CHAPTER 3

STUDY AREA, DATA COLLECTION AND CONCEPTUAL MODELING APPROACH

This chapter provides a detail description of the study area and four phases of modeling procedures: data collection, model creation, model calibration/validation, and, finally, model prediction. The data collection included two types of data, field data and existing data gathered from other studies and government agencies. The model creation phase incorporated all steps in model construction such as segmentation, determination of flow functions, temperature functions, initial conditions, and point and non-point source loads. The model calibration and validation phase demonstrated how the constants and coefficients were adjusted to calibrate the model. The model was subsequently validated with the second set of field data. Finally, the verified model was used as a tool to test different scenarios which could have happened during the fish-kill period.

3.1 STUDY AREA, WATER/LAND USES AND LOADINGS

This section describes in detail the location of the watershed, land uses and its water utilization by local people which result in point and non-point source loadings.

Location

The Pong River is considered in the tributary system of the Greater Mekong River Basin which covers Tibet, China, Laos, Burma, Vietnam and Thailand. The Pong River basin of 1,518,900 hectares (15,189 km^2) is the largest watershed in Northeast Thailand, which is mainly influenced by two types of monsoon wind, the wet southwest monsoon and dry northeast monsoon. The wet southwest monsoon causes the precipitation in September and October. In April and May, the precipitation in this region is affected by tails of typhoons from the China Sea. The average annual rainfall is from 1200-1500 mm (Johnson, 1980; Wijnhoud *et al.*, 2003).

The water from the Pong watershed provides water for electricity generation, agriculture, aquaculture, domestic uses, industrial and recreational purposes. Because of its many uses, the standard of water quality for this river is established as Class 3 as shown in Appendix C by the National Environment Board of Thailand. Being in Class 3, the Pong River water is considered "medium clean" and more suitable for agricultural use. It can be used for consumption if it is treated properly to meet the drinking water standards. Figure 3.1 shows the Lower Pong Watershed within the whole Pong Watershed, which starts from the Ubolratana Dam. The river reach (highlighted) between the Dam and the Nong Wai Weir is under this study. The sampling locations are shown in Figure 3.2.

Sampling points

There were 12 samplings points which were chosen on the basis of their accessibility. They were 1) inside the Dam (water gates), 2) below the Dam (0.2 km from the dam), 3) Known-Sung bridge (1.7 km from the dam), 4) Ban Known-Jik (4.5 km), 5) Ban Nong-Pur (12.0 km), 6) Ban Kum-Bon (15.2 km), 7) Pumping station (17.5), 8) 200-m above Chot (22.3 km), 9) Chot (22.5 km), 10) 200-below Chot (22.7 km), 11) Sua-Ten (24.8), 12) Ban Kum-Pae (26 km), 13) Ban Bua-Noi (29.5 km), and 14) Nong Wai Weir (34 km).

At the Known-Sung bridge, the water was sampled from the bridge in the middle of the river. At sampling points of Chot, Sua-Ten, and Bua-Noi, aquaculture of Nile tilapia was practiced in the river. At the 200-m above and below Chot sampling points, water was picked up from the middle of the stream from a small boat. The rest of the samples were picked up from approximately 2-5 m. from the banks of the river by stepping on boats or other wooden platforms.

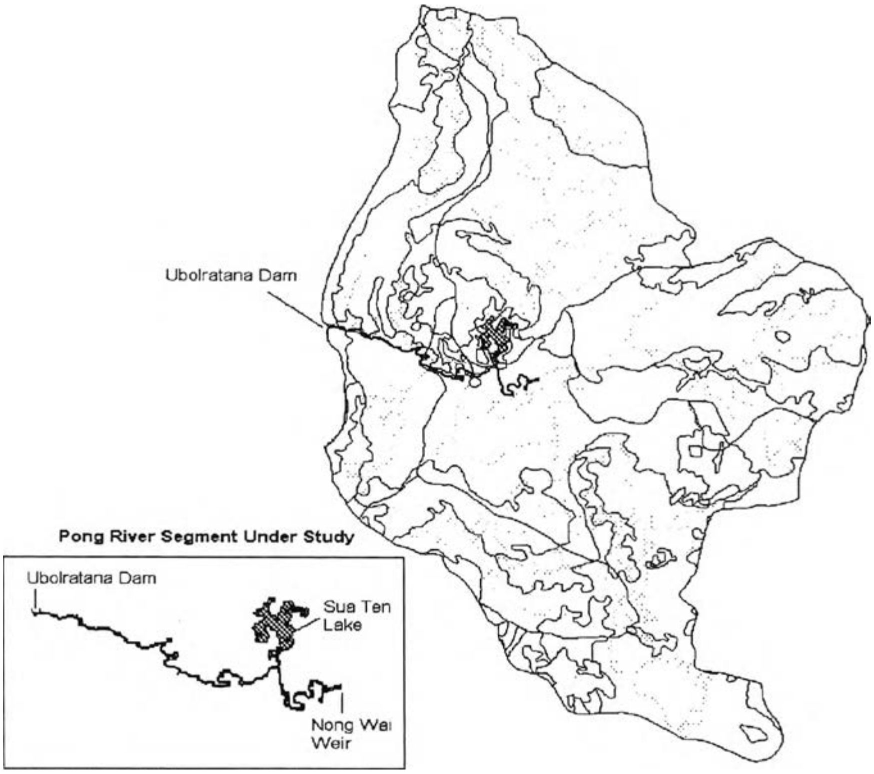


Figure 3.1 Lower Pong Watershed with the River Reach Understudy (inset).

Water Uses

For an agricultural country like Thailand, the Pong River provides the source of income and occupation. It is the "river of life" because all aspects of human activities in this region, either directly or indirectly, involve the use of water from this river. As human activities have increased the use of this river by many folds in the past decade, its assimilation capacity may be in question. This river, therefore, must be monitored regularly, with respect to water quality parameters, to ensure that it can still sustain "life."

Initiated by the U.N. Food Task Force of the Trilateral Commission in the 1977 Report of "Expanding Food Production in Developing Countries," the Ubolratana Hydropower Dam was constructed at approximately 140 kilometers from the upper bound of the Pong River Basin in 1964 to generate electricity and prevent flooding in the Lower Pong River Basin (Trilateral Task Force, 1977).

In addition to the Dam, a weir was constructed at Nong Wai, approximately 35 kilometers from the Dam, to supply large volumes of water for over 48,000 hectares (300,000 rais) of agricultural land. The Nong Wai Weir was supposed to expand food production and improve the economy in this part of the country because it would allow farmers to grow rice twice a year, instead of just once from having to rely on the monsoon rain.

Besides electricity generation and irrigation, the river water between the Dam and Nong Wai Weir has been used by the pulp and paper mill nearby. A mill with a capacity of 70,000 tons/year needs approximately 44,000 m^3/day of water from the river for its operation (CMS, 1999). Up to 1998, the river had also been used for diluting the mill's effluent via the Chot lagoon. Nowadays, the mill uses their treated wastewater to irrigate their Eucalyptus plantation.

Furthermore, the river has been used for aquaculture. Net-pen aquaculture of Nile tilapia started in this river segment in 1997. There are currently four aquaculture sites, namely Huai Sai (HS), Chot (CT), Sua Ten (ST), and Kum Pae/Bua Noi (KP/BN) with capacities of 10,000, 80,000, 200,000 and 100,000 fish, respectively. Their sites with respect to the river are shown in Figure 3.2. Most fish raised at these sites are sex-reversed all-male Nile tilapia (Yi *et al.*, 2003).

Each net pen, with a dimension of 4-m W x 4-m L x 3-m D, can raise from 1000-1200 fingerlings. The fish is fed about two to three times a day. For 1000 fingerlings at 50 g each, two kilograms of fish feed is given three times a day. For larger-sized fish, up to 20 kg is given per day. Fish feed has a composition of 30-33% protein and 3% fat. Floating pellet of feed is given to fish at least twice daily at rates of 3–10% body weight at 8:30 AM and 3:30 PM.

Water from this river is also used for domestic uses. The water from this river is pumped and treated by bottling companies; therefore, it is not used directly for drinking.

Finally, the river is used for recreational activities. During the Songkran Festival from April 12th-15th of every year, a mass of people use water in this area for their celebration and water-related plays. Since the massive fish kill in 1997, the regular recreational activities of people below the aquaculture sites (below the Nong Wai Weir) dropped. People have now been concerned about their safety and the water quality in this river segment.

Land Uses

According to the 1:50000 military maps updated by spot satellite imagery in 1992, the use of the Pong River watershed can be grouped as shown in Table 3.1. Agricultural uses in this watershed accounted for approximately 71%. Johnson (1980) showed that within ten years from 1965-1975 after the Dam was built, the forest land in the Upper Pong watershed declined by 47% and the agricultural land increased by 184%. The draw-down zone, which was the area between the highest and lowest water levels around this reservoir, was leased to farmers for agricultural activities, mostly rice-farming (Johnson, 1980). The trend of landscape change in the Pong Watershed was similar to the whole Northeast Thailand (Walsh *et al*, 2001) and Southeast Asia (Fox, 1990).

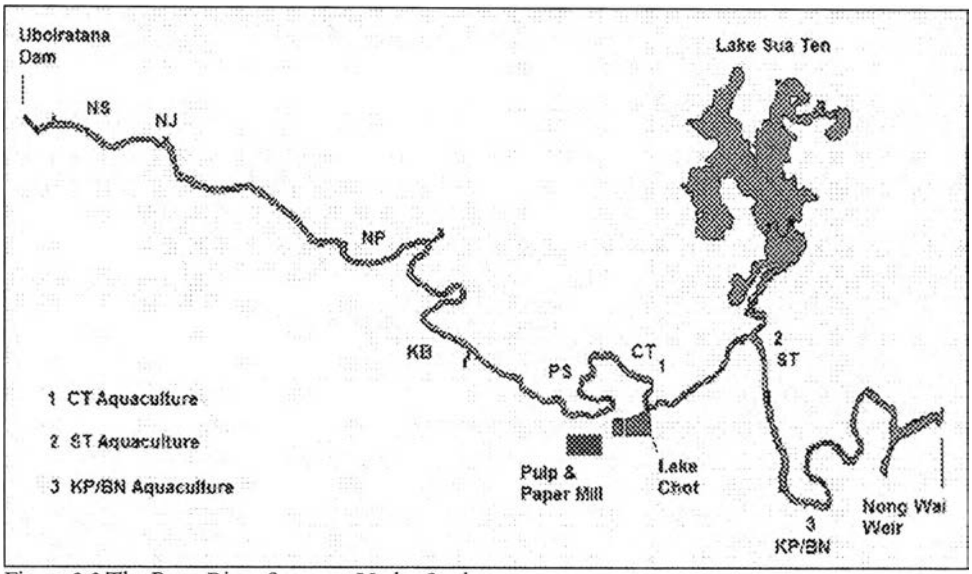


Figure 3.2 The Pong River Segment Under Study.

Table 3.1 Land Uses of Pong Watershed in 1992. (Source: 1992 Updated Spot Satellite Imagery Military Map)

Land Use	Rai	Hectare	%
Paddy field	2,930,000	46,880	32
Paddy field/Orchard	1,600,000	25,600	17.5
Orchard	1,400,000	22,400	15.3
Orchard/Forest	600,000	9,600	6.5
Forest	2,200,000	35,200	24
Uncultivated land	200,000	3,200	2.4
Water body	220,000	3,520	2.3
Total	9,150,000	146,400	100

(1 hectare = 6.25 rai)

Agricultural runoff

Agricultural runoff is often cited as the reason why water quality in a water body has deteriorated (Vezjak *et al.*, 1998; Comin *et al.*, 1997, Anderson and Flaig, 1995). Agricultural runoff contributes pesticides and nutrients such as nitrogen and phosphorus from fertilizers which are necessary for the algal growth. When the algal growth is significant in the river, the river bottom is covered with green substances. Green bottom was the exact description of the Pong River in this study, by survey. The reservoir could also be affected by the agricultural runoff from the draw-down zone. The agricultural runoff BOD_5, NH_3-N, NO_3-N, and TKN in Thailand has been reported at concentrations of 2.67, 0.32, 0.01 and 2.4 mg/L, respectively (Simachaya, 1999).

Golf Course Runoff

Phosphorus and nitrogen leached from high-porosity golf greens can adversely affect surface water quality. In particular, phosphorus in runoff is mostly in the soluble form which is immediately available to algae (Sharpley and Menzel, 1987). Marshall *et al.*, (2001) demonstrated that sandy soils in golf greens resulted in higher movement of NO_3-N to subsurface waters than finer textured soils. Experiments were carried out in greenhouse and field lysimeter to determine the effects of different formulas of fertilizer sources on P and N leaching from simulated golf greens. Phosphorus appeared in the leachate later than nitrate-nitrogen, and the highest concentrations were for the soluble 20-20-20 and the 16-25-12 starter fertilizers, with 43% of the applied P eluting in the leachate (Shuman, 2003).

Aquaculture Point Source Loading

Both fish feed and fish excretions contribute nitrogen and phosphorus to the river. Commercial fish feeds are often formulated to contain a slightly higher level of a nutrient than is required by the species for maximum growth. Unfortunately, the extra nutrient contributes in part, to the excess waste from fish. Phosphorus utilization in various tilapia culture systems is found to range from 10 to 20% (Schroeder *et al.*, 1991). Approximately 80% of the phosphorus in wastes from aquaculture is in solid form as feces or uneaten food (Ramseyer and Garling, 2000). Significant amounts of phosphorus and other nutrients may leach from small fecal fragments within an hour.

Fish feed is usually formulated to contain between 30-32% protein depending on the brand. Protein is the source of nitrogen input into the aquaculture system. Fish utilization of nitrogen is between 20-32% (Brunty *et al.*, 1997), and the rest of nitrogen is released into the water.

Industrial Point Source Loading

The pulp and paper mill produced approximately 15,750 m^3/day of effluent with the water-quality parameters as shown in Table 3.2. There was a long period of spillage of untreated wastewater into the Chot lagoon connected to the Pong River.

Table 3.2 Water-Quality Parameters in Mill's Effluent Before and After Treatment. (Source: EMS, 1995)

Parameters	Untreated Wastewater from Plant No.1	Untreated Wastewater from Plant No.2	Treated Wastewater
pH	6.42	6.82	7.78
COD (mg/L)	-	-	31
BOD_5 (mg/L)	289	138	5.5
SS (mg/L)	589	341	22
DS (mg/L)	1,938	1,783	1,510
TKN (mg/L)	14.4	44	2.3
TP (mg/L)	11.5	-	5.2
PO_4-P (mg/L)	35.3	12.7	15.8
Phenols (mg/L)	0.24	0.055	0.045
Sulfide (mg/L H_2S)	-	-	0.08

3.2 EXISTING DATA SURVEY AND DESCRIPTION

There were two types of data needed in this study. They were existing and field data. The existing data were collected from literature and various government agencies. Due to the time and budget constraint, the main source of information used in this study were existing data. Where the existing data were not available, the field data were collected. Thus, the objective of the field data collection was to fill data gaps in the data sources. Both existing and field data could be categorized into three groups, water quality data, water transport data, and pollutant loads.

3.2.1 Water Quality Parameters

The existing data on the conventional nutrients were considered for investigation in this study because, as mentioned in Chapter 2, the water quality is usually the major contributing factor to the fish kills. A detailed water quality data was imperative for this study. Fortunately, weekly-sampled data of the conventional nutrients, namely NH_3-N, NO_3-N, BOD_5, DO and ON (determined from TKN) in the 1999 and 2000 water quality monitoring studies were available from the Department of Industries (Wongphathanakul *et al.*, 1999, 2000). During the monitoring study, there were fish kills from May 9th-10th, 1999, and none in 2000. The advantages of using the 1999 and 2000 monitoring data were that they were monitored on a weekly basis, and relevant information such as the water temperature and visual descriptions of the water were included. Moreover, the fish kill could be examined by comparing the water quality between these two years.

Interesting observations from the 1999 study are described as follows. In the 1999 study, there were two water quality measurements on May 3rd, which did not correspond to one another. They were high BOD_5 and high DO at the same time. For examples, in segments NS and NJ, BOD_5 were 4.3 and 4.68 mg/L, while DO were 6.5 and 6.9 mg/L, respectively. DO should have been low in correspondence to high BOD_5. Figure 3.3 shows an example of the contradicting trend at segment NS in 1999.

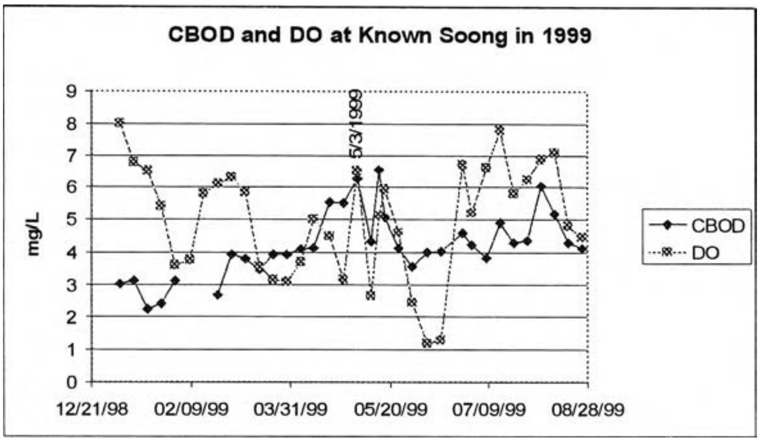


Figure 3.3 CBOD and DO at NS in 1999. On May 3rd, 1999, CBOD and DO did not correspond to each other. They were both high.

There were high NO_3-N concentrations in the reservoir from April 26th - May 10th, 1999 and on July 28th, 1999 from possible nitrate leaching and/or runoff (Figure 3.4). From the rainfall data at two meteorological stations in Appendix D, there was altogether approximately 0.21 m of average rainfall from January 1st - April 26th, 1999, and 0.14 m of average rainfall in July. Although NO_3-N was non-toxic, it could indirectly cause algal nuisance because it was the secondary nutrient for algal growth. The increase of NO_3-N in the reservoir corresponded to the increasing trend observed in Thailand. In the northeastern watershed, NO_3 -N increased from 0.46 mg/L in 1978-1981 to 1.91 mg/L in 1996 (Tonmanee and Kanchanakool, 1999).

High NH_3-N was observed in the reservoir from May 17th - 31st, 1999, as shown in Figure 3.4. NH_3-N can kill fish at high concentrations or cause algal growth as NH_3 was its primary nutrient. However, high NH_3-N in the Dam from May 17th and 31st, 1999 could not be responsible the fish kills because the fish kills preceded high NH_3-N. The cause of high NH_3-

N from May 17th-31st, 1999 could be due to either the agricultural runoff or algal death. If NH_3-N in the Dam was due to the agricultural runoff, it should have also appeared with NO_3-N from April 26th-May 10th, 1999 (Figure 3.5).

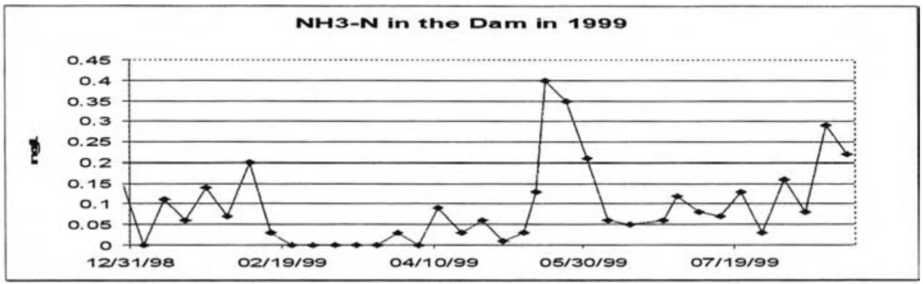


Figure 3.4 NH_3-N into the Reservoir on April 26th and May 10th, 1999.

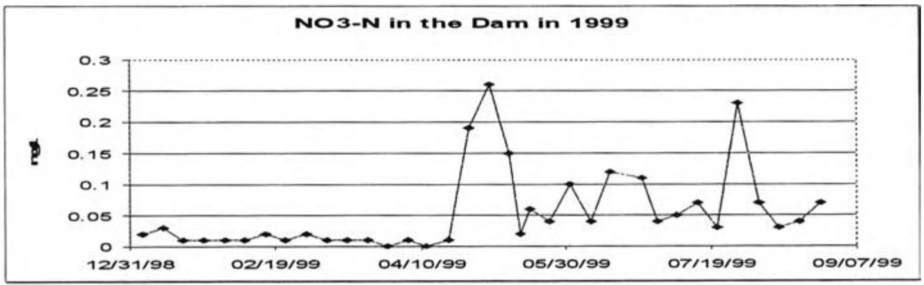


Figure 3.5 NO_3-N into the Reservoir on May 3rd and July 28th, 1999.

It should also be pointed out that in the 1999 and 2000 monitoring studies, the water samples were not filtered before the measurement of BOD_5. It was possible that BOD_5 might be contaminated with live algae as this river was eutrophic. The algorithm of BOD_5 in equation 3.3 includes the contribution of BOD_5 from only dead algae, not live algae. If the BOD_5 data from the 1999 and 2000 were to be used for constructing the model, the possible contamination should be taken into consideration; whenever the algal bloom was suspected, the BOD_5 and DO data should be excluded.

In addition to conventional nutrients, metals and pesticides had also been monitored in this segment of the Pong River from 1999 - 2001 by PCD. Their data on metals and pesticides are summarized in ranges and shown in Table 3.3 (PCD, unpublished results). There seemed to be no violation of the standard quality with the metals and most of the pesticides. Conclusions could not be made on organochlorine pesticides such as α-BHC, aldrin, heptachlor-epoxide, and dieldrin since their standards were established below the detection limit. Their extremely low concentrations agreed with other findings in the other main rivers of Thailand (Boonyatumanond *et al.*, 2001). Endosulfan was not allowed to be used in the rice fields and restricted for other uses in Thailand due to the 1993 decision in the Philippines of the United Nations Food and Agriculture Organization (Hoechst, 1991; IRPTC, 1993; PRC, 1994). Conclusion should not be made yet whether the metals or pesticides caused the fish kills because they were not sampled just before the fish kill incident. Considering the fact that there was no mining operation in this river segment, the likelihood that heavy metals were the cause was very small. The presence of pesticides during the fish kills was checked by GC/MS in this study which will be discussed in chapter 4.

Table 3.3 Ranges of Metal and Pesticides Found by PCD from 1999 - 2001.

Water Quality Parameters	Range	NEB Standard*1
Cd (μg/L)	<0.01 - 0.18	50
Cr (μg/L)	<0.15 - 0.97	50
Mn (μg/L)	0 – 65	1000
Ni (μg/L)	<1 – 9.2	100
Pb (μg/L)	<0.45 – 1.6	50
Zn (μg/L)	<0.01 - <10	1000
Cu (μg/L)	<0.3 – 1.1	100
Hg (μg/L)	<0.01	2
α-BHC (mg/L)	<0.005	0.00002

Heptachlor (mg/L)	<0.01	0.2
Aldrin (mg/L)	<0.02	0.0001
Heptachlor-epoxide (mg/L)	<0.005	0.0002
Dieldrin (mg/L)	<0.01	0.0001
Endrin (mg/L)	<0.01	No STD
p,p'-DDT (mg/L)	<0.01	1

*1 National Environmental Board of Thailand

3.2.2 Flow Data

The flow data was obtained from the Electricity-Generating Authority of Thailand (EGAT) which was in charge of releasing water from the Dam. As the daily Dam release was in the unit of MCM (mega-cubic meter), the average daily flow was determined by multiplying the daily Dam release by 1,000,000 to convert to the appropriate unit and dividing it with the total number of seconds in a day (86,400 seconds).

Figures 3.6-3.7 show the daily volumes released from the Dam in 1999 and 2000. According to Figure 3.6, the daily volumes between April 22nd and June 17th, 1999, except on April 26th were below one mega-cubic meter. A minimum volume released by the Dam was established at one mega-cubic meter by EGAT, to sustain living organisms in the river (EGAT, 2002). It was important to point out that the fish kills from May 9th and 10th, 1999 occurred during the lowest water volume released from the Dam.

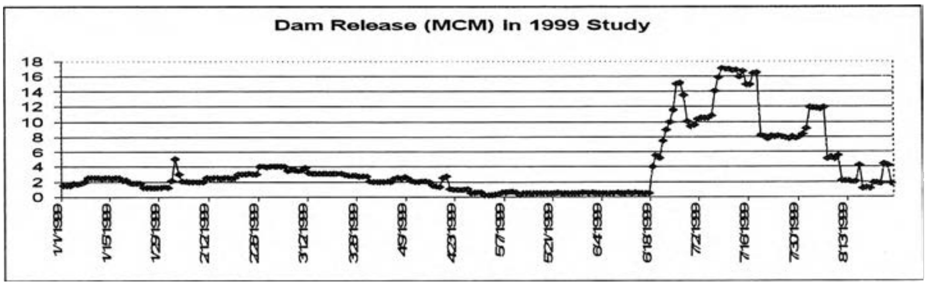


Figure 3.6 Daily Release in MCM from the Reservoir in 1999.

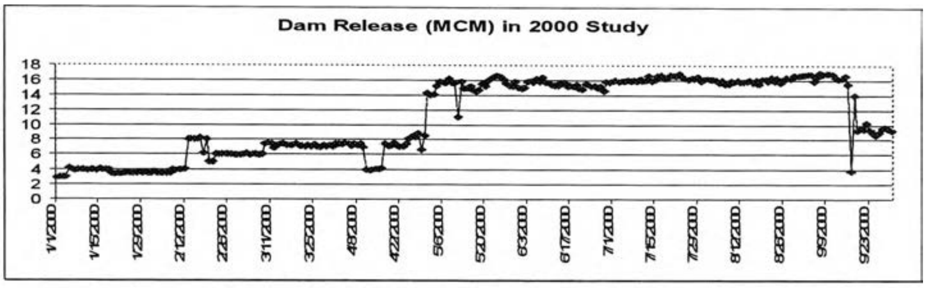


Figure 3.7 Daily Release in MCM from the Reservoir in 2000.

3.2.3 Meteorological Data

The 1999 and 2000 weather data of daily rainfall and mean dry temperature were obtained from the Computer Center at Khon Kaen University. The rainfall data were collected by the Department of Meteorology at the Khon Kaen and Ta Pra stations. The maximum, minimum and mean dry temperatures were only collected at the Khon Kaen station. No known reliability was reported. The rainfall data was only used for checking that the amount of runoff calculated in Section 3.1.4 corresponded with the rainfall data. The rainfall and the daily runoff for 1999 and 2000 are shown in Appendices D and E. As this study attempted to create a refined dynamic model to study the fish kill, the daily mean dry temperature for 1999 in Appendix F from April 26th - May 10th were used to interpolate the missing water temperatures for studying the predictive capability of the model.

3.2.4 Water temperature

The water temperature determines the rate at which all biological mechanisms proceeds in the water quality model. In this study, the water temperatures were obtained from the 1999 and 2000 studies, which recorded the water temperature at each site. Appendix G shows the temperatures of the water samples in 1999 and 2000. It should be pointed out that on May 3rd, 1999, a week before the fish kill event, the water temperature rose to 31 ^{0}C, which was the second highest in the year; the highest temperature in 1999 was 32 ^{0}C on July 21st, 1999.

3.2.5 Runoff Data

Urban and agricultural runoff contributes to the poor quality of the river. The daily runoff data for the river segment of this study were obtained from the Department of Royal Irrigation (RID) at Nong Wai. Equation 3.1 was used to measure the total daily runoff into the segment between the Dam and the Weir. Equation 3.1 assumes that the difference between the Dam release and Weir release is the lateral (point source from drains and diffuse source) inflow (Honisch *et al.*, 2002). Since the mill completely stopped releasing its effluent to the Chot lagoon in 1998, and the study area was agricultural farmland, this study assumed that most of the lateral inflow came from the agricultural runoff.

$$Q_{lat} = Q_{Dam} - Q_{Weir} \qquad [3.1]$$

where:

Q_{lat} = Lateral inflow (m^3)/day)

Q_{Dam} = Dam release (m^3/day)

Q_{Weir} = Weir release (m^3/day)

The amount of water pumped from the river by the mill (44,000 m^3/day), was added to the lateral inflow to account for the loss. The above equation was correct as long as the water level in the river was kept constant. In this study, the daily water levels were relatively the same. The runoff data in 1999 and 2000 are shown in Tables 3.4 and 3.5.

3.2.6 Cross Sectional Data

The cross sectional data of the Pong River segment under this study was necessary for the construction of the model, assignment of sampling locations and determination of the initial volume of each small segment. The cross sectional data was obtained from EGAT, which were measured in 1985. Appendix H shows the cross sectional areas and the sampling location in each segment. From the cross sectional data, the initial segment volumes were defined with the sampling sites as shown in Appendix I, and discussed in the section of the model developing steps. These initial volumes were later adjusted during the calibration of the transport model.

3.2.7 Non-Point Source Loading Data

BOD_5, NH_3-N, NO_3-N, and TKN in the agricultural runoff of Thailand were determined by Simachaya (1999). Data on other land uses were obtained from available documents from the Pollution Control Department, Thailand (1997), and adapted from Newell *et al.* (1992), as shown in Table 3.4.

Table 3.4 Conventional Nutrients from Literature and Available Documents.

Land Use	Land-Use Code*[1]	mg/L				
		BOD_5	NH_3-N	NO_3-N	TKN	ON*[2]
Urban*[3]	U	15	0.50	0.20	1.80	1.1
Agriculture*[4]	A	2.67	0.32	0.01	2.40	2.07
Forest*[5]	F	1.5	0.05	0.01	0.10	0.02
Industry*[3]	I	20.0	0.50	0.20	1.20	0.50
Golf course*[3]	G	1.5	0.30	0.2	1.25	0.75
Water body*[4]	W	1.6	0.10	0.20	0.86	0.56

Remarks:
*1 Code for the GIS database
*2 ON = TKN - NO_3-N - NH_3-N (Ambrose, 1997)
*3 from the Pollution Control Department, Thailand (1997)
*4 from Simachaya's Study (1999)
*5 adapted from Newell *et al.* (1992)

3.2.8 Point Source Loading Data from the Mill's Effluent

Before 1998, one of the major point sources of pollution was the pulp mill's effluent, and its water quality parameters were previously shown in Table 3.2. After 1998, the mill claimed that it completely used all of its effluent to irrigate its Eucalyptus plantation. Since this study attempted to construct a model from the 1999 and 2000 data, the point source loading due to the mill was thus inapplicable for this study. If there was a small amount of effluent's spill into the river, the model already accounted for it by using the water quality parameters from The Chot lagoon as a boundary input into the river.

3.2.9 Sediment Oxygen Demand (SOD)

The concentration of SOD in the Pong River was previously measured to be 0.50 $gO_2/(m^2 \cdot d)$ (Wirojanagud, 2002) which was similar to the average SOD of 0.60 $gO_2/(m^2 \cdot d)$ from the Tha Chin River (Simachaya (1999). The concentration of SOD was initially set to 0.50 $gO_2/(m^2 \cdot d)$ in this study.

3.2.10 Carbonaceous Biological Oxygen Demand (CBOD)

CBOD is one of the parameters required by WASP 6.1. Since only the BOD_5 data were available in the 1999 and 2000 studies, CBOD were estimated by multiplying BOD_5 with a factor of 1.46, as suggested by US EPA (1987).

3.3 FIELD DATA COLLECTION AND DESCRIPTION

A field collection of data on the phenols, and other compounds which might be toxic and could be detected with GC/MS during the fish kill were considered for investigation in this study. Field data collection is the most expensive step in any water quality study. Before planning on what data should be collected, a search of existing data should be performed first. After the sample collection, the laboratories at Khon Kaen University were used for analyzing the field samples, if not specified.

3.3.1 Non-Point Source Loading of PO_4-P from Paddy Fields

In the 1999 and 2000 water-quality data, there was one very important parameter which was left out; it was PO_4-P. This parameter was crucial for the study of the fish kill because it could provide information on the eutrophication problem of the river, and thus the possibility of the algal bloom. In the Pong Watershed, sugarcane was grown in addition to rice and fertilizers were applied two to three times per year in the sugarcane plantation. In this study, a field measurement of PO_4-P in the runoff was conducted on July 27th, 2003, which was after there was heavy rainfall with subsequent fish kills at the ST aquaculture. Water samples from the regular paddy field and the paddy field near a sugarcane plantation were collected around Lake Sua Ten for the PO_4-P analysis.

3.3.2 Point Source Loading of NH_3-N from Aquaculture

Aquaculture contributes nitrogen and phosphorus to the river. In this study, the calculation of NH_3-N excretion from aquaculture was based on the following field survey. For 1000 fingerlings at 50 g each, two kilograms of fish feed were given to the fish per meal. The fish were fed three times a day. For 1000 adult tilapias, 20 kilograms of fish feed were given to the fish per day. The composition of nitrogen in protein was 16.5%. Approximately twenty-five percent of nitrogen was assumed to be retained in the fish, and seventy-five percent was released as excretions in both dissolved form (80%, ammonia) and feces (Hargreaves, 2003).

NH_3 loading is shown in Table 3.5 and its calculation in Appendix J. The results of NH_3 loading are calculated in accordance to a literature review in aquaculture (Hargreaves, 2003), with a feed formulation of 30% protein. This feed formulation was found on the package of the feed. The loadings of BOD and PO_4 could not be estimated as easily as that of NH_3 because the amount of BOD and PO_4 in each feed could not specified by the feed industry. Their compositions depend on the source of the raw materials. Apparent phosphorus availability (APA) values range from 19.5 to 50.5% for fish meals (Riche and Brown, 1996).

Table 3.5 NH_3-N released from aquaculture at each location in 1999.

Location	Segment	No of Fish	Total feed of 30% protein (kg/day)	NH_3-N released (kg/day)
CT	7	80,000	1040	30.9
ST	9	200,000	2600	77.2
KP/BN	10	100,000	1300	38.6

In 1999 and 2000, there were only three aquaculture sites, namely CT, ST, and KP/BN. The HS aquaculture started in 2002. Since this study constructed the model from the 1999 and 2000 data, only the NH_3-N loading from the CT, ST, and KP/BN aquacultures were added to the model as the point source.

3.3.3 Point Source Loading of Phenols from the Possible Spill

Toxic chemicals could be the cause of fish kills. This study focused only on a class of phenols because it was one of the parameters in the water quality standard and it has been proven that it was produced by the pulp mill as shown in Table 3.2. Although in 1999, the pulp mill claimed that it completely stopped releasing its effluent into the river, phenols were analyzed in this study in case that the mill spilled some effluent into the river, or that there were some phenols left in the sediment from the past.

Phenols were not monitored in the 1999 and 2000 studies. Thus, both water and sediment samples were collected and phenols measured from July of 2002 to April of 2003 at the same sampling sites as in the 1999 and 2000 studies. In addition, phenols were measured at locations designated as B, C and D in Figure 3.8 to check if there were phenols coming from the mill through Creek Chot.

The sediment was collected with a jaw-like (grab) sampler. Whenever the water samples were not immediately measured for phenols, they were preserved under the same condition as the 1999 and 2000 studies. The procedure for measuring phenols was obtained from the Standard Methods (1995a) 5530, as recommended by the National Environmental Board of Thailand and U.S. EPA. This method is colorimetric with the use of 4-aminoantipyrene. It offers "extreme sensitivity" for measuring phenolic compounds between 1 and 250 □g/L in water with sensitivity of 1.0 □g/L, and in sediment at a concentration as low as 2 □g/L. The materials and methods for phenols analysis are discussed in Appendix K.

The phenolic data from July of 2002 to April of 2003 were separated into two sets for calibration and validation. The TOXI model was calibrated with phenols data from July – December of 2002 and validated with data from January - April of 2003. Theoretically, after calibration and validation with the data set of 2002 and 2003, the model could be used to investigate whether phenols could be the cause of fish kills in 1999 – by using the highest possible concentration of phenols (0.045 mg/L) released by the mill in Table 3.2. If a higher concentration of phenols was predicted in 2000 than in 1999, and fish did not die in 2000, then it is unlikely that phenols were the cause of the fish kill in 1999.

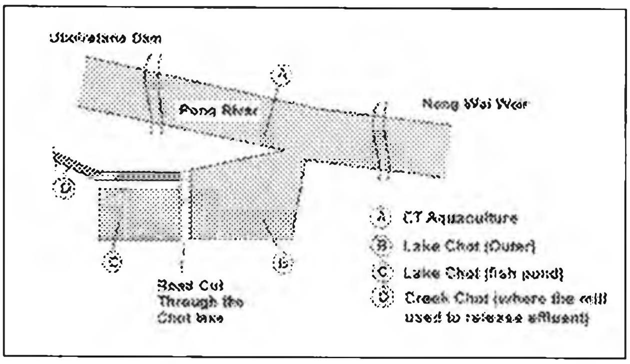


Figure 3.8 The Chot lagoon in 1998. (Notice that the old Chot Lake was cut by a road; the creek was reconnected to the Pong River without going through the fish pond.)

3.3.4 Analysis of Pesticides and Other Chemicals during Fish Kills

Other possible chemicals, such as pesticides, were also analyzed by GC/MS in the river water during the fish kills. A Shimadzu's GC-17A gas chromatograph and a QP-5000 EI quadruple mass spectrometer with a silica capillary column coated with SUPELCO's SPB-1 of 0.25 μm film thickness, was employed according to the method shown in Appendix L. to monitor all suspected organic chemicals. For the GC17A/QP-5000 model, compounds in the range of 0.1 - 0.3 ppt could be detected (Boonyatumanond *et al.*, 2001). The identification of the peaks was initially performed by comparing their fragmentation patterns with known compounds from a large library database. One-gallon water samples from locations NS, NJ, NP, KB, PS, CT, ST, KP/BN as well as locations A, B, C and D in Figure 3.8 were collected and analyzed by GC/MS from March to August of 2002. Water samples from locations B, and D were sampled to check if this creek was contaminated with any organic chemicals released from the mill. Samples from location C were picked up because this location used to be heavily contaminated with untreated effluent from the mill in the past; even though this pond was dredged and converted into a fish pond, there was a report of fish kills in this pond from local people. Similar to phenols, when the water samples were not immediately analyzed, they were preserved in a refrigerator before analysis.

3.3.5 Cyanobacteria and Trophic State

Highly eutrophic river could develop the algal bloom and cause fish kills; therefore, the eutrophic state and cyanobacteria were monitored in this river in 2003. Secchi depth was the parameter measured with a Secchi disc for determining the eutrophic state. As mentioned in Chapter 2, high algal population makes the water less clear and reduces the water depth which the Secchi disc could be seen under the water.

For the cyanobacteria analysis, water samples from location A, B, C and D in Figure 3.8 in the vicinity of the CT aquaculture were collected, preserved by 1% Lugol's iodine solution, and sent to the Department of Microbiology, Khon Kaen University for algal identification and enumeration. The phytoplankton identification and enumeration steps were performed similar to Hu *et al.* (1979). The water samples were concentrated to 30 mL for identification and biomass estimation, after sedimentation for 48 hours. Before counting, the samples were agitated in a high-speed blender for 10-30 seconds to split the colonies into single cells. 0.1 mL concentrated samples were counted directly with a microscope at 400 magnification.

After all data had been gathered and an algal bloom was suspected in the river, modeling would be the most useful tool for the study, as Thomann *et al.* (1987) state, "Without a modeling framework, the discussion of that bloom and its potential causes would have been reduced to an examination of the data, and qualitative conclusion."

3.3.6 Experimental Tilapia Aquaculture

Since there had also been reports of fish kill in the fish pond (location C) in Figure 3.8, an experimental aquaculture of Nile tilapia was set up in this pond and at the CT aquaculture to compare if the fish kill would occur at the same time. If the fish kill occurred at the same time, its cause must have come from the same source. If such was the case, the possibility that the source could be detected by GC/MS should have been higher in the pond than at the CT aquaculture, because the pond could not be easily diluted with the river water as there were only two underground concrete pipes connected between the pond (Inner part of the Chot lagoon) and Outer part of the Chot lagoon.

In this experiment, two schools of 50 Tilapia were raised in separate net pens at points A and C to compare the difference of the fish kill from May 19th to July 7th, 2002. The fish were fed regularly with commercial fish feed twice a day by local aquaculturalists.

3.4 CONCEPTUAL MODELING APPROACH

A model is a "conceived image of reality" or a theoretical construct relating some stimulus to a response (Wool, 2002). In the water-quality modeling, the stimulus is the loading of nutrients into the river, and the response is the water quality in each segment of the river. The relationship between the loading and the resulting water quality is determined by adjusting the transport variables and transformation constants of the water quality parameters until the predicted and observed results are in agreement. This study used WASP 6.1 to develop the model; therefore, the following sections were dedicated to elaborate on the algorithms behind the model, factors affecting modeling approach and steps in developing a model.

3.4.1 WASP 6.1

Water Quality Analysis Simulation Program version 6.1 or WASP 6.1, is the latest, enhanced window version of the original WASP model (Di Toro *et al.*, 1983; Connolly and Winfield, 1984; Ambrose, R. B. *et al.*, 1988). WASP 6.1 is a dynamic compartment-modeling program for aquatic systems, including both the water column and the underlying benthos. It can simulate the impact of natural phenomena and man-made pollution on the quality of water for environmentalists and decision-makers.

In the basic module, the time-dependent processes of advection, dispersion, point and diffuse mass loading and boundary exchange are represented. Water quality processes are represented in special kinetic subroutines. WASP is designed to permit easy substitution of kinetic subroutines into the overall package to form problem-specific models.

WASP 6.1 has four kinetic sub-models to simulate four classes of water quality problems, namely, eutrophication, toxic organic chemical/simple metal, mercury, and thermal/fecal coliform. The eutrophication sub-model called, "EUTRO" is involved with conventional pollution of BOD, DO, phosphate, organic phosphorus, ammonia, nitrate, organic nitrogen, and chlorophyll a. The toxic chemical sub-model, called "TOXI" is involved with organic chemicals, simple metals and sediments. For the Mercury sub-model, elemental mercury, divalent mercury, and methyl mercury can be simulated. Finally, the thermal/fecal coliform sub-model, called "HEAT", is involved with heat and the coliform population.

In the mass balance equations of the EUTRO sub-model, all water quality parameters involved in direct or diffuse loading, advective and dispersive transports, and kinetic transformation must be accounted for. The mass balance equation for BOD, according to Mill *et al.* (1985), is shown in equation 3.2.

The classic steady-state equation, called Streeter-Phelps equation, which is used to estimate DO downstream is shown in equation 3.3.

$$\frac{\partial L}{\partial t} = -\frac{1}{A}\frac{\partial(QL)}{\partial x} - k_L L + L_r\left({}^{\partial Q}\!/_{\partial x}\right)/\,A + L_{rd} \qquad [\,3.2\,]$$

$$D = D_0 e^{-K_a t} + \frac{W}{Q}\left(\frac{K_d}{K_a - K_r}\right)\left[e^{-K_r t} - e^{-K_a t}\right] \qquad [\,3.3\,]$$

where:

L_r = CBOD entering through distributed source (M/L)

L_{rd} = mass flux of CBOD entering with no associated flow (M/L·T)

K_L = deoxygenation rate (L/T)

Q = total river flow (L/T)

x = distance in longitudinal axis (L)

A = cross sectional area (L^2)

D = DO deficit downstream (M/L)

D_o = initial DO deficit (M/L)

K_a = atmospheric reaeration rate (1/T)

t = time of passage from source to downstream location (T)

W = total pollutant loading rate (M/T)

K_d = biochemical oxygen demand (BOD) deoxygenation rate (1/T)

K_r = BOD loss rate (1/T)

The Streeter-Phelps equation can be more complex if it is coupled to other state variables such as sediment oxygen demand (SOD), phytoplankton, and ammonia. The more complexed equation of DO is given by Mills *et al.* (1985) as shown below:

$$\frac{\partial C}{\partial t} = -\frac{1}{A}\frac{\partial (QC)}{\partial x} - k_L L - k_N N + k_a (C_s - C) - S_b + P - R \qquad [\,3.4\,]$$

where:

C = DO (M/L)

A = cross sectional area (L^2)

Q = discharges (L^3/T)

x = distance in longitudinal axis (L)

t = time (T)

K_a = reaeration coefficient (L/T)

K_L = deoxygenation rate (L/T)

K_N = nitrification rate (L/T)

C_s = saturation value of DO (M/L)

S_b = sediment oxygen demand (M/L T)

L = ultimate BOD (M/L)

P = rate of oxygen production due to photosynthesis (M/L/T)

N = NBOD concentration (M/L)

R = rate of oxygen consumption due to photosynthesis (M/L/T)

The equation for NH_3-N without phytoplankton growth and death, is given in equation 3.5. NH_3-N is affected by the nitrification and mineralization of organic matters. For nitrate, factors affecting the level of NO_3 are nitrification, denitrification, mineralization and atmospheric deposition. The equation for NO_3-N without phytoplankton, is given in equation 3.6.

$$\frac{\partial C_1}{\partial t} = K_{71}\Theta_{71}^{T-20}\left[\frac{Chl\,a}{K_{mPC} + Chl\,a}\right]ON - K_{12}\Theta_{12}^{T-20}\left[\frac{DO}{K_{NIT} - DO}\right]NH_3 \qquad [3.5]$$

Mineralization Nitrification

$$\frac{\partial C_2}{\partial t} = k_{12}\Theta_{12}^{T-20}\left(\frac{C_6}{K_{NIT} + C_6}\right)C_1 - k_{2D}\Theta_{12}^{T-20}\left(\frac{K_{NO_3}}{K_{NO_3} + C_6}\right)C_2 \qquad [3.6]$$

Nitrification Denitrification

where:

C_1 = NH_3-N (M/L)

C_2 = NO_3-N (M/L)

C_6 = DO (M/L)

K_{71} = Mineralization rate at 20^0C (T^{-1})

$\Theta_{71}{}^{T-20}$ =temperature coefficient for K_{71}

K_{mPC} = Half-saturation constant for phytoplankton limitation (M O_2/L)

ON = Organic nitrogen (M/L)

K_{12} = Nitrification rate (M O_2/L)

$\Theta_{12}{}^{T-20}$ =temperature coefficient for K_{12}

K_{NIT} = Half-saturation constant for O_2 limitation of nitrification (M O_2/L)

k_{2D} = Denitrification rate (M O_2/L)

K_{NO_3} = Half-saturation constant for O_2 limitation of denitrification (M O_2/L)

Chl a = Chlorophyll a (µg/L)

Factors affecting ortho-phosphate are phytoplankton death, growth, recycle, mineralization of organic matters and atmospheric deposition. The equation for ortho-phosphate is shown in equation 3.7. Factors affecting organic phosphorus are sorption, settling, phytoplankton death, mineralization of organic matters and atmospheric deposition. The equation for organic phosphorus is shown in equation 3.8.

$$\frac{\partial C_3}{\partial t} = D_{P1}\partial_{pc}\left(1 - f_{op}\right)C_4 + k_{83}\Theta_{83}^{T-20}\left(\frac{C_4}{K_{mPc} + C_4}\right)C_8 - G_{P1}a_{pc}C_4 \quad [3.7]$$

Death Mineralization Growth

$$\frac{\partial C_8}{\partial t} = D_{P1} a_{pc} f_{op} C_4 - k_{83} \Theta_{83}^{T-20} \left(\frac{C_4}{K_{mPc} + C_4} \right) C_8 - \frac{V_{s3}(1 - f_{D8})}{D} C_8 \quad [\,3.8\,]$$

Death Mineralization Settling

where:

C_3 = PO_4-P (M/L)

C_4 = Phytoplankton carbon (M/L)

C_8 = Organic phosphorus (M/L)

D_{P1} = Phytoplankton loss rate (T^{-1})

a_{pc} = phosphorus to carbon ratio

f_{op} = fraction of dead and respired phytoplankton recycled to OP pool

K_{mPC} = Half-saturation constant for phytoplankton limitation (M O_2/L)

G_{p1} = Specific phytoplankton growth rate (T^{-1})

k_{83} = Dissolved OP mineralization at 20^0C (T^{-1})

$\Theta_{83}{}^{T-20}$ = temperature coefficient for k_{83}

V_{s3} = organic matter settling velocity (L/T)

f_{D8} = fraction dissolved organic phosphorus

D = segment depth (L)

3.4.2 Factors Affecting Modeling Approach

There are two factors that determine the modeling approach. They are the flow/transport and water quality model complexities as discussed below.

1. Flow/Transport Model Complexity

The complexity of the model relating to the flow or transport could be divided into a) the spatial and b) temporal domains because these domains determine the accuracy of the model in terms of place and time.

a. Spatial domain

This domain is concerned with the required spatial resolution of the model. The spatial resolution for each model application is different due to the length of the river and location. Thomann and Mueler (1987) states that the number of segments depends upon the freshwater flow, hydraulic geometry, wastewater input, and numerical computational constraints. The spatial scales of various water quality parameters are illustrated in Figure 3.9, which gives the maximum distance that a segment should not exceed. If the segment length exceeds the maximum distance, all changes of the parameter would happen within one segment, and defeat the purpose of modeling.

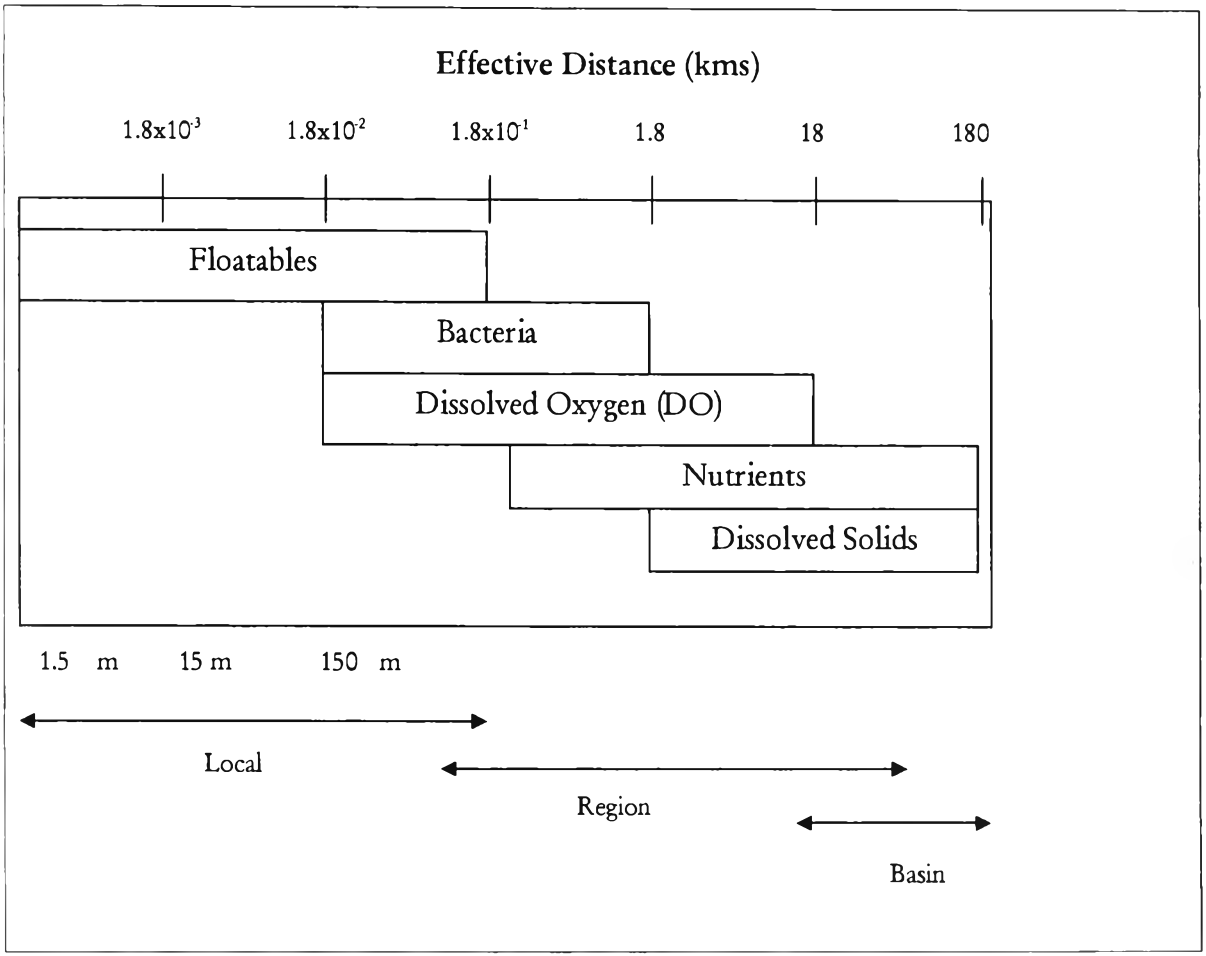


Figure 3.9 Spatial Scales of Water Quality Parameters (adapted from Lung, 1993).

b. Temporal domain

Similar to the spatial domain, the appropriate time scale for modeling a particular parameter is crucial. The temporal scale for different water quality parameters is shown in Figure 3.10. If the time scale of the model is too large, the model would show no changes in the parameter.

Various water-quality problems may be simulated under different temporal conditions as summarized in Table 3.6. There are three categories of temporal conditions, namely i) steady-state, ii) dynamic, and iii) quasi-dynamic (or quasi-steady state).

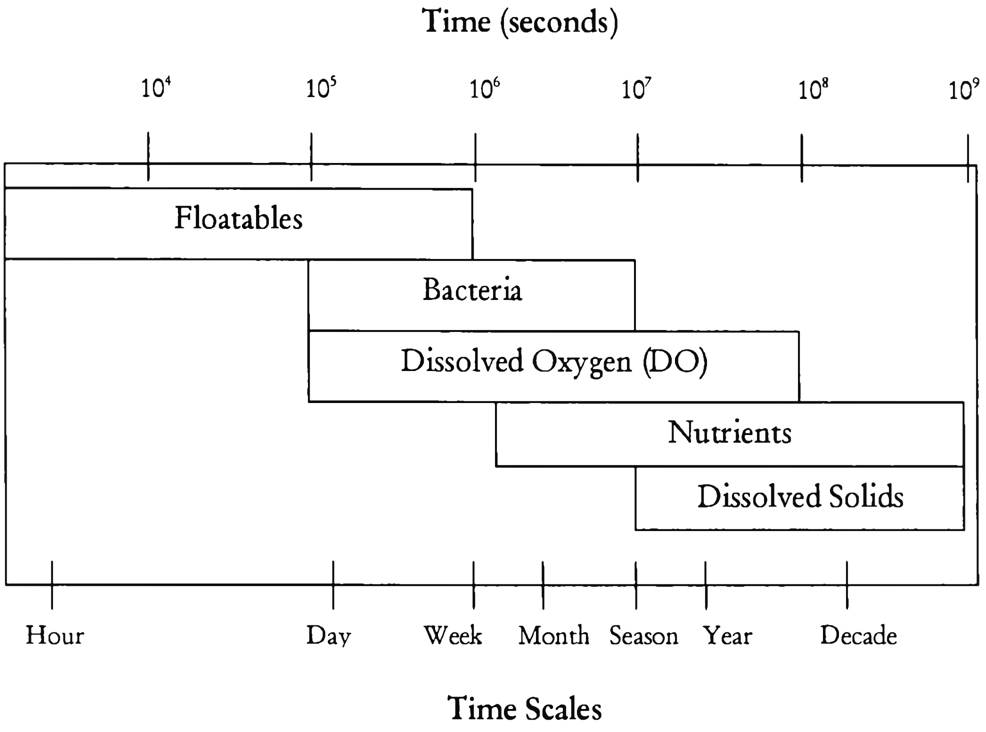


Figure 3.10 Temporal Scales of Water Quality Parameters (adapted from Lung, 1993).

i. Steady-State condition

Under the steady-state condition, the change in the concentration of the water quality parameter is constant as a function of time in the system under study (Chapra, 1997).

ii. Dynamic condition

In the dynamic model, time-dependent flows are used. The dynamic simulation can predict the water quality due to the flows and loads. A good dynamic model requires a coupling of hydrodynamic and water-quality models. The typical approach is to run the hydrodynamic model first and save the output (flows, volumes, depths, velocities) for use by the quality model.

A dynamic simulation is performed when flows are highly variable, such as the flows below the hydropower facilities, the impact of transient inflows such as the storm event and agricultural runoff is to be analyzed or when critical conditions are not known.

iii. Quasi-steady condition

In the quasi-steady condition, a dynamic condition of water quality parameter is simulated but with steady flows (descriptive flows), or the steady-state condition of water quality parameter is simulated with time-variable flows.

Table 3.6 Summary of Temporal Conditions

Condition	Flows	Water Quality	Examples of WASP application
Steady State	Constant	Constant (WASP run in dynamic with constant forcing model until predictions do not vary)	Like traditional WLA analysis (DOSAG, QUAL2)
Quasi-Steady State	Constant	Dynamic	Like QUAL2 analysis with diurnal variations.
Quasi-Steady State	Time-variable inflows but uniform flows through area	Constant or dynamic	Like running QUAL2 with varying flows
Dynamic State	Time Variable	Time Variable	Continuous simulations required where there are variable inflows, loadings, etc.

In this study, the main objective is to determine the cause of the fish kill in aquaculture. Due to the nature of the fish kill which occurs only at a certain period of time in a year, and with varying degrees of severity, a dynamic modeling was preferred to the steady-state modeling because the dynamic modeling could re-create the fraction of time during which the water quality was impaired. In this model, the daily Dam and runoff flows were also used to create a dynamic model.

2. Water Quality Model Complexity

The complexity of the model relating to the water quality parameters can be divided into two types: a) state variables and b) kinetics

a. State variables

The state variables (i.e., conventional nutrients, organic chemicals or metals) involved in the simulation determine what water-quality model (i.e., EUTRO, TOXI, HEAT, or COLIFORM) and of what complexity level is needed. Table 3.7 shows different complexity levels for the simulation of usual nutrients with WASP 6.1. With the available 1999 and 2000 monitoring data of BOD_5, DO, NH_3-N, NO_3-N, and ON, the EUTRO model at complexity level 3 was chosen for this study.

b. Kinetics

The state variables involved in the simulation also determine the types of processes. Processes such as sedimentation and scouring can be added to account for the interaction between the water column and the benthic layer to exemplify an even more complexed model. Since the 1999 and 2000 monitoring reports did not measure the parameters in the sediment, the use of the benthic layers in the model was only for sensitivity analysis. The lack of the sediment data in this study which made the model less complexed did not, however, make this model any less accurate than the more complexed model, as will be discussed below.

Table 3.7 The Level of Complexity for WASP6 Simulation Model of Usual Nutrients.

System	Variable	Symbol	Complexity Level					
			1	2	3	4	5	6
1	Ammonia Nitrogen	NH_3-N		X	X	X	X	X
2	Nitrate Nitrogen	NO_3-N			X	X	X	X
3	Phosphate	PO_4				X	X	X
4	Phytoplankton	*Chl a*				X	X	X
5	Carbonaceous BOD	CBOD	X	X	X	X	X	X
6	Dissolved Oxygen	DO	X	X	X	X	X	X
7	Organic Nitrogen	ON			X	X	X	X
8	Organic Phosphorus	OP				X	X	X

Complexity Level	Explanation
1	"Streeter-Phelps" BOD-DO with SOD
2	"Modified Streeter-Phelps" with BOD
3	Linear DO Balance with Nitrification
4	Simple Eutrophication
5	Intermediate Eutrophication
6	Intermediate Eutrophication with Benthos

Source: Ambrose et al. (1993b)

Model Complexity versus Accuracy

A more complexed model does not imply that it is more accurate in its prediction. Increasing model complexity does not usually result in an increase in the model credibility because the ratio of the model credibility and complexity decreases as the model complexity increases (Thomann, 1992). The model is most credible when it is only moderately complexed. In terms of the temporal condition of the model, a dynamic model may not offer more accurate results when a steady-state model will suffice.

3.4.3 Model Developing Steps

After the complexity level 3 of the model was decided and the necessary data (BOD_5, DO, NH_3-N, NO_3-N, and ON) were collected from either existing or field data, the model was developed. The first step was to calibrate the transport model by adjusting the segment volumes and dispersion coefficients in the TOXI sub-model. After the transport model was calibrated, the same segment volumes and dispersion coefficients were used with the EUTRO sub-model to calibrate conventional nutrients from the 1999 monitoring data. The model was finally validated with a different set of nutrients from 2000.

Data input

WASP 6.1 requires that twelve sets of data must be defined through their particular screens. They are 1) model identification and simulation control, 2) systems, 3) segments, 4) segment parameter scale factors, 5) exchange fields, 6) flows, 7) boundaries, 8) loads, 9) time step, 10) print interval, 11) time function, and 12) kinetic constants. Under the model identification and simulation control, the type of sub-model (i.e., EUTRO, TOXI, Mercury or HEAT) must be selected. The type of sub-model defines the parameters and the systems needed for the simulation.

Conventional Nutrients

In this study, the EUTRO sub-model was selected under the model identification and simulation control when conventional nutrients were considered. Under the systems, parameters of DO, CBOD, NO_3, NH_3, and ON were identified, as these were the only parameters measured in the 1999 and 2000 studies. They could be simulated, bypassed or kept constant as a function of time. This model simulated all parameters although *Chl a* and phosphate were not measured. The effect of the advection and dispersion on a particular parameter could also be determined by comparing the parameters before and after checking on the advection or dispersion bypass boxes.

Under the segments, segment volumes, environmental and constituent concentrations were defined. The segment data entry form had four tables associated with them: 1) Segment Definition, 2) Environmental Parameters, 3) Initial Conditions, and 4) Fraction Dissolved. The segment definition was where the names, segment types (surface, sub-surface, benthic, or sub-benthic) and physical characteristics of the segments were defined. In this model, the initial segment volumes and segment names, which were named after the sampling locations, are shown in Appendix I. By using the 1:50000 map, cross sectional and GIS data, the river reach was divided into small segments of equal volume, with a different sampling location in each segment. Benthic segments were also added to the bottom of each water column for sensitivity analysis of the scouring effect, as shown in Figure 3.10.

These segments should have relatively the same volume in order to make the model stable. After the process of segmentation, the locations of point-source loading and where the small streams meet the river should be in the middle of the segment. These locations should also be above the sampling sites in order to make the measurement representative of the segment (Wool *et al.*, 2000).

Also under the segments, the environmental parameters were the segment-specific information which WASP 6.1 assumed for the model. Some of these parameters could directly define segment-specific information (i.e. SOD), while others could indicate environmental time-dependent functions (i.e. temperature) for the segment. The initial conditions and fraction dissolved give information on the initial concentrations and dissolved fraction of each water quality parameter at the beginning of the simulation. In this study, all dissolved fractions, except that of *Chl a*, were set to zero. The initial concentrations of salinity were set at zero. These values were derived from the concentrations found in the reservoir at the beginning of the simulation. The values of the water temperature time functions for all segments were set to 1, for WASP 6.1 to use the temperatures from the temperature function 1 for calculating its predictions. The temperature function 1 for 1999 and 2000, followed Appendix G. They were obtained from the reported water temperatures at the second sampling point below the Dam (Pong2) in the monitoring studies. The water temperature in each segment was relatively the same; therefore, the water temperature at Pong2 was assumed to be representative of the water temperature at all segments.

Under the segment parameter scale factors, parameters and their scale factors are considered in the simulation. The Use box must be checked before an environmental segment parameter is considered by WASP6.1. Un-checking this box will remove the parameter from the simulation. By default the scale factor was set at 1.0 in this study. The scale factor was used in sensitivity analysis to determine the effect of a particular parameter on the simulation result.

Under the exchange fields, two types of exchanges are defined, surface and pore water. To use one of these exchange fields, the Use box must be checked and a scale entered. When the use box is unchecked the information for the particular exchange field is not passed to the model during execution. In this study, the use box of surface water was checked and a scale factor of 1 was entered.

Under exchange coefficients, cross sectional areas and dispersion coefficients are specified for each segment pair. The dispersion coefficients can be calculated from equation 3.9 (based on Mill *et al.*, 1985).

$$E_L = \frac{Q(x_2 - x_1)}{A \ln(C_2 / C_1)} \qquad [3.9]$$

where:

E_L = Dispersion coefficients (L^2/T)

Q = Flow (L^3/T)

$x_2 - x_1$ = Distance (L) between x_2 and x_1

C = Salinity concentration (M/L^3)

A = Cross sectional area (L^2)

Salinity is a very useful parameter for calibrating a tidal river model. The model can be calibrated by adjusting the dispersion coefficients to make the predicted and observed salinity values in close agreement. For this study, however, the Pong River is a freshwater river. According to equation 3.9, the dispersion coefficient would be near zero. To maintain the mass balance over the river length, the dispersion coefficient at freshwater reaches was set at 1 m^2/s (Cusimano, 1997; Hashim, 1995).

Under the flows, WASP 6.1 is instructed about the flow continuity and how segments are lined up to form a river reach. Six types of transport processes can be defined by users. 1. Surface Water Flow – This group transports both the particulate and dissolved fractions of a constituent. 2. Pore Water – This group only moves the dissolved fraction of a constituent. 3. Solids Transport 1 – This group moves solids field 1. 4. Solids Transport 2 – This group moves solids field 2. 5. Solids Transport 3 – This group moves solids field 3. 6. Evaporation/Precipitation – This field adds or subtracts water to the segment. No constituent mass is altered. Up to 10 flow functions for each of the six flow fields can be defined.

In this study, only the surface water flow was used. The decision on the number of flow functions was based on both the map and field survey data of the number of tributaries for the runoff to enter the segment. The flow functions for segments which have no tributaries for the runoff, were omitted.

The water quality parameters from the Chot lagoon and Lake Sua Ten were added to the boundary of flow function 7 and 8, respectively. An additional segment called "Golf" with a small volume was added near the first segment (Known Soong) to allow runoff from the golf course to enter the river. The connection order of the flow functions are graphically demonstrated in Figure 3.11.

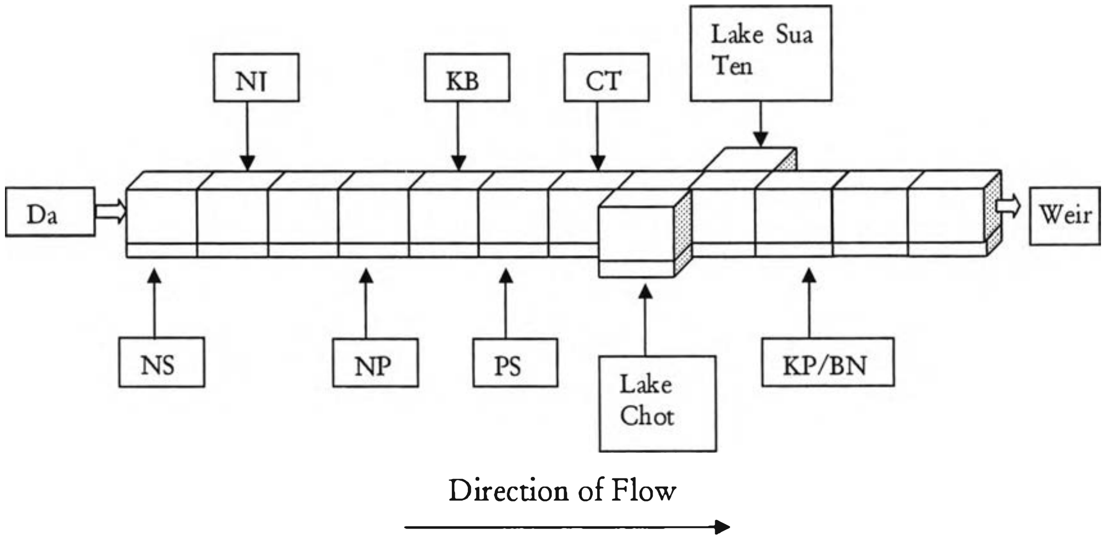


Figure 3.11 Flow Diagram of the Pong River Under Study.

Under boundaries, time-dependent concentrations of water quality parameters are entered into the flow functions. WASP 6.1 automatically determines where the boundary segment is in the flow function from the order in which the segments are aligned. In this study, a lumped-parameter modeling approach was used. This approach, mostly used in large basins (Shiba *et al.*, 1996) assumed that the spatial variability of the environment and its catchment characteristics were relatively unimportant. The lumped-parameter approach was appropriate when there were insufficient data to drive a distributed parameter model (Beven, 1989).

In this study, the concentrations in the Reservoir were entered as the boundary concentrations upstream. The boundary concentrations for the KJ, NP, KB, PS, CT, and KP/BN segments were assumed to reflect the agricultural area, and thus typical concentrations from the agricultural area in Table 3.1 were used. For the NS segment where a golf course was located, the typical nutrient concentrations of the studied parameters found in the golf course in Table 3.4 were used. Finally, the boundary concentrations for the Chot lagoon and Lake Sua Ten were obtained from the typical water body concentrations shown in Table 3.4.

Under loads, time-dependent loadings of water quality parameters may be entered in any of the segments. Point source loadings from industry and aquaculture are the two major sources of pollution into this river. In this model, using the 1995 effluent's data of the mill to construct the model would not reflect reality because the pulp mill had already started to use their effluent to irrigate their Eucalytus plantation in 1999. Moreover, the 1999 and 2000 monitoring reports from the Department of Industries already took this point source - in case of a spill - into consideration by measuring the nutrients in the Chot lagoon where the mill's effluent must be diluted.

The other point source loading was from aquaculture. NH_3-N loadings were entered at the Chot, Sua Ten and Kum Pae/Bua Noi segments in the model. In 1999 and 2000, the Huai Sai aquaculture did not start yet. Phosphorus and BOD_5 loadings from aquaculture were not entered in the model because there were no standard methods for calculating these loadings from aquaculture.

Under time step, the starting and ending times of simulation with the increment of time step are defined. In this study, a box of WASP-calculated time step in the simulation control was selected because when a user-defined time step of 0.20 day had been tried, the model became unstable.

Under print interval, the interval at which WASP 6.1 records the predicted data internally to an external file is defined. A post-processor program can retrieve this data later to produce graphs and tables. In this study, an interval of 0.2 day was used.

Under time functions, time-variable environmental information such as water temperature, daily solar radiation, fraction daylight, and wind speed are defined. In this study, time-dependent water temperatures, shown in Table 3.7 and daily solar radiation functions were entered in the model. The water temperature was obtained from the 1999 and 2000 studies, while the typical daily solar radiation was obtained from the WASP6 Manual (Wool *et al.*, 2000). Since the Pong River is at the latitude of 15-17 ^{0}N, the seasonal means of daily solar radiation at 30^{0}N were used. The mean daily solar radiations in the winter, summer, and rainy seasons were 530, 750, and 680 Langleys, respectively.

Under constants, global kinetic constants for each water quality parameter are defined. In this study, these constants were adjusted in the calibration process until the predicted and observed results were in good agreement.

These twelve types of data mentioned above, coupled with the mass balance equations define the water quality modeling of conventional nutrients.

3.4.4 Model Calibration and Validation

Model calibration is the process of running the model using a set of input data such as boundary nutrients and flows, and then comparing the results with actual measurements of the system. If the results do not "curve-fit" reasonably well with actual measurements, then some components of the model such as kinetic rates, temperature-dependent coefficients and interrelated variables must be adjusted.

Goodness of Fit

In this study, the goodness of fit between the predicted and observed values was determined by coefficient of determination (R^2) from multiple regression analysis, which was a built-in capability of the post-processor of WASP6.1. The root mean square error (RMSE) in equation 3.10 was also determined, as RMSE was one of the most widely employed methods of evaluating the differences between the predicted and observed values in modeling (Ambrose and Roesch, 1982; Thomann, 1992, Martin *et al.*, 1990). Ideally, RMSE should be as small as possible.

$$RMSE = \left[\frac{\sum (C_0 - C_p)^2}{N}\right]^{\frac{1}{2}} \qquad [3.10]$$

where:

C_p = predicted value

C_0 = observed value

N = number of measurements

The "goodness of fit", according to EPA (1995), is defined with respect to three qualitative criteria. First, the predicted and observed data should have similar profiles. Second, RMSE in the studied model should be comparable to those in other models. Third, RSME should be relatively the same as the temporal variability and measurement variability. For instance, the dissolve oxygen RSME should be close to the diurnal fluctuation.

In model calibration, McCutcheon (1989) suggested the following procedure for conventional nutrients:

1) Calibrate the hydrodynamic part of the model first to reproduce measurement of discharge, velocity and flows;

2) Select dispersion coefficient by trial and error;

3) Calibrate any processes that are not affected by water quality parameters such as salinity; and

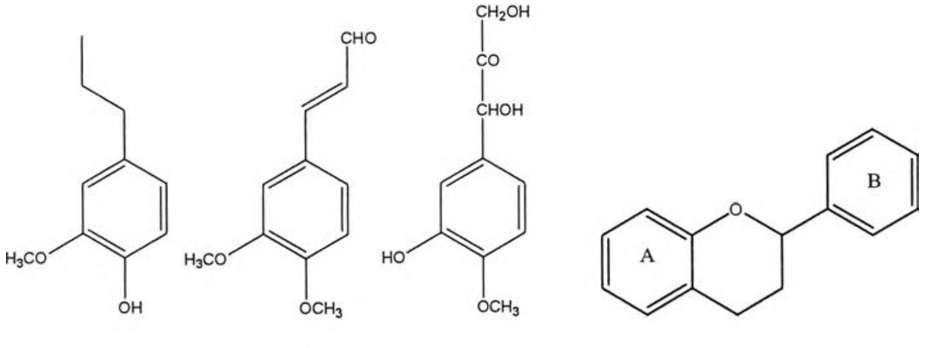
4) Calibrate conventional nutrients.

Although the hydrodynamic model was not used in this study, the temporal and spatial accuracy of the water quality parameters in the model were not sacrificed because the hydrodynamic aspect of the model was calibrated with lignin/tannin as a conservative trace.

Lignin is a complex phenolic polymer with the typical phenylpropane monomers, as shown in Figure 3.11. Tannin is a phenolic polymer with the molecular weight ranging from 500 to 3000 g/mol (White, 1957) and basic monomer structure, as shown in Figure 3.12. They both are components of vascular plants. Tannin is often found in the tree bark, while lignin is found in the cell wall of wood cells. When cellulose or protein is bonded to lignin/tannin, they become more resistant to biodegradation. Moreover, lignin/tannin gives plant rigid structures

(Sarkanen and Ludwig, 1971). They are indistinguishable by the Standard Methods due to their structural similarity; therefore, they are often reported together.

Lignin is an unequivocal signature of vascular plants on land (Hedges and Mann, 1979). Its presence in the river water is natural because it comes from leave litter and debris in the agricultural runoff (Schlesinger and Melack, 1981; Degens *et al.*, 1991; Dittmar and Lara, 2001). Lignin has been used as a conservative trace in other studies due to its stable aromatic structure (Kattner et al., 1999; Dittmar and Lara, 2001). The half-life of lignin derived from mangrove leaf was approximately 150 years in the upper 1.5 m of the sediment (Dittmar and Lara, 2001). The half-life of lignin is several months in water with sufficient oxygen (Opsahl and Benner, 1995). Similar to lignin, tannin also has the similar aromatic structure and stability towards biodegradation (Ganjegunte et al., 2004). While lignin is found in the tree bark, tannin is found in the wood cell wall. Due to their structural similarity, lignin and tannin were indistinguishable by the Standard Methods and were often reported together.



(a) (b)

Figure 3.12 Basic structures of (a) lignin and (b) tannin

The TOXI sub-model was used to calibrate the flow by leaving all kinetic constants and transformations unchecked to reflect the unchanging property of the trace. The EUTRO sub-model could not be used to calibrate the flow because EUTRO did not contain the mathematical equations to describe any other chemicals besides the conventional nutrients. After the flow was calibrated with lignin/tannin to obtain the appropriate volumes for all segments, the same model was used to calibrate the runoff. Finally, conventional nutrients were calibrated and validated with the EUTRO sub-model.

Flow Calibration

To calibrate the Dam flow, the lignin/tannin data from the Dam on February 1st and 22nd, 1999 were used as the boundary concentrations, as there was no or very small amount of runoff on these two days. The Dam flows on these two days were in the range of low flows in 1999, making them even more suitable for this model because the purpose of this model was to predict the bloom during the low-flow period around May 3rd, 1999. Although the period of the lowest flow in 1999 was from April 27th-June 17th, it was not possible to use the lignin/tannin data from this period to calibrate the flow due to the heavy rain and runoff, which would significantly change the lignin/tannin concentrations from the Dam. No chemical and physical transformation was assumed to occur with lignin/tannin in the river during the calibration of flow. The dispersion coefficient was, as mentioned above, set at 1 m^2/s, and finally the conventional nutrients were calibrated. The volume for each segment was adjusted, starting with the first segment, until the best fit between the predicted and observed lignin/tannin at each sampling site on February 1st and 22nd, 1999 was obtained.

Runoff Calibration

After the Dam flow was calibrated for the spatial and temporal accuracy of the model's prediction, the rest of the lignin/tannin data in each year were calibrated to obtain the runoff for each segment. Runoff lignin/tannin of 0.3 mg/L for a dry year in 1999 and 0.1 mg/L for a wet year in 2000 were found to give best calibration results. A range of runoff was assigned to each segment and test runs were conducted until the best fit between the predicted and observed lignin/tannin data was achieved at all sampling sites. The sum of the daily runoff assigned to each segment must be equal to the total daily runoff, provided by RID. The runoff for 1999 and 2000 were calibrated separately to determine the different runoff for each year.

The model with accurate flow and runoff, particularly under the low-flow conditions, was then used to calibrate the conventional nutrients of CBOD, DO, NH_3-N, and NO_3-N. Runoff CBOD, DO, NH_3-N, and NO_3-N from agricultural land in Thailand, were 3.90, 0.32 and 0.01 mg/L, respectively (Simachaya, 1999). Runoff PO_4-P measurement was conducted during the mild fish kills and found to be 2.01 mg/L in the paddy field, and 5.02 mg/L near the sugar cane field, using the vanadomolybdophosphoric acid method in accordance with the Standard Methods.

A preliminary calibration of the model with a full set of the 1999 data using the deoxygenation rate within a reasonable range of literature values, demonstrated that the predicted CBOD on May 3rd, 1999 were inconsistent with the observed CBOD in all segments. As the bloom was suspected, particularly on or near this date, high density of live algae could alter the observed CBOD and other nutrients if algal uptake was not considered; data from April 21st-June 15th, 1999 were thus omitted during the model calibration.

Model validation is the process of testing the calibrated model using one or more independent set of data. If the results "curve-fit" well with the actual measurements, then the calibrated model is considered to be validated. If the validation process fails, the previously-calibrated model must be re-calibrated, and validated again with a third independent data set. Validation is important because it assesses whether the model retains its generality. The model which loses its generality also loses its ability to predict the results in future years (U.S. EPA, 1999).

3.4.5 Model Prediction

The model, which has been calibrated and validated, can provide useful information as follows:

1) Real-time simulations were performed to re-create the conditions of the week before and during the fish kill, and tested with scenarios. Dynamic modeling could predict whether the algal bloom occurred before the fish kill or not. Since an algal bloom was one of the possible causes of the fish kill, and *Chl a* was not monitored during the fish kill in 1999, *Chl a* could not be calibrated; therefore, the predicted relative magnitude of uncalibrated *Chl a* in 1999 was only used for comparison with that of *Chl a* in 2000 when there was no fish kill. A significant increase in *Chl a* in 1999, compared to 2000, might signal a bloom. Thus, in this study, two different series of scenarios were simulated for comparison to determine the cause of the fish kills.
2) With the sensitivity index (SI) derived from the sensitivity analysis, the model can predict which rate constants, coefficients and other variables merit particular attention for better environmental management of the river and fish-kill prevention. SI is the ratio between the percentage change of the water quality parameter and that of the constant, coefficient or specific variable. Heathcote (1998) graphically demonstrated SI by plotting the relationship between the percentage change of each constant and the associated water-quality parameter. Often, the constants and coefficients are multiplied or divided by a certain number to obtain the specific

change. Martin *et al.*, (1996) divided the constants and coefficients by 1.25 to do their sensitivity analysis. In this study, the sensitivity analysis was performed in a similar fashion as that of Simachaya (1999). All rate constants, coefficients and variables were kept constant as one variable understudy were increased and decreased by 50% and simulated to obtain the associated change in the parameter. Since this model was under dynamic conditions and the changes in concentrations were not constant, the percentage changes of all parameters must be compared on the spatial and temporal basis. Data in segments NP and CT on February 22nd and March 1st, 1999 were thus selected randomly for the comparison of the sensitivity analysis.

3) Recommendation based on modeling for the prevention of future fish kills could be outline and illustrated with scenarios.