanding of their distribution in the various environmental compartments such as air, soil, water and biota. These properties include the molecular weight, the water solubility, the vapor pressure and the log K_{ow} (the logarithm of the octanol/water partition coefficient).

Tables 14 and *15* indicate other properties of environmental interest, namely log K_{oc}, persistence and groundwater ubiquity score (GUS) index (Gustafson, 1989) of pesticides in the Batangas Bay Region and Xiamen Seas where log K_{oc}, which is derived from Kd (soil absorption—the larger the Kd, the greater the binding capacity), is the ratio of sorbed to solution pesticides in water-soil slurry. It is a measure of the relative affinities of the pesticide for water and soil surface. Log K_{oc} is adjusting Kd for proportion of organic carbon in the soil (Karickhoff et al., 1979).

Persistence is defined as the degradation half-life in various media and GUS is a leachability index (e.g., potential for leaching and/or runoff, see following paragraphs). With the available data, a stepwise process for risk assessment could commence with a scoring system being the simplest approach.

Ranking for Pesticide Scoring Risk According to Intrinsic Properties: Toxicity, Persistence, Bioaccumulation and Leachability

A scoring system is basically used to give indices of risk among a group of substances ranging from very low to very high. In such a system a subject is asked to assess a degree of any unwanted environmental property. Each property is scored from 1 (good) to 3 (bad). The individual scores are then combined by multiplication to give indices of risk which take into account every unwanted property. Intrinsic unwanted properties of pesticides include toxicity that could provoke fish kills or damage to aquatic life, persistence that increases the risk of effects and the potential for mobility over time, bioaccumulation that could cause increasing concentrations in fish and leachability which is an index of the ability of the molecule to reach the aquatic environment.

Each of these properties can be characterized by a single parameter and quantified into acute toxicity to fish, half-life for persistence, K_{ow} for potential of bioaccumulation (metabolism should also be taken into account),

Table 10. Ecotoxicological Characteristics of Pesticides in Batangas Bay.

Pesticides	LC_{50} (mg/L) Fish	EC_{50} (mg/l) *Daphnia*	ADI (mg/kg bw)	LD_{50} (mg/kg)	NOEL (mg/kg) (a.i./diet)
Fungicides					
benomyl	0.17	0.640	0.02	>10,000	500
mancozeb	2.2	-	0.03	> 5,000	-
Herbicides					
butachlor	0.14	2.4	-	2,000	-
cyhalofop-butyl	1.54	> 100	-	> 5,000	-
2,4 - D isobutyl ester	1.1	235	0.3	639	1.0
fenclorim	0.6	2.2	-	> 5,000	10.4
glyphosate	86	780	0.3	5,600	300
paraquat	2.5	-	0.004	157	34
Insecticides					
Organophosphates					
azinphos-ethyl	0.03	0.0002	0.00025	12.0	0.1
chlorpyrifos	0.003	0.0017	0.01	135	0.01
diazinon	2.6	1.4	0.002	300	0.02
malathion	0.1	-	0.02	775	100
methamidophos	25.0	0.27	0.004	20	2.0
parathion-methyl	2.7	0.0073	0.02	6	0.3
phenthoate	0.12	-	0.003	300	10
profenofos	0.08	Highly toxic	0.01	358	0.08
triazophos	0.01	0.003	0.0002	57	0.3
Carbamates					
carbaryl	1.3	0.006	0.01	500	200
carbofuran	0.0073	0.015	0.01	8.0	20
fenobucarb/BPMC	16	0.32	-	425	4.1
methomyl	0.9	0.0287	0.03	17	100
Pyrethroids					
cyfluthrin	0.0006	0.0006	0.02	20	50
cypermethrin	0.00069	0.00015	0.05	250	5.0
deltamethrin	0.00091	0.0035	0.01	135	1.0
esfenvalerate	0.00069	0.00024	-	75	-
fenvalerate	0.0036	-	0.02	451	250
lambdacyhalothrin	0.00021	0.00036	-	19	0.5
Others					
fipronil	0.34	0.19	-	100	-
imidacloprid	211	85	0.057	150	100
Molluscicide					
niclosamide	0.1	0.2	3.0	5,000	200

a.i.= active ingredient

and GUS for potential leachability. While the relevance of the first two properties (toxicity and persistence) is quite easy to understand, the others need some explanation. There is a good correlation between the bioconcentration factor (BCF) in fish and K_{ow} (Chiou, 1985). In a general form, the equation is:

$$BCF = (a \log K_{ow} + b)\ (Im)$$

where (Im) is the index for metabolic transformation, with a value between 0 and 1.

When a chemical is not metabolized, the Im is 1; however, if it is easily transformed and excreted, Im is 0. Values of log K_{ow} higher than 3 are considered to be a risk in relation to bioaccumulation.

The GUS index was elaborated by Gustafson (1989) to assess the capability of pesticides to contaminate underground sources

Table 11. Ecotoxicological Characteristics of Pesticides in the Xiamen Seas.

Pesticides	LC_{50} (mg/l) Fish	EC_{50} (mg/l) *Daphnia*	ADI (mg/kg bw)	LD_{50} (mg/kg)	NOEL (mg/kg) (a.i./diet)
Fungicides					
carbendazim	0.61	0.13-0.22	0.01	>15,000	300
chlorothalonil	0.044	0.070	0.03	>10,000	1.8
copper sulfate					
mancozeb	2.2	-	0.03	>5,000	-
metalaxyl	>100	>100	0.03	633	2.5
thiophanate-methyl	7.8	20.2	0.08	7,000	160
thiram	0.13	0.21	0.01	1,800	2.5
zineb	2	-	0.03	>5,200	>5,200
Herbicides					
butachlor	0.14	2.4	-	2,000	-
dimethachlor	3.9	14.2	-	1,600	700
glyphosate	86	780	0.3	5,600	300
metsulfuron	>150	>150	0.25	>5,000	50
propyzamide	>4.7	>5.6	0.08	6,985	200
Insecticides					
Organochlorine					
dicofol	0.183	0.14	0.002	595	5
Organophosphates					
dichlorvos	0.450	0.00019	0.004	50	10
dimethoate	6	4.7	0.01	300	1
methamidophos	25.0	0.27	0.004	20	2.0
omethoate	9.1	0.022	0.0003	25	4
parathion-methyl	2.7	0.0073	0.02	6	2
triazofos	0.01	0.003	0.0002	57	0.3
trichlorfon	0.52	0.00096	0.01	250	100
Carbamates					
carbofuran	1.7	0.015	0.01	80	20.0
isoprocarb	10-20	0.03	-	450	300
Pyrethroids					
bifenthrin	0.00015	0.00016	0.02	55	1.5
esfenvalerate	0.00069	0.00024	-	75-458	-
fenpropathrin	0.00195	-	0.03	70	-

a.i.= active ingredient

of drinking water and is based on the following empirical equation:

$$GUS = \log (t/2 \text{ soil}) (4 - \log K_{oc})$$

where t/2 is the half-life in soil expressed in days; and K_{oc} is the soil sorption coefficient.

Chemicals are classified as improbable leachers when the GUS value is lower than 1.8, probable leachers when the value is higher than 2.8 and transition leachers when the value lies in between. The GUS index for molecules such as glyphosate or 2,4 D, however, could be misleading, due to their dissociation constants, and therefore different mechanism for soil/ molecule relationships.

A score table *(Table 16)* was prepared for the ranking of intrinsic properties of interest to water contamination (toxicity, persistence, bioaccumulation, leachability).

The results of this exercise in the Batangas Bay Region and the Xiamen Seas are shown in *Tables 17* and *18*, respectively.

If the metabolism of pyrethroids is rapid,

Table 12. Physico-chemical Properties of Pesticides, Batangas Bay Region.

Pesticides	Molecular Weight (g/mol)	Solubility (mg/l = g/m³)	Vapor Pressure (Pa)	log K_{ow}
Fungicides				
benomyl	290.3	4	0.0000049	(2.0)
mancozeb	>330.68	6.0	NEGLIGIBLE	*
Herbicides				
butachlor	311.9	20	0.0006	(2.5)
cyhalofop-butyl	357.4	0.7	0.0012	3.31
2,4-D isobutyl ester	221.0	311	0.011	2.58
fenclorim	225.1	2.5	0.012	4.17
glyphosate	169.1	12,000	NEGLIGIBLE	*
paraquat	186.3	700,000	0.0001	*
Insecticides				
Organophosphates				
azinphos-ethyl	345.4	4	0.00032	3.18
chlorpyrifos	350.6	1.4	0.0027	4.7
diazinon	304.3	60	0.012	3.3
malathion	330.3	145	0.0053	2.75
methamidophos	141.1	0.005	0.0023	-0.8
parathion-methyl	263.2	55	0.0002	3.0
phenthoate	320.4	11	0.0053	3.69
profenofos	373.6	28.0	0.000124	4.44
triazophos	313.3	30	0.00039	3.34
Carbamates				
carbaryl	201.2	120	0.000041	1.59
carbofuran	221.3	320	0.000072	1.52
fenobucarb/BPMC	207.3	420	0.0016	2.79
methomyl	162.2	57,900	0.00665	1.24
Pyrethroids				
cyfluthrin	434.3	0.0025	0.00000001	5.94
cypermethrin	416.3	0.004	0.00000023	6.6
deltamethrin	505.2	0.0001	0.0000001	4.6
esfenvalerate	419.9	0.002	0.0000002	6.22
fenvalerate	419.9	0.005	0.0000192	5.01
lambdacyhalothrin	449.9	0.005	0.0000002	7.00
Others				
fipronil	437.2	2.0	0.00000037	4.0
imidacloprid	255.7	510	0.0000002	0.57
Molluscicide				
niclosamide	327.1	1.6	<0.001	1.0

Pa= Pascal

bioaccumulation does not occur. Therefore it was decided to score them (1). This could also be true for several organophosphate substances. Carbendazim, thiophanate-methyl, butachlor, dicofol and carbofuran have the highest score in Xiamen and will be considered for further evaluation.

In general, fungicides utilized in Batangas are of little relevance for unwanted effects in aquatic environments. Among the herbicides, butachlor and fenclorim warrant attention and may require a more refined risk assessment, while glyphosate and paraquat, unless used directly in water, should not cause major problems, due to their affinity for soil. They do not enter in the score system because of their dissociation constants and, for glyphosate, low persistence. For insecticides, organophosphate and carbamate scores range from 2 for malathion and fenobucarb to 27 for chlorpyrifos and carbofuran. In general, one should try to prepare a more refined risk assessment for substances with a score value of 12 or higher. In any case,

Table 13. Physico-chemical Properties of Pesticides, Xiamen Seas.

Pesticides	Molecular Weight (g/mol)	Solubility (mg/l=g/m^3)	Vapor Pressure (Pa)	Log K_{ow}	Melting Point
Fungicides					
carbendazim	191.2	8	0.00009	1.5	304
chlorothalonil	265.9	0.9	0.000076	2.89	250
copper sulfate					
mancozeb	>330.68	6.0	NEGLIGIBLE	-	-
metalaxyl	279.3	8,400	0.00075	1.75	72
thiophanate-methyl	342.4	100	0.0000095	1.50	172
thiram	240.4	18.0	0.023	1.73	155
zineb	275.8	10.0	<0.01	1	-
Herbicides					
butachlor	311.9	20	0.0006	2.5	-5
dimethachlor	255.7	2,100	0.0021	2.2	47
glyphosate	169.1	12,000	NEGLIGIBLE	-	-
metsulfuron	381.4	279,000	0.00000000033	-1.74	158
propyzamide	256.1	15	0.000058	3.1	155
Insecticides					
Organochlorines					
dicofol	370.5	0.8	0.00053	4.28	78
Organophosphates					
dichlorvos	221.0	8,000	2.1	1.9	20
dimethoate	229.2	23,800	0.0011	0.7	49
methamidophos	141.1	2,003,000	0.0047	-0.8	46
omethoate	213.2	10,000	0.0033	-0.75	-
parathion-methyl	263.2	55	0.0002	3.0	35
triazofos	313.3	30	0.00039	3.34	3
trichlorfon	257.4	120,000	0.00021	0.43	78.5
Carbamates					
carbofuran	221.3	320	0.000072	1.52	153
isoprocarb	193.2	265	0.0028	0.36	94
Pyrethroids					
bifenthrin	422.9	0.1	0.000024	>6	58
esfenvalerate	419.9	0.002	0.0000002	6.22	60
fenpropathrin	349.3	0.0141	0.00073	6	47

it is relevant to investigate the quantitative use of an individual pesticide in the area.

A particular case is of pyrethroids which at a first glance show a high score, e.g., 27. However, it has been implied that they are easily metabolized and excreted by a variety of aquatic animals, from mussels to fish, therefore the bioaccumulation parameter (very high due to high log K_{ow}) should be modified in relation to their easy degradation by animal metabolism (Leahey, 1985).

A similar procedure could have been used to score risk to human health. The most undesirable consequences of the use of pesticides are mammalian toxicity, contamination of treated crops and drinking water, presence in air and/or volatilization towards other compartments, and bioaccumulation in non-target edible

Table 14. Affinity for Soil, Persistence, Leachability and Groundwater Ubiquity Score (GUS), Batangas Bay Region.

Pesticides	log K_{oc}	Persistence Soil t/2 (days)	Persistence Water Hydrolysis (days)	GUS Value	Persistence Soil Class	GUS Leachability Index
Fungicides						
benomyl	1.79	2	decomposed	0.66	days	improbable
mancozeb	-	6-15	17	-	days	-
Herbicides						
butachlor	2.29	42-70	-	2.99	months	probable
cyhalofop-butyl	3.1	< 10	slowly	0.9	days	improbable
2,4-D isobutyl ester	2.37	< 7	-	1.38	days	improbable
fenclorim	3.96	17-35	-	0.06	weeks	improbable
glyphosate	-	3-60	-	-	weeks	-
paraquat	-	-	-	-	-	-
Insecticides						
Organophosphates						
azinphos-ethyl	2.97	28	270	1.49	weeks	improbable
chlorpyrifos	4.49	60-120	1-100	-0.96	months	improbable
diazinon	3.09	11-21	185	1.10	weeks	improbable
malathion	2.54	7	-	1.23	days	improbable
methamidophos	1.01	7	5	4.23	days	probable
parathion-methyl	2.79	rapid (5)	40	0.85	days	improbable
phenthoate	3.48	10	-	0.52	weeks	improbable
profenofos	4.23	7	14	-0.19	days	improbable
triazophos	3.13	(7)	-	0.73	weeks	improbable
Carbamates						
carbaryl	1.38	7-28	12	3.26	weeks	probable
carbofuran	1.31	30-60	121	4.48	months	probable
fenobucarb	2.58	6-30	20	1.78	weeks	improbable
methomyl	1.03	rapid (5)	decomposed	2.07	days	transition
Pyrethroids						
cyfluthrin	5.73	rapid (5)	20	-1.21	days	improbable
cypermethrin	6.39	90	5	-4.67	months	improbable
deltamethrin	4.39	< 21	-	-0.52	weeks	improbable
esfenvalerate	6.01	90	-	-3.93	months	improbable
fenvalerate	4.8	90	-	-1.56	months	improbable
lambdacyhalothrin	6.79	90	-	-5.45	months	improbable
Others						
fipronil	3.79	-	-	-	-	-
imidacloprid	0.36	-	-	-	-	-
Molluscicide						
niclosamide	0.79	-	7	-	weeks	-

organisms. At first glance, none of these chemicals demonstrate a very high score. However, it has to be realized that this score system is only the first step of a risk assessment. A more appropriate evaluation of environmental distribution and fate and ultimately of potential exposure should be done using evaluative models. These have been developed in the succeeding chapters.

Environmental Distribution and Persistence According to Fugacity Models

A natural chemical (xenobiotic) has a cycle within environmental compartments, i.e., air, water, soil/sediment and biota (*Figure 5*). This occurs after its use or escape from an agricultural

Table 15. Affinity for Soil, Persistence, Leachability and Groundwater Ubiquity Score (GUS), Xiamen Seas.

Pesticides	Log K_{oc}	Persistence Soil t/2 (days)	Persistence Water Hydrolysis (days)	GUS Value	Persistence Soil Class	GUS Leachability Index
Fungicides						
carbendazim	1.29	8-32	-	3.5	weeks	probable
chlorothalonil	2.68	5-36	-	1.74	weeks	improbable
copper sulfate						
mancozeb	-	6-15	1	-	days	-
metalaxyl	1.54	70-90	-	4.7	months	probable
thiophanate-methyl	1.29	21-28	-	3.8	weeks	probable
thiram	1.51	2	18	0.7	days	improbable
zineb	-	(6)	-	-	days	-
Herbicides						
butachlor	2.29	42-70	-	2.99	months	probable
dimethachlor	1.99	14-60	-	3.1	weeks	probable
glyphosate	-	3-60	-	-	weeks	-
metsulfuron	-1.95	7-35	-	7.8	weeks	improbable
propyzamide	2.89	30	-	1.6	weeks	improbable
Insecticides						
Organochlorines						
dicofol	4.06	60-80	64-99	-0.114	months	improbable
Organophophates						
dichlorvos	1.69	7	3	1.95	days	transition
dimethoate	1.99	14-60	-	3.1	weeks	probable
methamidophos	-1.01	7	5	4.23	days	probable
omethoate	-0.96	7	17	4.19	days	probable
parathion-methyl	2.79	7	40	1.02	days	improbable
triazophos	3.13	(7)	-	0.73	days	improbable
trichlorfon	0.22	7	2	3.19	days	probable
Carbamates						
carbofuran	1.31	30-60	121	4.44	months	probable
isoprocarb	0.15	3-20	-	4.15	days	probable
Pyrethroids						
bifenthrin	5.79	65-90	-	-3.39	months	improbable
esfenvalerate	6.01	70-120	-	-3.93	months	improbable
fenpropathrin	5.79	7	-	-1.5	days	improbable

Table 16. Preliminary Risk Assessment for Pesticides.

Ranking of Intrinsic Properties					
Toxicity to Fish			**Persistence**		
LC_{50} > 10 mg/l		1	Limited (days)		1
LC_{50} 0.1-10 mg/l		2	Medium (weeks)		2
LC_{50} < 0.1 mg/l		3	High (months)		3
Bioaccumulation (log K_{ow})			**Leachability (GUS index)**		
Limited potential	(<3.0)	=1	Improbable leacher	(<1.8)	=1
Medium potential	(3.0-3.5)	=2	Transition leacher	(1.8-2.8)	=2
High potential	(>3.5)	=3	Probable leacher	(>2.8)	=3

Figure 5. Pathway for Environmental Distribution of Chemical Substances.

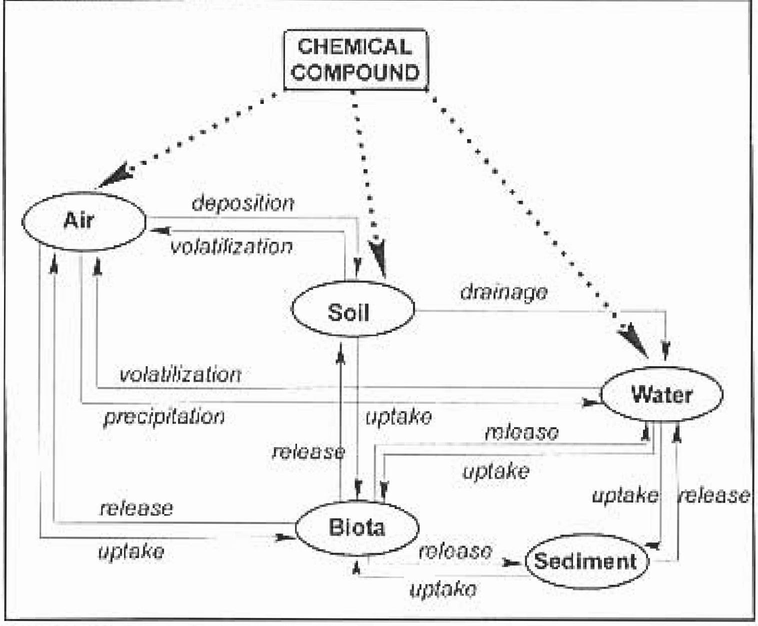
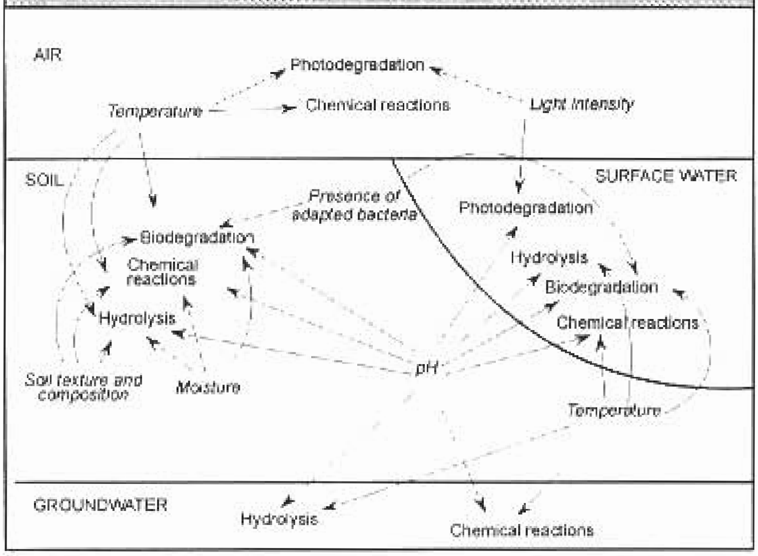


Figure 6. Degradation Possibilities in Various Compartments.



or an industrial process and is subjected to environmental partitioning. Substances will move from their point of entry to their final destination, i.e., the environmental compartment for which they have more affinity. Furthermore, chemicals may be transferred again to other compartments. Substances can undergo chemical transformations in every environmental compartment. The relevant degradation processes are shown in *Figure 6*. For example, if a substance with very high water solubility is discharged into the soil, it will remain there until it comes into contact with water. Thus, it will become a water contaminant. On the other hand, if a chemical with a high affinity for soil is discharged into water, it will soon reach and become bound to soil sediments.

Many volatile chemicals have the ability to move by advection with air and may reach remote areas far from their place of origin. In addition, many chemicals with a high affinity for living organisms can accumulate in plants and animals, either directly or via food chains, eventually giving rise to contaminated food. Information on physico-chemical properties of molecules is needed to predict environmental partitioning; in this connection, the most relevant parameters are water solubility, vapor pressure, octanol/water partition coefficient, etc.

All these parameters including basic physico-chemical characteristics can be found in scientific literature or obtained by means of laboratory measurements. They can also be calculated by means of property-to-property correlation or alternatively with the fragment constant methods and by means of topological indices (Lyman et al., 1992).

Dissociated chemicals do not enter into the previously described system, however, as a general rule, anions have a strong affinity for water and cations for soil. More complete

Table 17. Ranking Pesticides for Risk Assessment According to Intrinsic Properties, Batangas Bay Region.					
Pesticides	**Toxicity to Fish (LC_{50})**	**Bioaccumulation (log K_{ow})**	**Persistence**	**Leachability**	**Score**
Fungicides					
benomyl	2	1	1	1	2
mancozeb	2	-	1	-	2
Herbicides					
butachlor	2	1	3	3	18
cyhalofop-butyl	2	2	1	1	4
2,4-D isobutyl ester	2	1	1	1	2
fenclorim	2	3	2	1	12
glyphosate	1	-	2	-	2
paraquat	2	-	-	-	2
Insecticides					
Organophosphates					
azinphos-ethyl	3	2	2	1	12
chlorpyrifos	3	3	3	1	27
diazinon	2	2	2	1	8
malathion	2	1	1	1	2
methamidophos	1	1	1	3	3
parathion-methyl	2	2	1	1	4
penthoate	2	3	2	1	12
profenofos	3	3	1	1	9
triazophos	3	2	2	1	12
Carbamates					
carbaryl	2	1	2	3	12
carbofuran	3	1	3	3	27
fenobucarb	1	1	2	1	2
methomyl	2	1	1	2	4
Pyrethroids					
cyfluthrin	3	3 (1)	1	1	9 (3)
cypermethrin	3	3 (1)	3	1	27 (9)
deltamethrin	3	3 (1)	2	1	18 (6)
esfenvalerate	3	3 (1)	3	1	27 (9)
fenvalerate	3	3 (1)	3	1	27 (9)
lambdacyhalothrin	3	3 (1)	3	1	27 (9)
Others					
fipronil	2	3	-	-	6
imidacloprid	1	1	-	-	1
Molluscicide					
niclosamide	2	1	2	-	4

discussions on this subject can be found in Mackay (1991), Van Leeuwen and Hermens (1995) and Calamari (1996). However, looking at the single property of a given chemical is not sufficient to give a complete picture of its chemical distribution in the environment except for molecules that are with extreme values, e.g., very high solubility and high volatility. Moreover, integrating the various properties provides a means by which more information may be obtained which can be used to simulate more accurately what could happen in the real world.

In order to develop these concepts, models of compartmental analysis were proposed. The input to these models are physico-chemical parameters and partition coefficients, while the output is the expected percentage distribution in

Table 18. Ranking Pesticides for Risk Assessment According to Intrinsic Properties, Xiamen Seas.

Pesticides	Toxicity in Fish (LC_{50})	Bioaccumulation (log K_{ow})	Persistence	Leachability	Score
Fungicides					
carbendazim	2	1	2	3	12
chlorothalonil	3	1	2	1	6
mancozeb					
metalaxyl	1	1	3	3	9
thiophanate-methyl	2	1	2	3	12
thiram	2	1	1	1	2
zineb	2	1	1	-	2
Herbicides					
butachlor	2	1	3	3	18
dimethachlor	2	1	2	3	12
glyphosate	1	-	2	-	-
metsulfuron	1	1	2	3	6
propyzamide	2	2	2	1	8
Insecticides					
Organochlorines					
dicofol	2	3	3	1	18
Organophosphates					
dichlorvos	3	1	1	2	6
dimethoate	2	1	1	3	6
methamidophos	1	1	1	3	3
omethoate	2	1	1	3	6
parathion-methyl	2	2	1	1	4
triazophos	3	2	1	1	6
trichlorfon	2	1	1	3	6
Carbamates					
carbofuran	2	1	3	3	18
isoprocarb	1	1	1	3	3
Pyrethroids					
bifenthrin	3	3(1)	3	1	27(9)
esfenvalerate	3	3(1)	3	1	27(9)
fenpropathrin	3	3(1)	1	1	9(3)

the main environmental compartments. One of these models is briefly described below. It has a very solid scientific basis being calculated using the gas law equation of Mackay and Paterson (1981). Fugacity *(f)* is an old physico-chemical concept rediscussed in new terms and defined as the tendency, for a chemical substance, to escape from one phase to another. This property can be calculated in units of pressure (Pa).

Subsequently, it was proposed that an evaluative model of 1 km^2 as *unit of world* be divided into six compartments with defined quantities of material. It also introduced the concept of environmental capacity for each compartment ($Z = mol\ m^{-3}\ Pa^{1}$) from which the theoretical concentrations ($C = mol\ m^{-3}\ Pa^{1}$) could be calculated after an emission of a given amount of chemical compound.

$$C = fZ$$

The equilibrium being attained when the fugacities are equal in all compartments

$$f_1 = fZ_2$$

therefore: $C_1/Z_1 = C_2/Z_2$

and $C_1/C_2 = Z_2/Z_1 = K_{12}$

K is the partition coefficient determining the distribution of the substance between two phases.

The capacities of each compartment (Z) can be determined, as a function of partition coefficient. If equilibrium, well mixing, no reaction and no advection are assumed, the relative mass distribution and relative concentrations can be calculated. An improvement of the simple system described above, but basically on the same principle, has recently been proposed and in part utilized.

As stated by Mackay et al. (1996a, 1996b, 1996c), the focus of fate assessment is based on the understanding of the following key areas: how diverse are the properties of chemical control, its distribution among compartments, how it is transported, and transformed and its general persistence. Only the parent compound is treated. No other metabolites or degradation product will require separate evaluation.

The scenario adopted is at a generic environment of 25°C which is the common temperature for data acquisition. Because environmental conditions are evaluative, validation is not normally possible. Mackay et al. (1996a, 1996b, 1996c) suggested an evaluative area of 10^5 km^2 with about 10% being covered with water. The reasons for conducting an evaluative fate assessment are that it helps reveal general features of chemical behavior and focuses efforts on obtaining information on the most important characteristics of the chemical if it is of no concern, or is of definite concern. Key information obtained in this stage includes the tendency for intermediate transport (e.g., evaporation) and for bioconcentration, and the persistence of the substance, which is a function of reaction and advection rate. It should be noted that similar systems are nowadays utilized both in Europe and the USA.

A detailed description of the equilibrium criterion (EQC) model is given by Mackay et al. (1996a, 1996b, 1996c) where the data

Figure 7. Equilibrium Criterion (EQC) Model Level I.

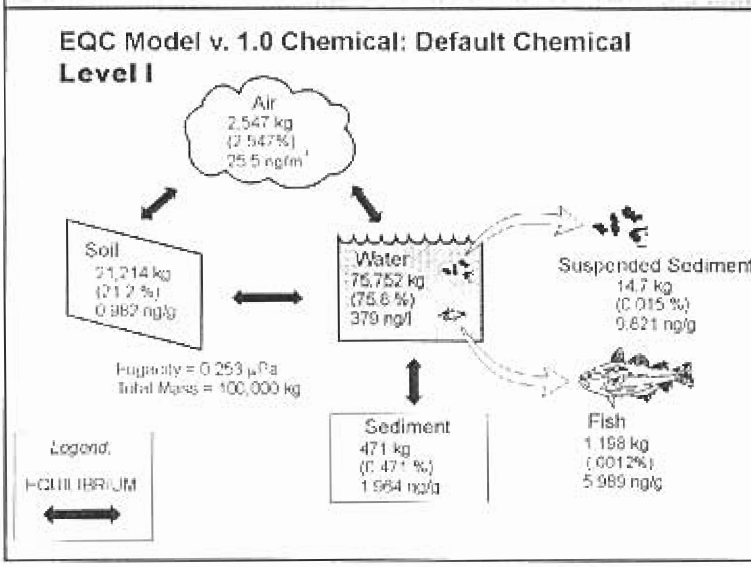
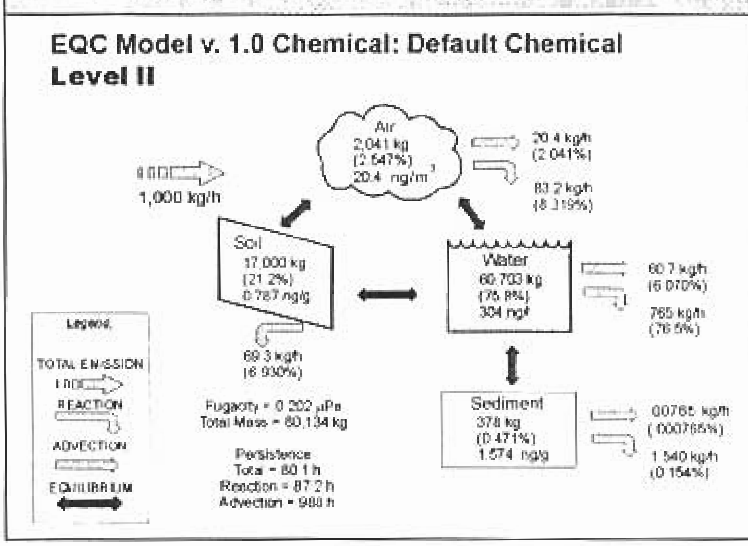


Figure 8. Equilibrium Criterion (EQC) Model Level II.



requirements, the units of world and the equation used to calculate partitioning, transport and transformation are referred to. Basically, Level I has a situation in which a fixed quantity of chemicals is introduced in a closed system under steady-state and equilibrium conditions. The model calculates their partitioning among compartments. Level II is similar to Level I calculation but the chemical is continuously discharged at a constant rate and achieves a steady-state and equilibrium condition where input and output rates are equal. Degradation rates in the compartments are calculated from half-life and advection by calculating the output rates through a fixed advection flow of air and water in the unit of world.

Table 19. Environmental Partitioning (in percentage) According to Equilibrium Criterion (EQC) Scenario Level I, Batangas Bay Region.

Pesticides	Air	Water	Soil	Sediments	Fish
Fungicides					
benomyl	0.00658	91.7	8.120	0.180	0.000458
mancozeb					
Herbicides					
butachlor	0.146	77.6	21.7	0.483	0.00123
cyhalofop-butyl	4.156	33.6	60.8	1.351	0.00343
2,4-D isobutyl ester	0.117	74.3	25.0	0.556	0.00141
fenclorim	1.491	6.841	89.6	1.991	0.00506
glyphosate					
paraquat					
Insecticides					
Organophosphates					
azinphos-ethyl	0.235	42.1	56.4	1.253	0.00318
chlorpyrifos	0.293	2.149	95.4	2.119	0.00538
diazinon	0.435	35.5	62.7	1.393	0.00354
malathion	0.161	66.1	32.9	0.732	0.00186
methamidophos	0.0000327	100.0	0.014	0.000312	0.000000792
parathion-methyl	0.01	52.5	46.5	1.032	0.00262
phenthoate	0.569	18.3	79.3	1.763	0.00448
profenofos	0.00129	3.853	94.0	2.089	0.00531
triazophos	0.028	33.5	65.0	1.443	0.00367
Carbamates					
carbaryl	0.00134	96.6	3.328	0.074	0.000188
carbofuran	0.000975	97.1	2.847	0.063	0.000161
fenobucarb	0.01	64.2	35.0	0.778	0.00198
methomyl	0.00037	98.4	1.515	0.034	0.0000855
Pyrethroids					
cyfluthrin	0.0000444	0.127	97.6	2.17	0.00551
cypermethrin	0.000134	0.028	97.7	2.172	0.00552
deltamethrin	0.274	2.690	94.9	2.108	0.00536
esfenvalerate	0.000563	0.066	97.7	2.171	0.00552
fenvalerate	0.346	1.063	96.4	2.142	0.00544
lambdacyhalothrin	0.0000401	0.011	97.7	2.172	0.00552
Others					
fipronil	0.000162	9.941	88.0	1.956	0.00497
imidacloprid	0.00000202	99.7	0.328	0.00729	0.0000185
Molluscicide					
niclosamide	3.54	95.6	0.847	0.019	0.0000478

Table 20. Environmental Partitioning (in percentage) According to Equilibrium Criterion (EQC) Scenario Level I, Xiamen Seas.

Pesticides	Air	Water	Soil	Sediments	Fish
Fungicides					
carbendazim	0.042	97.2	2.721	0.06	0.000154
chlorothalonil	0.265	58.6	40.3	0.895	0.00227
mancozeb	-	-	-	-	-
metalaxyl	0.000479	95.2	4.739	0.105	0.00027
thiophanate-methyl	0.000638	97.2	2.722	0.06	0.000154
thiram	5.579	90.0	4.282	95.2	0.00024
zineb	-	-	-	-	-
Herbicides					
butachlor	0.146	77.6	21.7	0.483	0.00123
dimethachlor	0.00451	87.4	12.3	0.273	0.00069
glyphosate	-	-	-	-	-
metsulfuron	0.0000000009	99.9	0.111	0.00247	0.00629
propyzamide	0.00933	46.7	52.1	1.157	0.00294
Insecticides					
Organochlorines					
dicofol	0.27	5.461	92.2	2.048	0.0052
Organophosphates					
dichlorvos	1.08	92.3	6.491	0.144	0.000367
dimethoate	0.000214	99.5	0.442	0.00982	0.000025
methamidophos	0.000067	99.9	0.111	0.00247	0.000006
omethoate	0.00142	99.9	0.088	0.00197	0.000005
parathion-methyl	0.01	52.5	46.5	1.032	0.00262
triazophos	0.028	33.5	65.0	1.443	0.00367
trichlorfon	0.00009	99.8	0.238	0.00528	0.0000134
Carbamates					
carbofuran	0.000975	97.1	2.847	0.063	0.00016
isoprocarb	0.041	99.8	0.202	0.0405	0.0000114
Pyrethroids					
bifenthrin	0.00226	0.110	97.6	2.17	0.0055
esfenvalerate	0.00056	0.066	97.7	2.171	0.0055
fenpropathrin	0.401	0.110	97.3	2.161	0.0055

The EQC Models Level I and Level II were utilized. A synopsis of the environmental partitioning in percentage among various compartments for the pesticides applied on agricultural fields in Batangas and Xiamen and the residence time in the unit of world are presented in *Tables 19* and *20*, respectively. In *Figure 7*, the output of the model is shown as an example with a default chemical. The water compartment holds more than 75.8% of the chemical, while 21.2% is in the soil and 2.5% in the air. This last figure is worth noting as it could indicate a certain mobility through the atmosphere. Contents in the other compartments are significantly smaller.

Tables 21 and *22* present persistence time in days according to EQC Scenario Level II for the Batangas Bay Region and Xiamen Seas. The Level II diagram (*Figure 8*) shows the same distribution. Additional information is provided by the grey arrows that indicate degradation and advection in the various compartments, for example, degradation in water, 76%; advection in air, 2%; etc. This figure contains a small table under the heading of persistence, where the total is the overall residence time in the compartments. Global persistence is best indicated by reactions and the tendency to mobility by the advection time. Bearing this information in mind, one can look at the synopsis of the results of the EQC modelling calculation.

Herbicides and fungicides, with the exception of fenchlorim and cyhalofop-butyl, have a preference for water; organophosphates have a variety of behavior, from very low affinity for water (as in the case of chlorpyrifos) to very high (for methamidophos). Carbamates have affinity for water while pyrethroids partition mainly for soil. Some chemicals are volatile; for example, 0.2-0.4% of dichlorvos, fenpropathrin and dicofol indicates volatility.

Information on the persistence of some pesticides such as overall residence time, reaction time and advection time is given in *Tables 21* and *22*. Pyrethroids demonstrate a very scarce mobility, months of persistence and high residence time. In general, carbamates are short living and relatively mobile molecules, while organophosphates have very diverse behavior. One should look at these tables in order to obtain more detailed information relevant to the exposure assessment.

Table 21. Persistence Time (in days) According to Equilibrium Criterion (EQC) Scenario Level II, Batangas Bay Region.

Pesticides	Overall	Reaction	Advection
Fungicides			
benomyl	65	65	45
mancozeb			
Herbicides			
butachlor	46	363	51
cyhalofop-butyl	15	21	55
2,4-D isobutyl ester	21	34	55
fenclorim	34	41	191
glyphosate			
paraquat			
Insecticides			
Organophosphates			
azinphos-ethyl	38	65	94
chlorpyrifos	111	128	813
diazinon	26	34	104
malathion	20	30	61
methamidophos	6	7	42
parathion-methyl	11	13	79
phenthoate	16	18	173
profenofos	10	10	1,066
triazophos	14	15	123
Carbamates			
carbaryl	12	18	43
carbofuran	34	166	43
fenobucarb	19	28	65
methomyl	1	1	42
Pyrethroids			
cyfluthrin	7	7	24,458
cypermethrin	129	129	57,500
deltamethrin	29	30	776
esfenvalerate	130	130	36,083
fenvalerate	115	132	912
lambdacyhalothrin	130	130	75,833
Others			
fipronil			
imidacloprid			
Molluscicide			
niclosamide	8	11	31

Table 22. Persistence Time (in days) According to Equilibrium Criterion (EQC) Scenario Level II, Xiamen Seas.

Pesticides	Overall	Reaction	Advection
Fungicides			
carbendazim	41	1,037	43
chlorothalonil	35	72	68
methalaxyl	43	2,383	44
thiophanate-methyl	41	1,270	43
thiram	12	20	29
Herbicides			
butachlor	46	364	53
dimethaclor	43	426	48
metsulfuron	42	33,500	42
propyzamide	43	81	89
Insecticides			
Organochlorines			
dicofol	89	107	508
Organophosphates			
dichlorvos	4	5	40
dimethoate	42	11,833	42
methamidophos	6	7	42
omethoate	15	25	42
parathion-methyl	15	18	79
triazophos	14	13	123
trichlorfon	3	3	42
Carbamates			
carbofuran	34	166	43
isoprocarb	41	8,042	42
Pyrethroids			
bifenthrin	112	112	23,625
esfenvalerate	137	137	25,583
fenpropathrin	10	10	1,002

Risk Assessment in Relation to Pesticide Loads

As it would be a very difficult task to make detailed simulations for every pesticide used in the Batangas basin and bearing in mind that only a few are applied in relevant quantities, it was decided to concentrate modelling activities on only the most relevant chemicals. It has been further observed that chemicals belonging to the same group have the same mode of action and the total effect is considered to be toxicologically additive when present in mixtures (Vighi and Calamari, 1996). Thus, one single chemical could well represent a chemical group.

Treatments and Loads of Pesticides

In the Batangas Bay Region, a total of 2,256 kg/year of butachlor out of 2,990 kg/year total herbicides was used in the area and was selected as being representative for the category. Chlorpyrifos (2,552 kg/year out of the total 7,000 kg/year of organophosphates) was selected for having a high score in the ranking system (worst possible case). Carbaryl (5,125 kg/year out of the total 6,000 kg/year) and cypermethrin (ca. 300 kg/year out of the 500 kg/year total) were taken as representative for carbamates and pyrethroids, respectively. *Tables 23a* and *23b* summarize agronomical data and the physico-chemical properties of the pesticides utilized for the most refined risk assessment modelling of the Batangas Bay using the SoilFug model (Di Guardo et al., 1994a, 1994b).

In Xiamen, among the fungicides applied, thiophanate-methyl is used most (10 t/year). However, for simulation purposes, it was decided to include carbendazim (7.5 t/year) because of its high toxicity to fish and *Daphnia*. Copper sulfate was excluded from the evaluation as it is not applied directly to water. It has limited risk due to metal absorption into soil. Butachlor used at 12 t/year was taken as representative for herbicides. Glyphosate, despite its high toxicity to many plants, is a molecule with a short life and has very low mobility due to its dissociation (Grossbard and Atkinson, 1985). With this in mind, it was not considered. The acaricide dicofol

Table 23a. Simulated Treatment and Loads of Pesticides in Batangas Bay.

Pesticides	Kg a.i. per year	Type of Crop	Application (kg/ha)	Number of Treatments	Treated Area (ha)	Simulated Treatment (kg/ha)
Organophosphates	7,000	any	0.15	2	24,000	0.30
Carbamates	6,000	mango corn	0.40	2	8,000	0.80
Herbicides	3,000	rice	0.50	1	6,000	0.50
Pyrethroids	500	any	0.01	2	24,000	0.02

a.i. = active ingredient

Table 23b. Properties of Pesticides in Batangas Bay.

Pesticides	MW (g/mol)	Water Solubility (mg/l)	Vapor Pressure (Pa)	Bioaccumulation ($\log K_{ow}$)	Soil Persistence (t/2) (days)
Chlorpyrifos	350	1.4	.0027	4.7	90
Carbaryl	201	120	.00004	1.6	14
Butachlor	312	20	.0006	2.5	56
Cypermethrin	416	0.004	.00000023	6.6	90

Pa = Pascal

Table 23c. Rainfall Data from August to November 1996 (9 Rain Events) in Batangas Bay.				
Rain event	Day to rain	Duration (days)	Amount of Rainfall (mm in)	Amount of Runoff (mm out)
1	1	4	57	29
2	7	5	12	6
3	2	5	17	8
4	2	2	18	9
5	7	14	198	100
6	4	3	15	7
7	19	4	18	9
8	3	21	208	106
9	7	12	168	84

Table 23d. Characteristics of Soil in Batangas Bay.	
Characteristics	Value
Depth (m)	0.60
Field capacity	0.50
Porosity	0.70
Organic carbon content (%)	1.8
Total basin area (ha)	87,000

has been included in the simulation as the only representative of organochlorine compounds due to its similarity to DDT, from which it is prepared. Dichlorvos has been taken as the most commonly used organophosphate (180 t/year) of active ingredient per year and associated with the very similar methamidophos (52 t/year) thereby providing a total organophosphate load of 230 t/year. Types of crops, quantities applied per hectare, number of treatments and treated areas were derived from *Tables 7* and *8*. Treatments are made year-round on vegetables and fruits. On the other hand, treatment on rich soil is from March to October (2 croppings). Rainfall simulations (*Table 23c* for Batangas Bay and *Table 24c* for the Xiamen Seas) were made using data from late April to December 1996. *Tables 24a* and *24b* summarize agronomical data on physico-chemical properties of the pesticides utilized for the most refined risk assessment modelling in the Xiamen area with the SoilFug model (Di Guardo et al., 1994a, 1994b).

As stated in the EQC series of papers (Mackay et al., 1996a, 1996b, 1996c), after a generic evaluation of the chemical of interest at a certain stage this evaluation should be complemented with information on the environmental media into which a substance is discharged or used to identify conditions where elevated concentrations could occur. These situations are highly site-specific and local models are needed. SoilFug is one such model, particularly appropriate for the situation under evaluation.

Table 24a. Simulated Treatments and Loads of Pesticides in Xiamen.						
Pesticides	Total (a.i./year)	Types of Crop	Application (kg/ha)	Number of Treatments	Treated Area (ha)	Simulated Treatments
Fungicides	18	any	1.0	1	18,000	1
Herbicides	12	rice	1.0	1	12,000	1
Organochlorines	4	fruit, vegetable	0.3	1	12,000	0.3
Organophosphates	230	mainly rice	2.4	8	12,000	2.4(8)
Carbamates	6.5	any	0.1	2	30,000	0.2

Table 24b. Properties of Selected Pesticides in Xiamen.					
Pesticides	MW (g/mol)	Water Solubility (mg/l)	Vapor Pressure (Pa)	Bioaccumulation (log K_{ow})	Soil Persistence (t/2) (days)
Carbendazim	191.2	8	0.00009	1.5	8-32
Butachlor	311.9	20	0.0006	2.5	42-70
Dicofol	370.5	0.8	0.00053	4.28	60-80
Dichlorvos	221.0	8,000	2.1	1.9	7
Carbofuran	221.3	320	0.000072	1.52	30-60

It should be noted, however, that exact scenarios for simulation can be built only for research purposes. In fact, the high number of variables inherent to such models do not allow for precise scenarios where large-scale areas are studied. This model, however, has been validated for research purposes (Di Guardo et al., 1994a, 1994b; Barra et al., 1995).

Table 24c. Rainfall Data from Late April to December in 1996 in Xiamen.

Rain Event	Day to Rain (days)	Duration (days)	Amount of Rainfall (mm in)	Amount of Runoff (mm out)
1	1	2	75	37.5
2	9	11	35	17.5
3	14	7	139	69.5
4	19	5	56	28.0
5	31	15	453	226 5
6	12	3	22	11.0
7	3	9	80	40.0
8	19	3	22	11.0
9	44	3	30	15.0

Table 24d. Characteristics of Soil in Xiamen.

Characteristics	Value
Depth (m)	0.3
Field capacity	0.3
Porosity	0.5
Organic carbon content (%)	0.02
Total basin area (ha)	140,500

A Short Ecotoxicological Profile of the Selected Pesticides

Ecotoxicological profiles of the active ingredients used in the Batangas Bay Region and the Xiamen Seas were synthesized on the basis of physico-chemical properties, application rate, toxicology, terrestrial/aquatic/atmospheric fate, environmental distribution and GUS.

Profiles related to toxicological characteristics and environmental properties for the Batangas Bay Region are given below:

- Butachlor: Like many other herbicides, butachlor is a leacher and can therefore easily reach the aquatic environment. In addition, it is also persistent. Low log K_{ow} gives an indication of scarce potential for bioaccumulation; toxicity to fish is of the level of mg/l. Metabolites are water soluble and could thus impair drinking water sources.

- Chlorpyrifos: This organophosphate compound has a high affinity for soil due to its elevated K_{oc}. It cannot be considered a leacher; however, a certain amount could reach the water. It is persistent, with orders of magnitude of months, and could theoretically be accumulated. It is well known, however, that organophosphates are easily metabolized and excreted. This chemical is highly toxic to aquatic fauna and it can be expected that once introduced into the environment, a limited amount of leaching could have undesirable effects on aquatic fauna.

- Carbaryl: This carbamate, the most used in the world, is very soluble, therefore it can be easily found in the aquatic environment. Despite its moderate persistence in soil (a few weeks) and in water (up to 12 days) it could be dangerous to aquatic organisms, particularly crustaceans, in case of rapid runoff occurrences after the treatments. No bioaccumulation is expected.

- Cypermethrin: According to its half-life and GUS values, cypermethrin (a synthetic pyrethroid) appears to be persistent (16 weeks in soil) and is a non-leachable molecule. Its low vapor pressure suggests that it does not volatilize significantly, while its high log K_{ow} value and its low solubility explain its scant affinity for water in which it is quickly degraded (5 days). Despite its high lipofilicity, it is not bioaccumulative, as the molecule is rapidly metabolized. Cypermethrin exhibits high toxicity to some non-target organisms, such as fish and aquatic crustaceans, but is considered to be only slightly toxic to birds and mammals. Aquatic fauna toxicity is, however, mitigated by the strong affinity for sediments and suspended solids that make the molecule not bioavailable.

Once the molecule has entered the environment, it is reasonable to expect that it will be almost completely absorbed by soil, in which it will be degraded in a few months.

Profiles related to toxicological characteristics and environmental properties for the Xiamen Seas are summarized below:

- Butachlor: Like many other herbicides, butachlor is a leacher and can therefore easily reach the aquatic environment and is also persistent. Low log K_{ow} gives an indication of scarce potential for bioaccumulation, toxicity to fish is of the level of µg/l. Metabolites are water soluble and could thus impair drinking water sources.

- Carbendazim: This systemic fungicide is a leacher and it can therefore be transported to the aquatic environment. It has no bioaccumulation potential, but its persistence (order of weeks) and its toxicity to aquatic fauna (less than 1 µg/l) could make it dangerous to the aquatic environment.

- Carbofuran: This insecticide and nematocide has high affinity for water and high mobility; it is toxic to fish and very toxic to crustaceans (at the level of µg/l).

- Dicofol: This organochlorine acaricide is poorly mobile, being mainly partitioned into the soil. It has a potential for bioaccumulation, is persistent (months) and is toxic to aquatic fauna.

- Dichlorvos: This organophosphate is very mobile. It has a high affinity for water, and can be found in the atmosphere, where it has a certain tendency to enter (1% EQC model). It has no bioaccumulation potential but is very toxic to aquatic fauna. It is, however, a short-lived molecule. Due to its characteristics, it poses a risk to humans because of its volatility, and to aquatic animals.

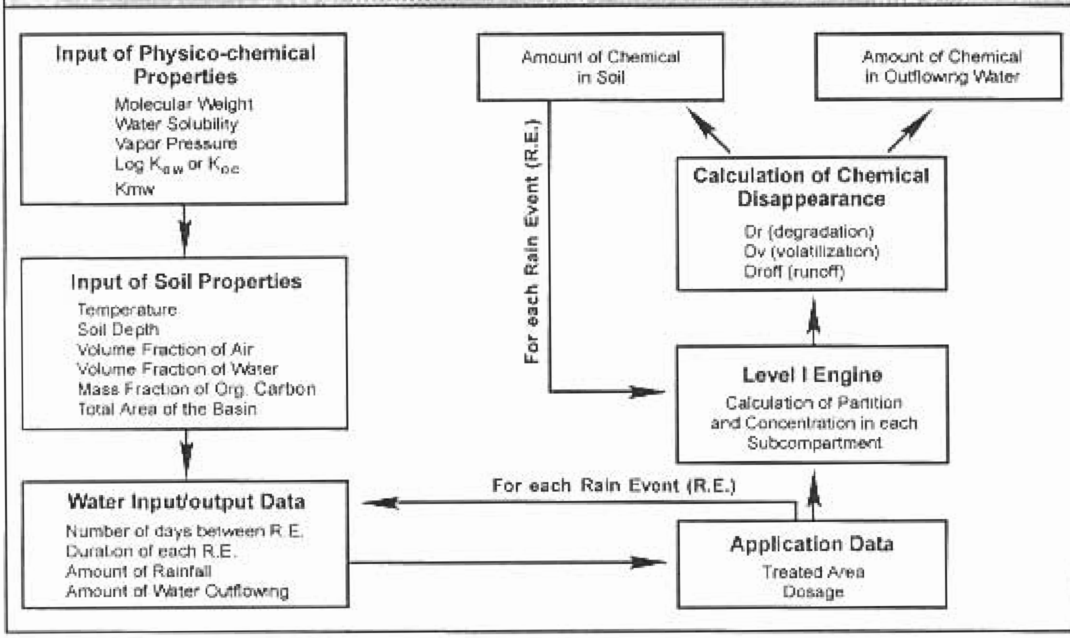
APPLICATION OF SOILFUG MODEL FOR ESTIMATING PESTICIDE RUNOFF

There are many pesticide runoff simulations. However, for the purpose of the present study, the SoilFug model of Di Guardo et al. (1994a) was used. SoilFug is a model for the prediction of potential surface water contamination derived from pesticide use on agricultural fields. It uses the fugacity approach to a basin scale soil environment and calculates the partition of the chemical applied to the soil phases and its possible contamination of surface water during the rain events, i.e., periods of time starting with a rainfall and ending with the return to the background water level in the adjacent stream. It requires a limited amount of chemical and environmental data, and it furnishes an average concentration of pesticide in outflowing waters *(Figure 9)*.

SoilFug is essentially an unsteady-state but equilibrium-event model. This is because it takes into account the disappearance of the chemicals according to different phenomena (degradation, volatilization, runoff) and calculates the partition among the different phases of the soil according to a Level I fugacity calculation (Mackay and Paterson, 1981) in the rain event period.

Briefly the model considers the following four different compartments in the soil: soil air, soil water, organic matter and mineral matter. For each of these compartments, a capacity (Z) can be calculated and therefore the fugacity can be worked out, once the volume and the chemical input are known. From the fugacity, chemical

Figure 9. Block Diagram of the Soil Fugacity (SoilFug) Model.



amounts and concentrations in each compartment can be calculated.

Input Data for the SoilFug Model

Input data for the SoilFug model are: physico-chemical properties of the pesticide, soil properties, water input/output balance, and pesticide treatments—each of which is elaborated below.

Physico-chemical properties

Physico-chemical properties of the pesticides, together with the half-life in soil, were the first data to be entered into the SoilFug model. They were drawn from the recent literature (Howard, 1991a, 1991b; Tomlin, 1995), with the exemption of the half-life figures, which were selected on the basis of extremes of the ranges of variability encountered under different conditions and taking into account the high temperatures of the Batangas basin.

Soil properties

The input data required for the soil scenario description of the model were temperature, depth, volume fractions of air and of water in soil at field capacity, organic carbon content, area of the basin and the number of simulations, i.e., the number of rain events. The actual values of these parameters, as used for the simulations, are given in *Tables 23* and *24* for the Batangas Bay Region and Xiamen, respectively. The data were derived from the coastal environmental profiles of the Batangas Bay Region and Xiamen (ITTXDP, 1996; MTE, 1996), the Department of Agriculture in Batangas and Xiamen University.

Water input/output balance

The mass balance of the water was calculated on the basis of rain events and outflow. The basic data for the water input calculation were the number of rain events, the duration of the rain events and the quantity of rain. A rain event was arbitrarily considered to be a period during which consecutive instances of rainfall were separated by no more than two days. Each rain event had to be sufficient to produce a measurable outflow, since the model was required to estimate the quantity of pesticides in advective water moving out of the basin. In addition, each rain event has to allow for the repartition and the re-equilibration of the chemicals between the soil phases and the rain water.

Outflows were estimated by taking into account the amount of rainfall over the whole basin and the evaporation rates of about 50%, considered to be reasonably representative of the basin. In the Batangas Bay Region, the actual values used for the simulation of rain events are given in *Table 23c*. The simulation lasted for 120 days. On the other hand, the actual values used for the Xiamen Seas are listed in *Table 24c*. The simulation lasted for 250 days.

Pesticide treatments

The other parameters necessary for the running of the model were the periods and numbers of pesticide applications, pesticide dosage, days between pesticide applications and rain events, area treated and half-life of the pesticides. The actual values of these parameters for the simulation are given in *Tables 23a* and *24a* for the Batangas Bay Region and the Xiamen Seas, respectively. In assembling these values for the SoilFug model, it was assumed that all the treatments were done in the wet season (worst case) when there was maximum possible runoff and simulations related to single treatments (maximum load).

Output of the SoilFug Model

From the sets of data described above, based on the model, it was possible to calculate the average concentrations of the different pesticides in water during each rain event, taking into account not only the partitioning phenomena between soil and water, but also the estimated persistence of each molecule (i.e., its half-life). The final output was a series of graphs showing the predicted concentration of the different pesticides at the basin outlet. These graphs are presented in *Figure 10* for the Batangas Bay Region and *Figure 11* for the Xiamen Seas, and are discussed in the succeeding sections, together with the ecotoxicological significance of the estimated concentrations.

Risk Assessment for the Batangas Bay Aquatic Ecosystem

The results of the SoilFug model calculations demonstrated that certain quantities of the most commonly used pesticides (none of which have bioaccumulation potential) could have been present in the estuary of the main rivers that enter the Batangas Bay (e.g., Calumpang River) at analytically detectable levels (cypermethrin excluded). The ecotoxicological significance of the calculated concentrations are discussed separately for the four representative chemicals.

The herbicide butachlor has a calculated concentration in water of about 2.5 μg/l, about 100 times less than the actual toxic concentration for fish. It can be analytically detectable, and exceeds the European Union Standard for Drinking Water for Human Consumption (0.1 μg/l). Concentrations in soil declined three times during the study period mainly due to soil degradation with a little contribution of runoff.

The concentration of chlorpyrifos was calculated in water at 0.05 μg/l to around 0.025 μg/l, while its acute toxicity is reported to be 3 μg/l for fish and 1.7 μg/l for *Daphnia*, about 100 times higher than the calculated data. Dissipation is mainly via degradation, which in soil is a slow process.

Carbaryl could cause adverse effects on river fauna when it peaks for a few days between 8 and 12 μg/l, i.e. exceeding the acute toxicity for *Daphnia* at 6 μg/l. Degradation is fast in water and soil and dissipation in soil occurs also through runoff.

The concentration of cypermethrin in water started from about 0.04 ng/l and slowly declined to less than 0.02 ng/l. According to the literature on cypermethrin, the acute concentration for aquatic fauna is at 0.7 ng/l for fish and 0.15 ng/l for *Daphnia*, respectively. Considering, however, the strong affinity for suspended solids and sediments, one could consider the risk from this chemical as low. Concentration in soil was about 0.025 mg/l and

Figure 10. Concentration Trends of Various Chemicals in Soil and Basin Water and Loss Processes Calculated by the Soil Fugacity (SoilFug) Model for Batangas Basin.

a. Butachlor

b. Chlorpyrifos

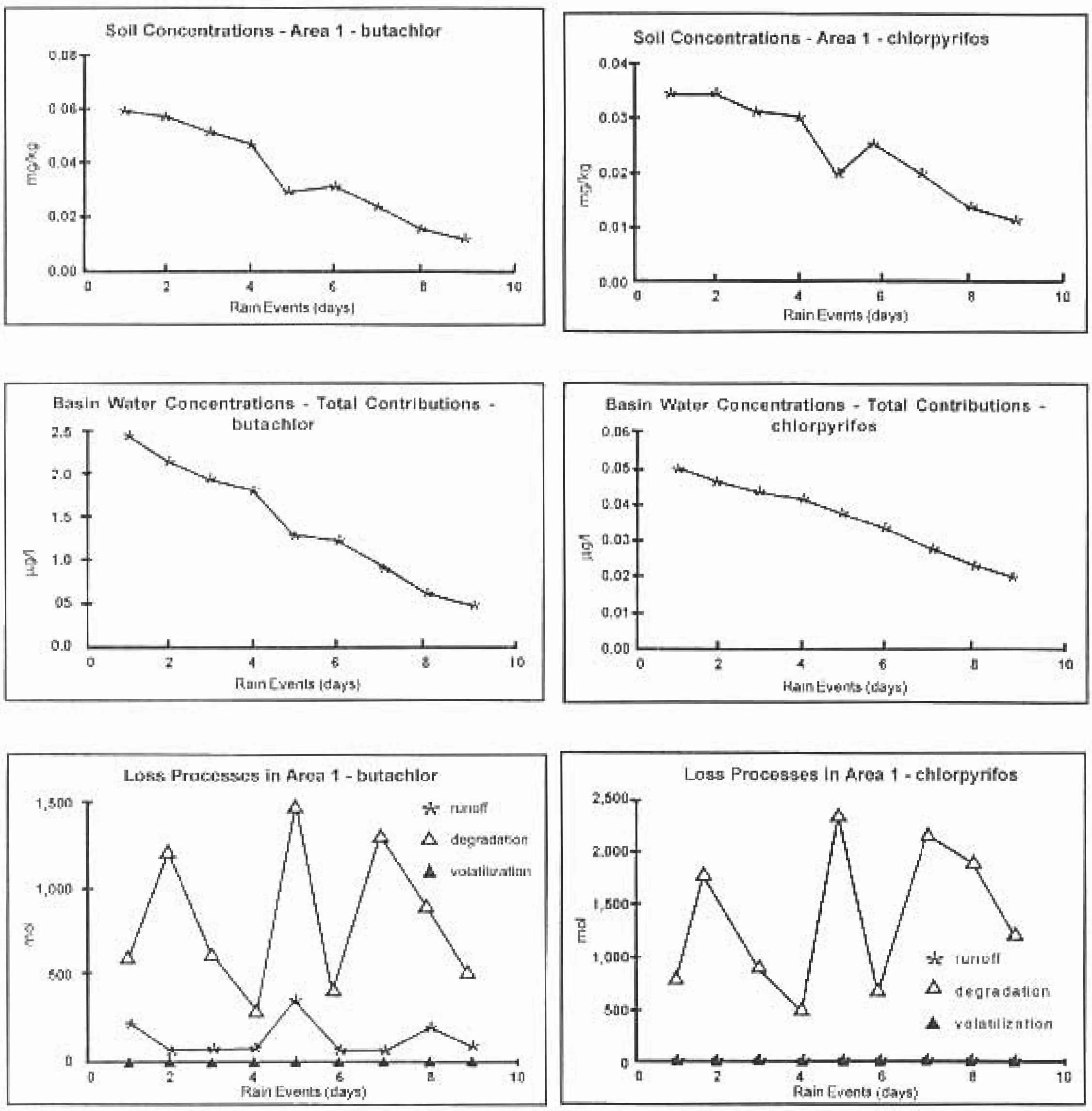
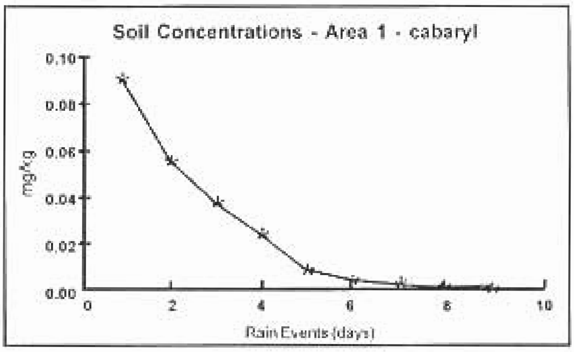
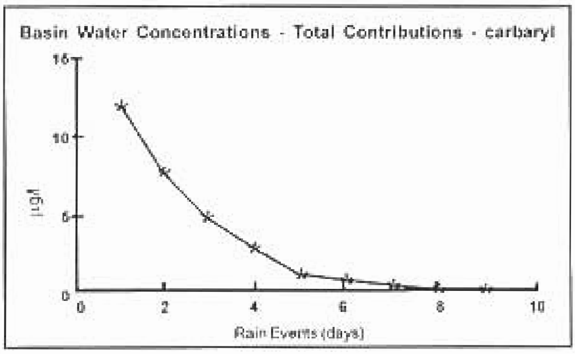
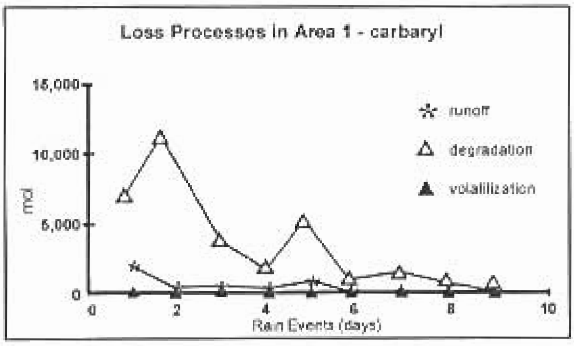


Figure 10. Concentration Trends of Various Chemicals in Soil and Basin Water and Loss Process Calculated by the Soil Fugacity (SoilFug) Model for Batangas Basin.

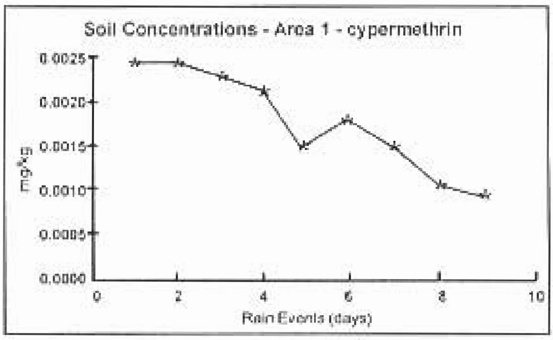
c. Carbaryl

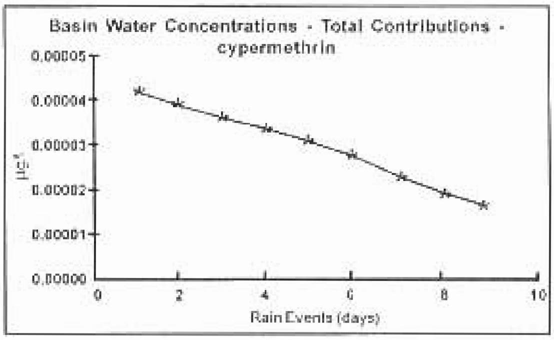


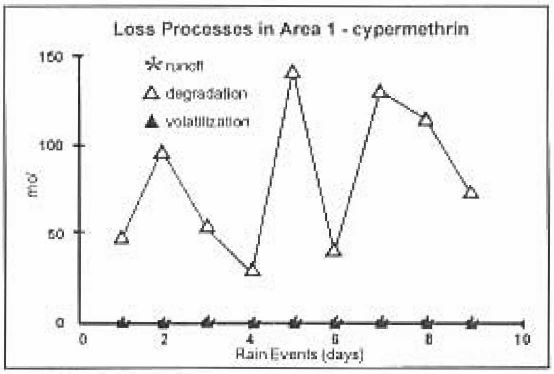




d. Cypermethrin







persisted for several months, with a low rate of degradation. No data are available for soil risk assessment. Loss processes are only by soil degradation. There is no volatilization; neither is there runoff.

If risk assessment is made simply by examining the ratio between predicted environmental concentration (PEC) and acute toxicity data for the four molecules, only carbaryl shows a risk for the aquatic fauna. The results were not cause of concern for the other three compounds, as the differences were in orders of magnitude. One should also note that the simulations were made according to worst case scenarios.

If, however, a more severe criterion is used to evaluate the model predictions, e.g., by applying the water quality objective for aquatic life established by the EEC Scientific Advisory Committee on Toxicology and Ecotoxicology (CSTE/EEC, 1994) at 0.1 µg/l for several organophosphate compounds, one can observe that this more stringent level of concentration could have been exceeded for several days after the treatments with chlorpyrifos.

It can therefore be concluded that on the basis of acute toxicity criteria considered in the first of the two types of assessment, there is no immediate cause of concern with regard to the river aquatic fauna with the exception of the short-lived carbaryl. However, if the more severe EEC criterion is applied to the assessment, the fact that the criterion was theoretically exceeded for several days has to be accepted as proof of contamination, and should therefore be viewed as an early warning.

The same consideration could also apply to marine waters, where less ecotoxicological data are available. Not one of the chemicals under study was a cause of concern for bioaccumulation. The extremely toxic cypermethrin has limited possibilities to reach marine water and, in any case, has a very high affinity for suspended solids and sediments. Butachlor and chlorpyrifos are actually no cause of concern but should be kept under observation as contaminants, as their calculated theoretical presence could be considered an early warning.

Carbaryl could provoke undesirable effects on river fauna. However, it has less probability to endanger marine fauna due to a dilution effect and to its very short half-life, being quickly hydrolyzed in water and even faster in alkaline conditions (i.e., in sea water).

Risk Assessment for the Xiamen Aquatic Ecosystem

The results of the SoilFug model calculations demonstrated that certain quantities of the most commonly used pesticides (none of which have bioaccumulation potential) could have been present in the estuaries of the main rivers entering the Xiamen Seas at analytically detectable levels. The ecotoxicological significance of the calculated concentration is discussed separately for the five representative chemicals.

The fungicide carbendazim has a calculated concentration in river water at the outlet of about 45 µg/l, acute toxicity for *Daphnia* being 130 µg/l. The ratio between predicted environmental concentration and acute toxicity on a sensitive crustacean is 0.35. If a no effect level is considered, for example only 10 times less the acute toxicity, a risk could be expected. The substance is dissipated from soil mainly by degradation and partially by runoff.

Butachlor has a calculated concentration of 8 µg/l while acute toxicity to aquatic organisms is of the order of hundreds µg/l. The former figure however exceeded the European Union Standard for Drinking Water for Human Consumption (0.1 µg/l).

Dicofol is persistent for about one year in soil but due to its affinity for soil, the leaching is limited (max 0.04 µg/l) and much lower than toxic levels. A certain amount of bioaccumulation could be expected (log K_{ow} 4.3) but it has been demonstrated that it can be metabolized by

Figure 11. Concentration Trends of Various Chemicals in Soil and Basin Water and Loss Processes Calculated by the Soil Fugacity (SoilFug) Model for the Xiamen Seas.

a. Carbendazim

b. Butachlor

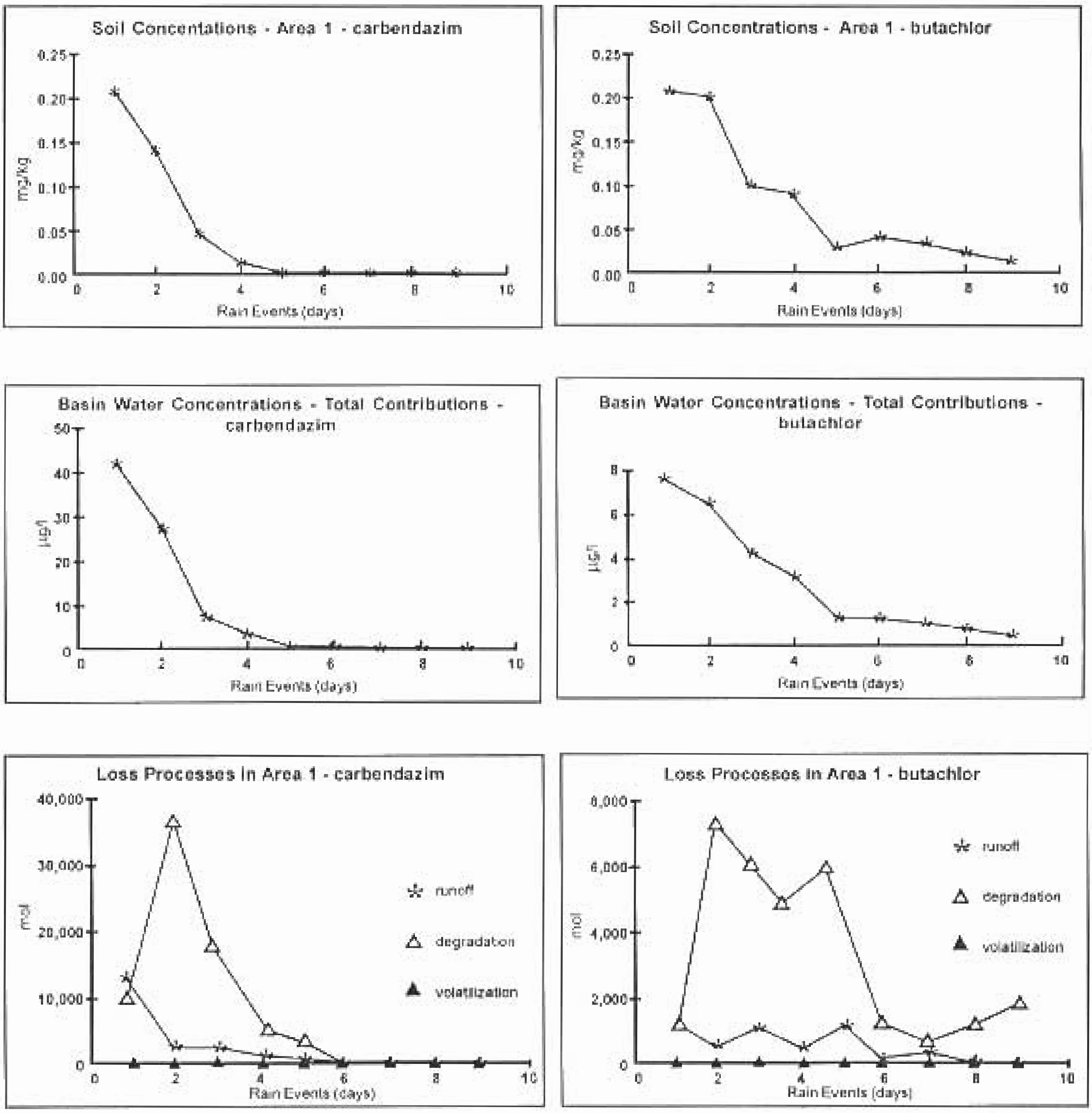
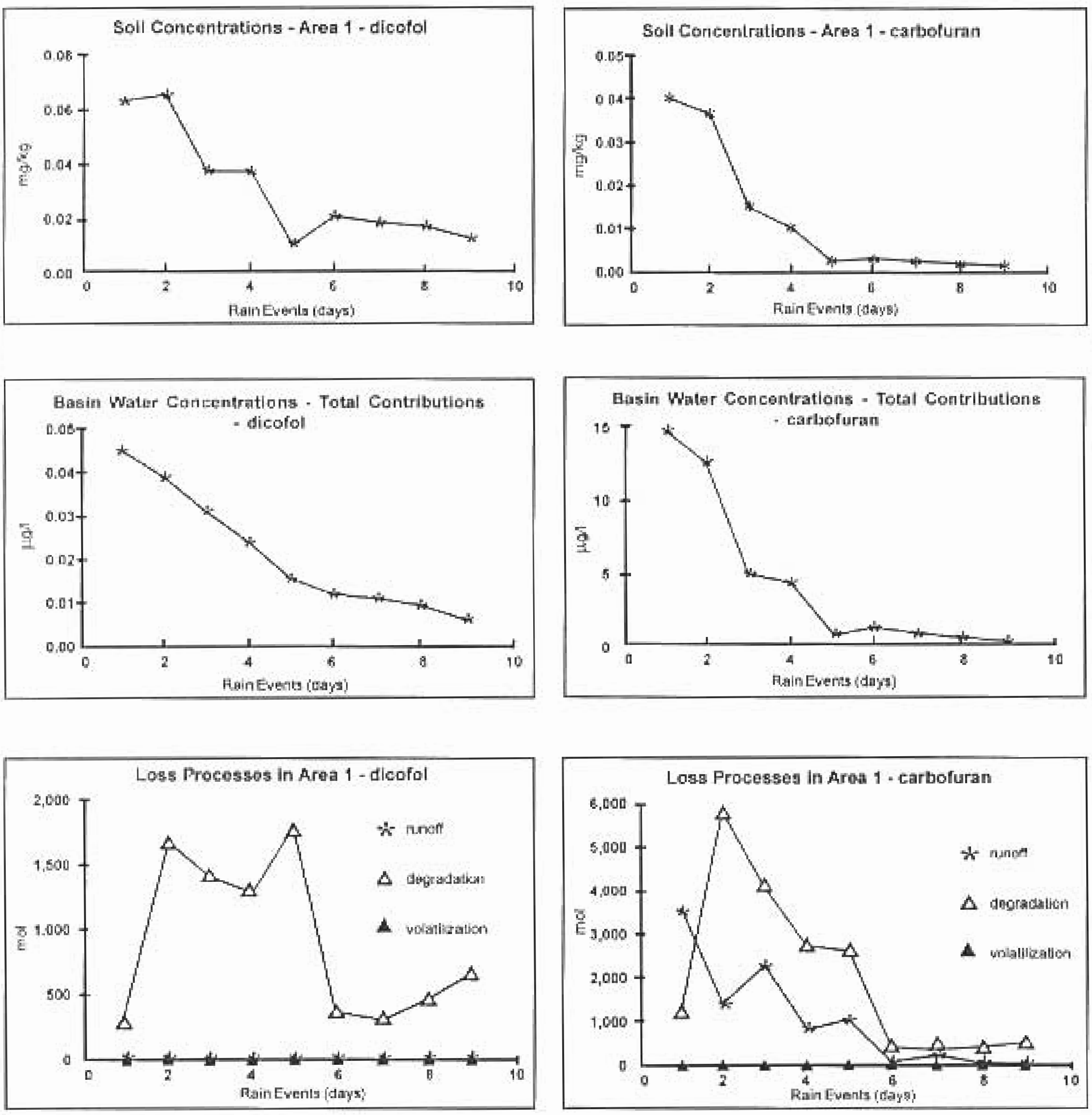


Figure 11. Concentration Trends of Various Chemicals in Soil and Basin Water and Loss Processes Calculated by the Soil Fugacity (SoilFugSoilFug) Model for the Xiamen Seas.

c. Dicofol

d. Carbofuran



mammalians and birds. Soil risk assessment was not possible due to the lack of data. Degradation occurs only through soil biodegradation. Carbofuran is dissipated via degradation and runoff. Water calculated concentration has a peak of 15 µg/l that is equal to acute toxicity to *Daphnia*. In this condition, the risk ratio for danger to aquatic organisms is high.

Only carbofuran shows a risk for the aquatic fauna, the result not being cause of concern for the other compounds. If, however, a more severe criterion is used to evaluate the model predictions, e.g., by applying the non-observed effect level, calculated assuming a factor of 10 in respect to acute toxicity, a risk factor can be expected for carbendazim and also butachlor. It can therefore be concluded, that on the basis of acute toxicity criteria, carbofuran is at risk of causing acute damages, while on the basis of an assumed no effect level of a factor of 0.1 of the acute toxicity, carbendazim and butachlor fall into the group of molecules that could provoke risk to the aquatic fauna. In Xiamen where mariculture is widely practiced, the risk of mass mortality is posed as a result of the existence of relatively short rivers which result in waters entering the sea at a faster rate.

A particular case is that of dichlorvos of which several applications are done according to normal agricultural practices. Simulation of three sequential applications was conducted. The results are shown in *Figure 11e*. Dichlorvos, despite its short half-life, was present in water at peaks of 40-20 µg/l (see for example Area 1-2-3) and for a period of several days (integrating the various contributions). Considering the higher total quantity applied (230 t/year), the application rate of 2.4 kg/hour and that treatments are repeated up to 8 times per year, this substance has probably caused and will continue to cause massive aquatic organism mortality. Its acute toxicity reported by Tomlin (1994) is 0.19 µg/l for *Daphnia*. Because this figure was very low, a quick literature survey was made and the low value was confirmed. In fact Vighi et al. (1991) reported a value of 0.22 µg/l while older data referred to 0.05 µg/l (Mayer and Ellersieck, 1986). Acute toxicity to fish is reported at 450 µg/l (Tomlin, 1994).

Considering the water quality objective for aquatic life, including coastal and marine waters, established by the European Union Scientific Advisory Committee on Toxicology and Ecotoxicology (CSTE/EEC, 1994) at 0.1 µg/l for several organophosphate compounds, one can observe that this level of concentration could have been exceeded for a number of months by several orders of magnitude.

RISK ASSESSMENT FROM PAST USE OF PERSISTENT PESTICIDES: A XIAMEN CASE STUDY

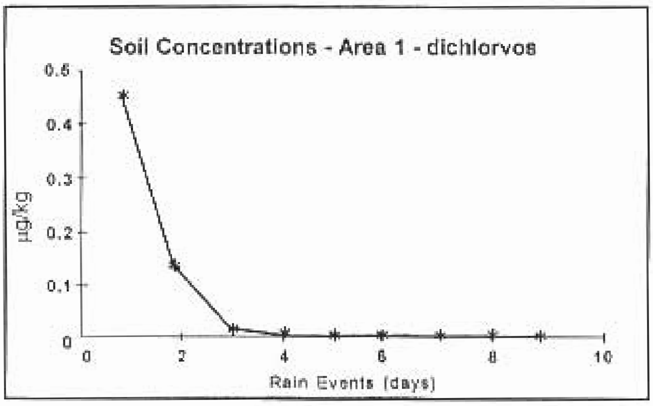
Available Analytical Data

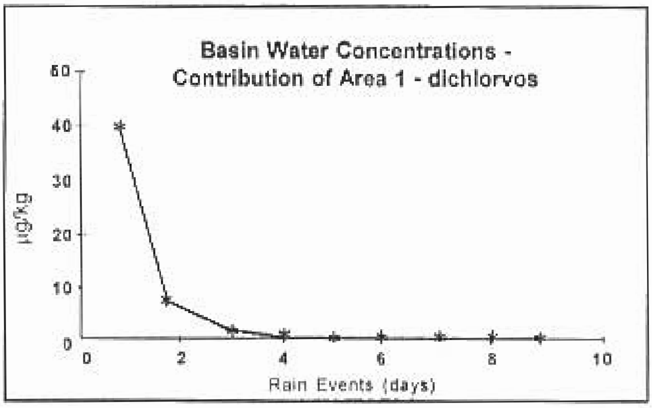
In the coastal environmental profile of Xiamen (ITTDXP, 1996), data exist from various sources on pollutant concentration in biota and sediment. Extensive studies lasting several years were recently published on surface sediments and core sediments from several stations around Xiamen Island (Hong et al., 1995; Chen et al., 1996a, 1996b; Zhang et al., 1996). A synopsis of these data is reported in *Tables 25* and *26* and the sampling stations are shown in *Figure 12*.

HCH concentrations were higher in the Western Seas and upper Tong'an Bay and lower in the Southern and Eastern Seas. The absolute concentrations are reflecting a limited utilization of the product. This fact is also confirmed by the decrease in concentration demonstrated by Chen et al. (1986) (1.5-27 µg/g) and by the concentration in sediment cores of two stations that are very similar to those reported and nearly constant from deepest to surface sediments. ΣDDT concentrations also reflect, in the majority of the stations, pollutant input from agricultural activities, probably from the recent past, considering the ratio of DDT to its metabolites of around 40 to 50%. Concentration over time is relatively constant and one could assume that there are constant inputs from agricultural soil from past use (as DDT has been banned). A few points, however, need to be clarified as recent

Figure 11. Concentration Trends of Various Chemicals in Soil and Basin Water and Loss Processes Calculated by the Soil Fugacity (SoilFug) Model for Xiamen.

e. Dichlorvos (repeated treatments)





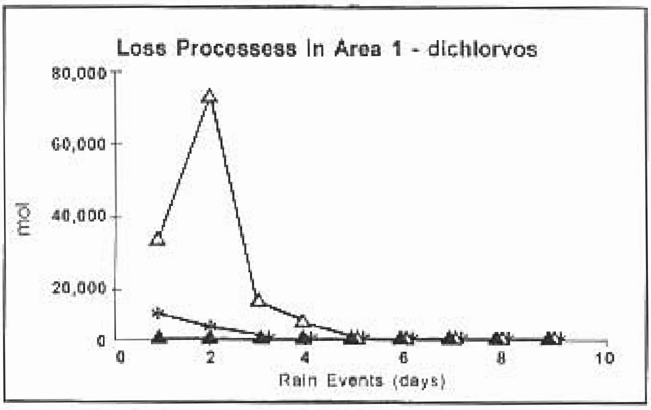


Figure 11. Concentration Trends of Various Chemicals in Soil and Basin Water and Loss Processes Calculated by the SoilFug (Soil Fugacity) Model for Xiamen.

e. Dichlorvos (repeated treatments)

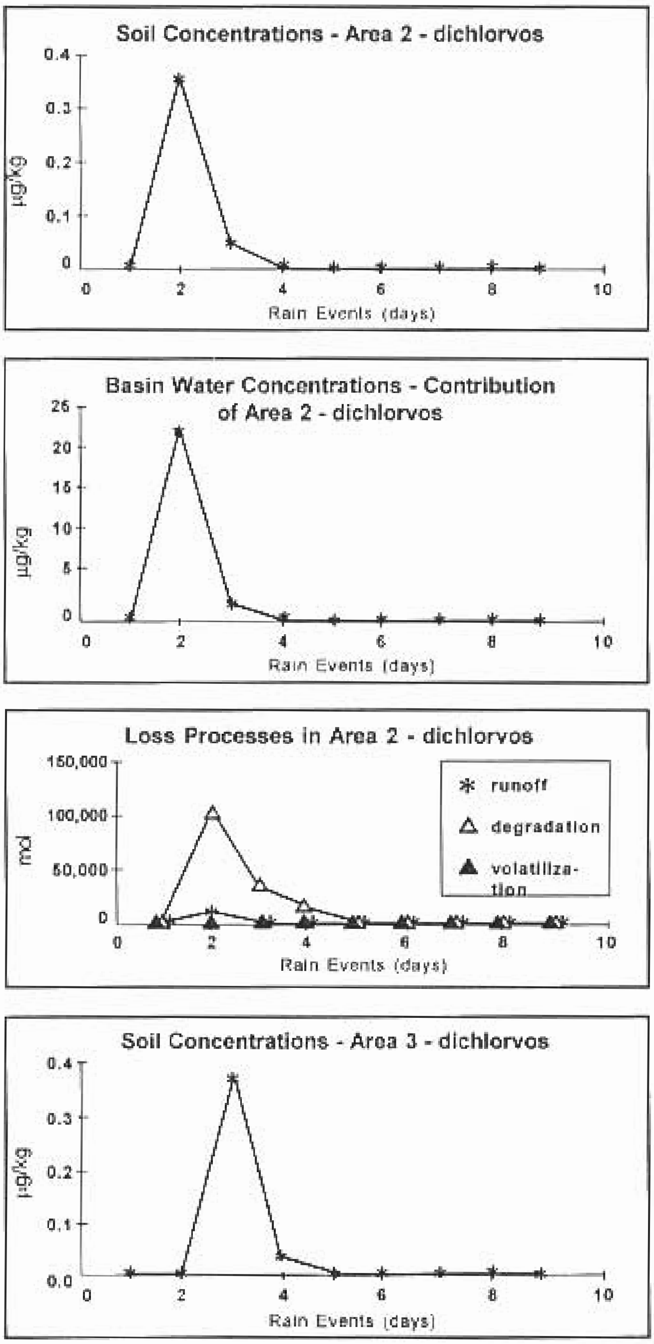
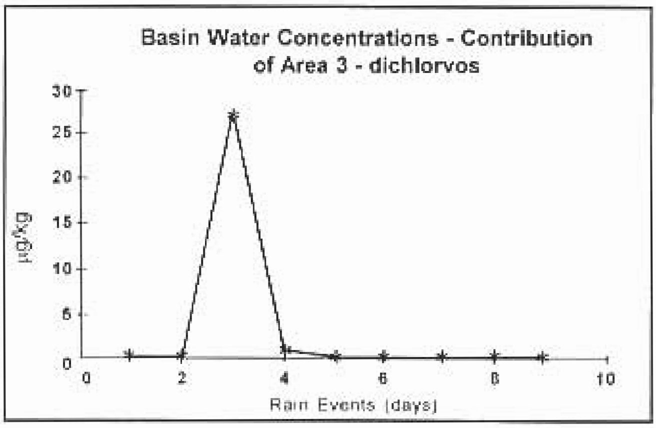
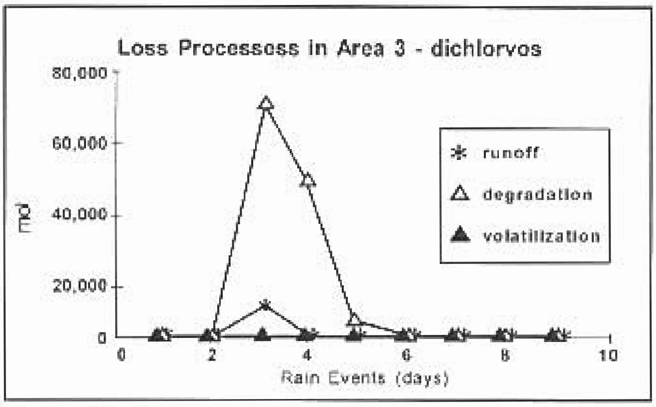


Figure 11. Concentration Trends of Various Chemicals in Soil and Basin Water and Loss Processes Calculated by theSoil Fugacity (SoilFug) Model for Xiamen.

e. Dichlorvos (repeated treatments)





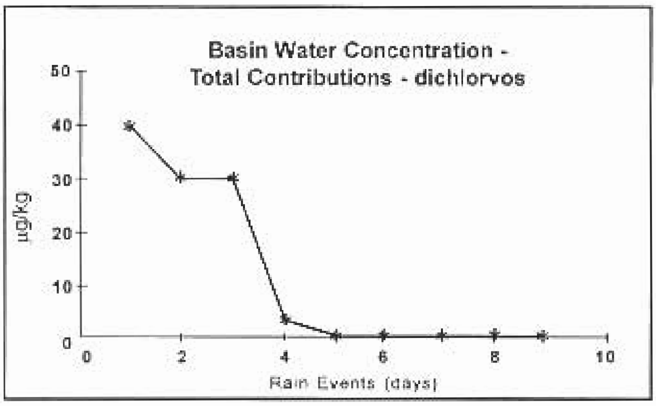


Table 25. Concentrations (ng/g dw) of HCH and DDT in Surface Sediments of the Sea Area Around Xiamen.

Station	αHCH	γHCH	ΣHCH*	ppDDT	ppDDD	ppDDE	ΣDDT
1	0.12	0.23	0.35	2.20	1.52	0.73	4.45
2	0.17	ND	0.17	263.00	35.00	12.60	311.00
3	ND	ND	0.78	7.75	7.13	2.25	17.40
4	0.08	0.63	1.12	8.08	4.45	1.65	14.20
5	0.07	0.19	0.26	2.35	3.02	1.32	6.69
6	0.14	ND	0.14	1.75	2.69	1.04	5.48
7	0.10	0.29	0.39	4.91	3.75	1.30	9.94
8	0.09	0.24	0.33	6.20	3.36	1.24	10.80
9	0.14	0.35	0.49	2.20	2.15	0.75	5.20
10	0.07	0.01	0.08	1.22	1.26	0.51	2.29
11	0.06	0.01	0.07	4.06	2.46	1.04	7.56
12	0.05	0.03	0.08	5.88	2.37	0.91	9.16
13	0.03	0.03	0.06	1.42	1.22	0.46	3.10
14	0.02	0.46	0.48	1.22	1.30	0.52	3.04
15	0.03	0.03	0.06	1.14	1.32	0.51	2.97
16	0.03	0.06	0.09	2.34	1.08	0.53	3.95
17	0.11	ND	0.11	2.36	2.02	0.61	4.99
18	0.02	0.01	0.03	1.42	1.51	0.60	3.53
19	0.03	0.02	0.05	3.36	1.57	0.72	5.85

βHCH sometimes contribute to the total HCHs
ND= no data

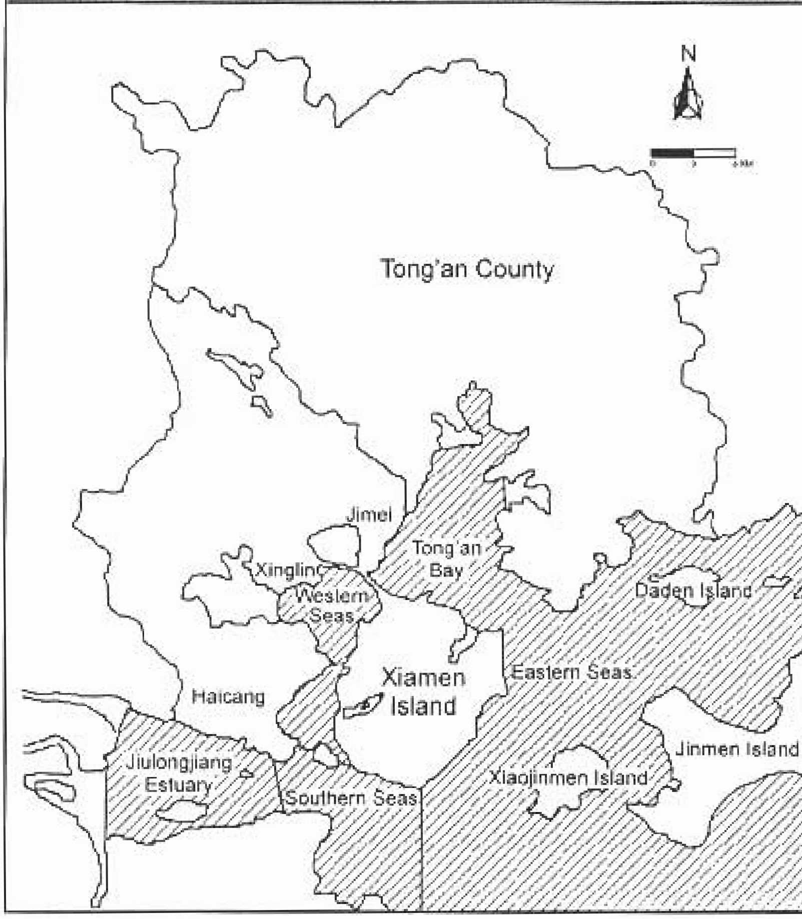
Table 26. Concentrations (ng/g dw) of HCH and DDT in Two Sediment Cores.

	Depth (cm)	αHCH	βHCH	γHCH	ΣHCH	ppDDE	ppDDD	ppDDT	ΣDDT
Eastern Sea	0-3	0.19	0.06	0.04	0.29	1.25	3.26	2.81	7.32
1	3-6	0.20	0.08	0.04	0.32	1.54	3.70	5.22	10.50
	6-9	0.08	0.05	0.03	0.16	1.54	2.95	2.84	7.33
	9-12	0.16	0.05	0.03	0.24	1.19	2.57	2.45	6.21
	12-15	0.07	0.05	0.03	0.15	1.19	2.05	1.40	4.64
	15-18	0.16	0.03	0.03	0.22	1.24	2.25	2.27	5.76
	18-21	0.05	0.03	0.04	0.12	1.18	1.61	2.00	4.79
Western Bay	0-3	0.07	0.06	0.04	0.20	6.00	47.60	105.00	159.00
5	3-6	0.06	0.10	0.02	0.18	1.70	3.46	2.68	7.84
	6-9	0.08	0.15	0.04	0.27	1.85	3.19	6.44	11.50
	9-12	0.06	0.08	0.03	0.17	0.86	2.01	1.01	3.88
	12-15	0.10	0.12	0.03	0.25	0.99	1.65	1.55	4.19
	15-18	0.09	0.18	0.04	0.31	1.73	3.37	3.22	8.32
	18-21	0.08	0.13	0.03	0.25	1.60	2.90	0.95	5.45
	21-24	0.11	0.09	0.03	0.23	1.18	2.81	1.51	5.50
	24-27	0.08	0.09	0.03	0.20	1.26	2.44	0.68	4.38
	27-30	0.14	0.13	0.04	0.31	1.12	1.87	0.66	3.65
	30-33	0.09	0.08	0.03	0.20	1.40	1.86	1.15	4.41
	33-38	0.10	0.11	0.03	0.24	1.59	1.82	1.01	4.42

inputs in Stations 2 and 5 of relatively high levels of DDT have been detected. This is probably due to occasional use against human parasites (mosquitoes, lice, etc.).

The absolute concentrations are not very high in the sediment. However, such concentrations could allow a partition toward marine organisms causing bioaccumulation and subsequently biomagnification. Some data on concentration in marine organisms have been published and will be referred to in the following paragraphs. The problem is to determine if the detected concentrations could have some unwanted effects on marine organisms, or if there is the possibility of problems for human health when such organisms are consumed.

Figure 12. Sampling Stations in the Xiamen Seas.



Physico-chemical Properties and Environmental Partitioning

The following properties for DDT and HCH of particular environmental interest are listed below:

	DDT	HCH
Molecular Weight	355	291
Water Solubility (g/m^3)	$4 \cdot 10^{-3}$	7.3
vapor pressure(Pa)	$2.5 \cdot 10^{-5}$	$5.6 \cdot 10^{-3}$
log K_{ow}	5.7	3.8

These molecules will be modelled as the compound in the environment. Both of them have been very persistent; DDT for several years; γHCH for a few years.

An EQC run has shown the following partition for Level I:

	DDT (%)	HCH (%)
Soil	96.600	82.600
Sediment	2.146	1.837
Suspended Solids	0.067	0.057
Water	0.218	14.800
Air	0.978	0.666
Biomass	0.005	0.004

These molecules have both a strong

tendency to partition into soil/sediment systems, a limited affinity for air (0.97 and 0.66%, respectively) but lindane also has a certain affinity for water.

An Attempt for a Mass Balance for DDT and HCH in the Xiamen Seas

For a risk assessment in relation to the past use of DDT and HCH, it is not only necessary to have the actual concentration in sediments or in selected marine organisms, but to have an idea if there are new inputs, whether the situation is stable (steady-state among components) and how much of the total quantity present could constitute the load towards other environmental compartments. The relative constancy of concentrations in sediment cores indicates that no new inputs are occurring (except the limited situation discussed above).

The total load can be calculated by modelling the marine ecosystem around Xiamen and utilizing the actual concentration in sediments to calculate the load in the sediment and then the equilibrium concentration in generic aquatic organisms. The model is similar to a fugacity model Level I with the volumes of compartments represented by marine waters (no soil), sediments, air above marine areas and the biomass of aquatic organisms that could be present in the Xiamen Seas.

The relative volume of the seas around Xiamen are listed below:

	Area ($x10^6m^2$)	Water volume ($x10^8m^3$)
Western Bay	47.5	1.7
Jiulongjiang Estuary	85	3.4
Southern Seas	88	3.5
Tong'an Bay	91.7	2.8
Eastern Seas (part)	90	1.0
Total	392.2	12.4

Sediment depth that could exchange the chemicals was assumed to be 0.20 m, the total sediment volume being $78.4 \cdot 10^6$ m^3, with an organic matter content of 1.5%.

The volume of the air compartment was calculated at 392.2 $m^3 \cdot 10^9$ assuming the air column to be 1,000 m high. The biomass in the scenario could be taken as 30,000 tonnes; that is, the annual production of aquaculture summed up with 20,000 tonnes of standing biomass of various types (fish, benthos, etc.).

If 100 moles of DDT and HCH, respectively, were introduced into this system, the partitioning in the Xiamen scenario would be as follows:

	Volume (m^3)	% Distribution	
		DDT	HCH
Air	$392.2 \cdot 10^9$	0.064	0.43
Sediment	$78.4 \cdot 10^6$	99.58	84.15
Water	$12.4 \cdot 10^8$	0.227	15.20
Biomass	$50 \cdot 10^3$	0.128	0.208

The average total DDT in the first 20 cm sediment cores (removing the surface outliers) has been calculated at 6.665 μg/g dw. Assuming 10% dw on wet weight, it will be 0.665 μg/g or 0.665 mg/m^3. This value multiplied by $78.4 \cdot 10^6$ m^3 gives about 52 kg of DDT in sediments in the seas around Xiamen. If only 0.128% is in the aquatic biomass, it could be about 66 g in this last compartment. This value in a biomass of 50,000 t gives $1.32 \cdot 10^{-3}$ mg/kg wet weight of aquatic biomass and 0.013 mg/kg in dry weight.

Fish from the Xiamen area have a ΣDDT content of 0.031 mg/kg dw; fish from Daden Island have 0.045; while mussels and oysters from Xiamen have 0.004 and 0.017, respectively (Center of Environmental Science Study, Xiamen University, Prof. L. Zhang, pers. comm.). Repeating the same calculation for total HCH with an average of 0.21 μg/g dw in the first 20 cm of sediments gives 1.65 g in the total sediments of the area and about 4 g in the aquatic biomass. This last value gives 0.0008 mg/kg dw.

Prof. L. Zhang also found analytical values of 0.001-0.015 in fish from Xiamen and Daden Island and 0.001 in both oysters and mussels.

The fugacity model used in the Xiamen scenario is a thermodynamic model that assumes equilibrium and, considering all the assumptions and approximations made, gives results with a certain coherence between calculated and measured concentrations and this could indicate a steady-state condition.

Risk Assessment for DDT and HCH in the Xiamen Seas

The Xiamen Seas are contaminated by DDT and HCH being present in sediments and aquatic organisms. If one considers the People's Republic of China Assessment Standard for Sediments (ITTXDP, 1996) of 0.5 μg/g, HCH concentrations are much lower while DDT concentrations are at the limit in some cases and lower in many others. In a very few cases, DDT concentrations exceed the maximum allowed value. Concentrations in aquatic organisms are within the acceptable standards for human consumption (0.1 mg/kg ww for DDT in EU; 5 mg/kg fish in the USA; for HCH, USA EPA indicates 0.1-0.5 mg/kg for various food).

From mass balance and sediment core analysis one can also infer that there is no major recent contamination. A constant flow from soil runoff is reflecting past use and a total load of about 50 kg DDT and 5 kg HCH in the seas around Xiamen. These concentrations will probably give rise to aquatic food contamination in the near future but with high probability to the same extent as now, within acceptable legal standards.

Conclusions and Recommendations

Initial risk assessment of the impact of major agricultural activities, focusing on the use of pesticides, has been reported. The process has undergone four major steps:

- listing the pesticides applied and evaluating those utilized in greatest quantity;
- ranking the pesticides for preliminary risk assessment in relation to their intrinsic toxicological/ecotoxicological properties and to the physico-chemical properties of environmental relevance;
- running models (EQC Level I, II) to understand the environmental distribution and fate of the chemical substances in a standard environment; and
- applying a site-specific model (SoilFug) utilizing the output of all the three steps listed above to produce site-specific data for risk assessment with a higher degree of realism.

To date, the exact ratio of predicted environmental distribution on observed effect level or water quality objective has not been calculated. In our opinion this ratio should be calculated only when the margin of uncertainty is reduced as low as possible. In our procedure, several factors of uncertainty were present. The estimation of loads of pesticides, the moment of the application in the field, the water balance (input/output) and the variability of soils, etc. are just a few examples of the types of environmental variables influencing the model.

The environmental persistence, the correctness and precision of physico-chemical data in addition to the limited and arbitrarily selected toxicological and ecotoxicological data, are examples of uncertainty regarding the molecular characteristic. It is to be stated, however, that even if precision was lacking, pesticides with the highest risk have been certainly identified, as well as trends and approximate concentrations that could be present in the estuary.

Batangas Bay Region

The observations that were made on the agricultural activities (in respect to pesticide use) in the Batangas Bay Region can be considered very positive: the total load of pesticides is 0.7 kg/ha on the agricultural soil with an average of 0.24 kg/ha on the overall basin. This reflects a relatively low consumption resulting from several components. The Department of Agriculture in Batangas is presently addressing the issue of integrated pest management. This is facilitated by property sizes that are about 2 ha per farm. Several of the most environmentally dangerous pesticides (i.e., organochlorines) have been banned or regulated, as well as some organophosphates with high human toxicity (MTE, 1996). Most of the pesticides available on the market are of the last generation, such as synthetic pyrethroids. Probably, the alternation and mixing of pyrethroids and organophosphates have curbed insect resistance to organophosphates which, under other circumstances, could easily develop. This practice has helped to reduce consumption and has increased the efficiency of treatments.

However, it should be said that the first signal of warning is already appearing from the initial risk assessment and that the consumption of some molecules such as carbaryl should be reduced. No data were available to make a risk assessment for the soil or to forecast the tendency of agricultural development in the near future.

Similarly, no data were available on previous use of persistent organochlorine pesticides such as DDT or HCH, or field data relating to concentrations in various environmental media. Regarding this subject only chemical analysis of organisms and sediments could give elements for risk assessment. Organotin compounds have been utilized in agricultural practices in the past but are now banned. Tributyltinoxyde (TBTO), which has been banned in some countries, is still used in many others as a component of antifouling paints and therefore can be released from ship hulls protected by such paints. The only way to make a risk assessment of organotin compounds is to organize a specific monitoring activity on such compounds. The research should not only analyze aquatic organisms and sediments but should also have a biological monitoring component examining the presence of imposex in benthic organisms. The project could provide important baseline data directly relevant to the future port development in the Batangas Bay Region.

XIAMEN, CHINA

The situation with respect to pesticide use in the Xiamen agricultural area is of major concern. The total load of pesticides on agricultural soil is 27 kg/ha on average. If the calculation is made on the overall catchment area, the load is still very high, 7.6 kg/ha. These values are very high even if compared with intensively exploited agricultural areas. The pesticide market is dominated by organophosphate insecticides which are very toxic to aquatic fauna and very mobile (although short-lived). Fish and aquatic organism kills have been reported, even if their causes have not been established.

Some of these chemicals are volatile and therefore there is a potential risk to human health. Intoxication of people not involved in agricultural production and of some farmers has also been documented. In recent years (1991-1997), hundreds of people have been involved in such events (Prof. L. Zhang, pers. comm.). Because of their high loads, some other groups of chemicals also pose risk to aquatic life. A vigorous action to reduce pesticide consumption and to redirect the market to use less impacting pesticides is absolutely necessary. A master plan to improve and change the actual agricultural practices should also be prepared.

Major points could be:

- Improving pesticide utilization;
- Rotation of insecticide treatments (e.g., organophosphates alternating with pyrethroids);
- Selection of less impacting products (e.g., less mobile organophosphates, synthetic pyrethroids and the new generation of pseudopyrethroids);
- Improving agricultural practices and, whenever possible, introduction of crop rotation systems; and
- Introducing integrated pest management practices.

In conclusion, the present state of pesticide utilization poses a high risk to the aquatic environment and human health, and relevant remedial measures should be undertaken quickly. Monitoring should be systematic and have a design for chemicals that pose high risk to health and the environment. However, because of their very short half-life, the possibilities of being able to detect them could be very limited. To avoid this problem, monitoring utilizing biomarkers (aquatic organisms) should be initiated. Considering the type of chemicals actually used, acetylcholinesterase activities in various marine organisms could be taken as the most appropriate indicator.

In respect to retrospective risk assessment for persistent organochlorine chemicals (DDT, HCH), the situation is not serious for HCH, and DDT is now posing minor risks. However, in consideration of the apparent constant inputs (see sediment cores analysis) for DDT and as the ratio of DDT to its metabolites is still 40 to 60%, a monitoring program should be organized, with strong emphasis on marine biota, particularly fish (data on fish were limited). These studies could be associated with the monitoring of other chemicals such as PCBs or PAHs that are expected to increase in relation to the industrial and commercial (maritime and terrestrial traffic) development in the near future. Regarding this subject, only analysis on organisms and sediments would be needed to give elements for risk assessment.

No data are available on tributyltinoxyde (TBTO) for Xiamen. The only way to make such a risk assessment is to organize an *ad hoc* monitoring investigation on organotin compounds for Xiamen similar to Batangas Bay.

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