CHAPTER 2

LITERATURE REVIEW

This chapter reviews available literature on the water quality parameters, water quality modeling, fish kills, and study area. In the first section, conventional nutrients such as BOD, DO, nitrogen and phosphorus, and toxic substances such as phenols are discussed. In the second section, various receiving water quality modeling programs and criteria for choosing the most appropriate model for the study, are reviewed. In the third section, a topic of fish kills is reviewed to provide fundamental background of the problem which this study attempted to solve. The final section provides description of the study area, pollution sources and waste loadings.

2.1 WATER QUALITY PARAMETERS

There are many water-quality parameters which can cause water pollution. They could be the conventional nutrients, such as BOD, DO, nitrogen and phosphorus, and toxic substances such as pesticides, metals and other organic chemicals such as phenols. The National Environmental Board (NEB) of Thailand has set the water quality standard for the Pong River as shown in Appendix C. After the fish kill incident of 1977 in the Pong River, the water quality parameters were regularly monitored by many researchers (Wongpathanakul et al, 1999, 2000; KKU 2002, 2003, 2004).

2.1.1 BOD (Biochemical Oxygen Demand)

BOD is a measurement of the amount of oxygen (O_2) required by aquatic microbes to oxidize organic matter (Tchobanoglous and Schroeder, 1985). In the river, BOD can come from both point and non-point sources of organic loading. BOD decreases as it travels downstream due to biodegradation and dilution. Factors which affect the decrease of BOD are the water temperature, hydraulic factors, and nature of carbonaceous materials (Bowie *et al.*, 1985).

BOD is commonly divided into two main groups: CBOD (carbonaceous biochemical oxygen demand) and NBOD (nitrogenous biochemical oxygen demand). CBOD is measured by adding nitrifying inhibitor to the water samples to stop nitrifying bacteria from digesting nitrogenous substances.

In the Pong River, previous monitoring reports did not indicate any exceedences of BOD_5 beyond the water quality standard (Wongpathanakul et al., 1999, 2000; KKU 2002, 2003, 2004).

2.1.2 DO (Dissolved Oxygen)

DO is the amount of oxygen in the water. It is the most important parameter for maintaining aquatic life; therefore, it is often used in the determination of the impact of receiving water quality and development of water quality management. DO should be more than 6 mg/L in rivers (US EPA, 1986a). DO of 5-6 mg/L may not kill aquatic organism, but it can lead to environmental stresses. The DO threshold for many species in the river is established at 3 mg/L by US EPA (1986). If DO drops below 2 mg/L for one to four days, most aquatic biota may die. Therefore, it is always preferable to maintain DO at a high level in the river to promote aquatic life (Bach *et al.*, 1989; US EPA, 1986a).

Factors which affect the DO level are hydraulic factors, salinity, oxidation of carbonaceous materials, nitrification, benthic sediment oxygen demand, photosynthesis of aquatic plants and algae, respiration, reaeration and water temperature (Havno *et al.*, 1995).

In the Pong River, one previous monitoring report indicated any exceedences of DO beyond the water quality standard (Wongpathanakul et al., 1999).

2.1.3 Nitrogen

The major sources of nitrogen contamination in the US and UK rivers are agricultural fertilizers (Dillaha, 1998; Luker *et al.*, 1993; Powlson, 2000). High nitrate leaching occur when organic manures or chemical fertilizers are applied to land in excessive amounts, or at inappropriate times, e.g. during seasons of high rainfall (Chambers *et al.*, 2000). Excessive nitrogen loading in the river can lead to undesirable eutrophication and low DO. Eutrophication is the aging state of enriched nutrients, and excessive growth of aquatic plants, both attached and planktonic to levels that are considered to be an interference with desirable water uses (Lee, 2000). Low DO is caused by oxygen consumption during nitrification. Nitrogen is represented as inorganics and organic nitrogen. Inorganic nitrogen includes ammonia (NH_3), nitrate (NO_3) and nitrite (NO_2). There are two forms of ammonia in water which are ammonia and ammonium. At high pH, ammonium is converted to ammonia which is toxic to fish and aquatic life (Russo, 1985).

NH_3 is converted to NO_3 in the nitrification process by nitrifying bacteria in oxygen-sufficient rivers. NO_3 is converted to nitrogen (N_2) by denitrifying bacteria.

During a heavy rain, nitrate leaching often occurs in agricultural area as the result of nitrate from the fertilizer is dissolved and flushed to the river. Factors affecting the level of NH_3 are nitrification, denitrification, phytoplankton recycle, mineralization of organic matters and atmospheric deposition (Ambrose *et al.*, 1993b).

In the Pong River, previous monitoring reports did not indicate any exceedences of NH_3 and NO_3 beyond the water quality standards (Wongpathanakul et al., 1999, 2000; KKU 2002, 2003, 2004).

2.1.4 Phosphorus

Similar to BOD_5 and nitrogen, phosphorus can come from both point and non-point sources. Organic phosphorus can be generated from dead algae, which later mineralizes to inorganic form of phosphorus, called ortho-phosphate. Treatment plants usually release phosphorus in the form of phosphate which is readily taken up by algae (Bowie *et al.*, 1985). During a heavy rain and flooding, subsurface phosphorus from organic soils, associated with fertilizer application and cultivation, can leach to the river at concentrations that can cause eutrophication (Turner and Haygarth, 2000; Heckrath *et al.*, 1995; Elrashidi *et al.*, 2001; Miller, 1979; Reddy, 1983; Reddy, 1987). Under anaerobic conditions, a significant decomposition of organic phosphorus matter can also occur (Racz, 1979).

In the Pong River, previous monitoring reports did not indicate any exceedences of phosphorus-containing molecules beyond the water quality standards (KKU 2002, 2003, 2004).

2.1.5 Pesticides as Toxic Chemicals

Pesticides are used in food production. They could contaminate the river water through runoff. Pesticides include all agents which prevent, control, and reduce insects, fungi, rodents, microbes and weeds. Chemically-related pesticides of three main groups, organophosphates, carbamates and organochlorines, will be discussed in this study. Organophosphate pesticides have the functional group of phosphate attached to the organic groups. They act by reducing the ability of cholinesterase, an enzyme, to function properly in regulating a neurotransmitter called acetylcholine (Brown *et al.*, 2004; Skládal, 1992; Donarski, 1989; Chapalamadugu and Chaudhry, 1992; FAO, 1989). Organophsphates are widely used, and not persistent in the environment (Jury *et al.*, 1987). Examples of this group are glyphosate and Dimathoate.

Carbamate pesticides have the carbamate functional group. Similar to organophosphates, they act by regulating acetylcholine (Pentyala and Chetty, 1993). They are also widely used and not environmentally persistent. An example of this group is Lannate. Organophosphorus and carbamate insecticides, which have replaced the more persistent organochlorines are generally more toxic (Lionetto *et al.,* 2003) and have been responsible for fish kills in the past (Finlayson and Lew, 1983, Zinkl *et al.*, 1991).

Finally, organochlorine pesticides have chlorine atoms attached to organic groups. They act by disrupting reproductive cycles of humans and wildlife (Colborn and Smolen, 1996). This type of pesticides was commonly used in the past, but has become unfavorable due to their environmental persistence and harmful effects on human (Minh *et al.*, 2004; De Felip *et al.*, 2004; Zhang, 2003). Some of these that have been banned are DDT and chlordane.

In the Pong River, previous monitoring reports did not indicate any exceedances of pesticides beyond the water quality standards (PCD, 1999, 2000, 2001, 2002; KKU 2002, 2003, 2004).

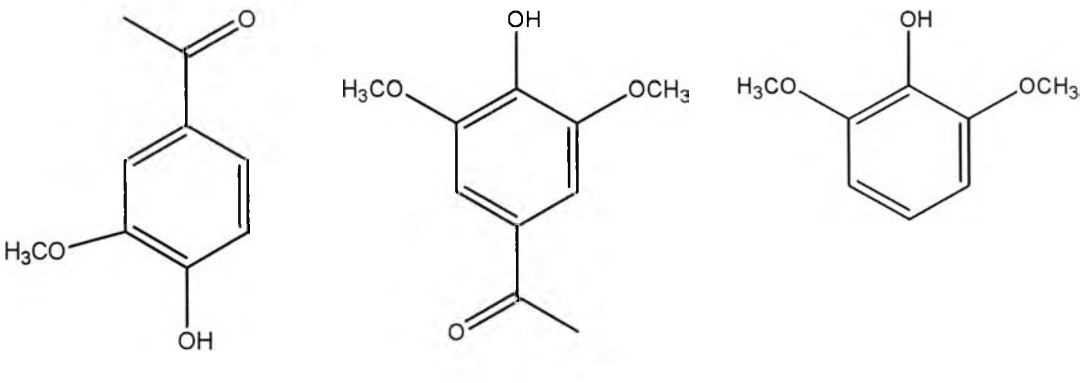
2.1.6 Heavy Metals as Toxic Chemicals

Numerous heavy metal contaminations in the river have been due to mining operations (Lewin *et al.*, 1977; Marron, 1992; Macklin *et al.*, 1994; Swennen *et al.*, 1994; Miller, 1997 and Hudson-Edwards *et al.*, 2003). Both human and animals are affected by the contaminations (Beiras and Albentosa, 2004; Tkatcheva *et al.*, 2000). In Brazil, people who live near the Hg-contaminated river showed high mercury in their hair, and developed sensory disturbance, tremor, and slight balancing failure (Harada *et al.*, 2001). Fish in the coastal waters from the Bay of Seine in the eastern English Channel to the Belgian border in the southern North Sea, were found to accumulate heavy metals in their liver (Henry *et al.*, 2004).

In the Pong River, previous monitoring reports did not indicate any exceedences of metals beyond the water quality standards (PCD, 1999, 2000, 2001, 2002; KKU 2002, 2003, 2004).

2.1.7 Phenols as Toxic Chemicals

Phenols are defined as hydroxyl derivatives of benzene. They are natural compounds involved in the formation of humic polyers. They originate from the decomposition of plant residues (Chua *et al.*, 1982; Stevenson, 1994). Other important sources of naturally occurring phenols are esters of phenolcarboxylic acids linked with lignin (Besle et al., 1995), hemicelluloses or pectins (Hartley and Ford, 1989), flavonoids (Borner, 1958; Barz, 1969), lignans (Sundman and Haro, 1966), tannins (Lorenz *et al.*, 2000) and phenolic glycosides in plant vacuoles (Daltion *et al.*, 1987). Chlorophenols are produced from naturally occurring phenols as a result of chlorine bleaching of wood pulp in the paper industry, through chlorination of domestic water supplies and swimming pools. In the rivers of Thailand, small amounts of phenols in the range of 0.02 to 4.35 ppb were found with GC/MS with the highest concentration of 4-nonylphenol at 1.9 ppb in the Tha Chin River (Boonyatumanond, 2001). The decay rate and mass balance of phenols as toxic compounds are described by an equation in Chapter 3. In the Pong River, there was no monitoring of phenols before.



Example of Different Phenols

2.2 RECEIVING WATER QUALITY MODELING

Water quality models have been used extensively in the receiving water bodies for many years. They are tools, particularly preferred by environmental managers because these tools can predict the water quality parameters under different critical conditions such as low flow and high temperature. Environmental planning and management decisions can be made based on these predictions.

There is no universal or all-purpose water quality model. The choice of one particular model over the others depends upon the appropriateness of the model in simulating the specific conditions and problems of the water body in question (Ambrose and Roesch, 1982; Beck, 1985; Stefan *et al.*, 1990). Most water quality models are based on the finite-segment approach, and mass balance equations (Atkinson *et al.*, 1998). In this approach, the river can be conceptually represented as a series of small segments or cells. Water travels from an upstream cell to a downstream cell and resides in each cell with complete mixing for a detention time.

There are two important points in considering possible flaws in modeling. First, the hydrodynamic results should be real-time calculations. Second, mass conservation around a point can not be transformed accurately into mass conservation for a finite-volume model. Therefore, interpolation and thereby errors are introduced into the water quality model calculation.

In a one-dimensional advection model, the equation used is:

$$\frac{\partial C}{\partial t} + U\frac{\partial C}{\partial x} = \frac{\partial}{\partial x}\left[D\frac{\partial C}{\partial x}\right] \qquad [\,2.1\,]$$

where:

C = concentration (M/L^3)

t = time (T)

U = mean longitudinal velocity (L/T)

x = distance (L)

D = dispersitivity (L^2/T)

If kinetic transformation of the water-quality parameter is considered, the equation can be expressed in the following form:

$$\frac{\partial(AC)}{\partial t} = \frac{\partial\left(-U_x AC + E_x A\frac{\partial C}{\partial x}\right)}{\partial x} + A(S_L + S_B) + AS_K \qquad [\,2.2\,]$$

where:

C = concentration (M/L^3)

A = cross-sectional area (L^2)

U_x = longitudinal advective velocity (L/T)

E_x = longitudinal diffusion (L^2/L)

S_L = point and non-point source loading rate (M/L^3/T)

S_B = boundary loading rate (M/L^3/T)

S_K = total kinetic transformation rate (M/L^3/T)

t = time (T)

x = distance (L)

In the river, lateral mixing is faster than other water bodies; therefore, it is assumed that the concentration is approximately uniform over the river cross section (US EPA, 1999). Although all water quality parameters are subjected to the same advection equation, each one (conventional nutrients or toxic chemical) is affected by its own kinetic and transformation factors.

2.2.1 Modeling of Conventional nutrients

The mathematical modeling equations of conventional nutrients are already shown Section 2.1. The first modeling of conventional nutrients started with DO more than 70 years ago (Wool et al., 2000). A simulation of DO can reveal the impact of episodic loads on the river. The complexity of the DO modeling can vary, depending on the purpose of the modeling. A simple DO model such as STREANDO IV (Zander and Love, 1990) is available in a spreadsheet form.

2.2.2 Modeling of Toxic Contaminants

For near trace levels of toxic contaminants, i.e., below half the solubility or 10^{-5} molar, all transformations such as biodegradation, hydrolysis, photolysis, volatilization, and oxidation, are described by first-order decay equation (2.7) in the WASP 6.1 Manual (Wool *et al.*, 2000). The simplest technique in modeling toxic contaminants is to lump all first-order transformation rates together and express them as one net decay rate. This technique is called, "the lump, first-order decay." The drawback of the lump, first-order decay method is that daughter products which are produced from the original, parent contaminants, can not be simulated (WASP 6.1 Manual). The second simulation technique is to consider each transformation individually. In this method, the first-order rate for each transformation must be identified. This technique takes much more time.

2.2.3 Choices of Computer Models

The Center for Exposure Assessment Modeling (CEAM) under U.S. EPA maintains a distribution center for water quality models and related software. Those models include QUAL2EU, WASP6.1, HSPF, EXAMSII, CORMIX, SMPTOX3, and DYNTOX. Table 2.1 shows the comparison of some of these models and other related models.

QUAL2EU

QUAL2EU is Enhanced Stream Water Quality Model with Uncertainty Analysis. It is an enhancement of QUAL2E because it includes the extensive capability for uncertainty analysis such as sensitivity analysis, first-order error analysis and Monte Carlo simulation. QUAL2EU is a one-dimensional model for rivers. Up to fifteen water quality variables, namely temperature, bacteria, BOD, DO, ammonia, nitrate, nitrite, organic nitrogen, phosphate, organic phosphorus, algae, and additional conservative substances, can be simulated (Brown and Barnwell, 1987). Inputs for this model such as flows and loadings must be in steady states, while temperature, algae photosynthesis and respiration can fluctuate. Experienced users may be able to simulate the model with non-steady loadings under steady flow conditions by establishing certain initial conditions or varying climatic conditions (Brown and Barnwell, 1987).

The limitation of QUAL2EU is that it is designed to be a relatively general program; thus it allows limited number of segments (25 segments), headwater elements (7 elements), junction elements (6 elements), and input and withdrawal elements (25 elements).

WASP 6.1

WASP 6.1 is Water Quality Analysis Simulation Program, Version 6.1. It allows users to create one, two and three-dimensional models (James, 1992; Lung, 1993; Orlob, 1992). This flexibility enables users to study the effect of processes such as sedimentation and scouring on the water quality parameters.

Moreover, WASP 6.1 offers users options for inputting variables such as exchange coefficient, reaeration, air and water temperature, zooplankton population, velocity, ammonia and phosphorus benthic fluxes, light extinction, wind, fraction daily light, daily solar radiation in the model either as constants or time-variable functions. Finally, WASP6.1 permits tailored structuring of the kinetic processes, all within the larger modeling framework without having to write or rewrite large sections of computer code (Ambrose *et al.*, 1988). The limitation of WASP 6.1 is that it does not handle the mixing zone, and floatables/sinkables.

HSPF

HSPF is Hydrological Simulation Program – Fortran. It is a one-dimensional, comprehensive hydrology and water quality simulation package. This model was originally designed for watershed modeling. Later, the water-quality processes and algorithm enhancement were added. Now HSPF can simulate the transport and fate of pollutants in rivers and reservoirs. Different sediment types such as sand, silt and clay can be studied

(Johnson *et al.*, 1984). HSPF has been applied all over the world. In Central Iowa, the range of the watershed areas that used HSPF was from 52 to 7,200 km^2 (Donigian, Bicknell, and Imhoff, 1995). The largest application is the 62,000 square mile tributary area to the Chesapeake Bay, U.S. The smallest application is the experimental plot of a few acres near Watkinsville, Georgia.

The limitation of HSPF is that it requires a comprehensive set of data which includes estimates of evapotranspiration, dewpoint temperature, wind, humidity, cloud cover, and tillage practices. This requirement makes modeling cost-intensive.

Mike 11

Mike 11, developed by the Danish Hydraulic Institute (DHI), is a 1-D dynamic simulation model of hydrology, water quality and sediment transport in estuaries and various water bodies (DeVries and Hromadka, 1992). It is widely used around the world, including the Nepal River in Nepal, the Paramatta and Georges Rivers in Australia, the Sarawak River in Malyasia, and the Chao Phraya Tidal River in Thailand (Marco Consultants, 1995).

The drawback of Mike 11 is that it is quite expensive. The model requires different modules which are sold separately. The hydrodynamic and eutrophication modules cost $15,000 and $6,700, respectively.

EXAMSII

EXAMSII is Exposure Analysis Modeling Systems II. It is an interactive model which allows users to specify and store properties of chemicals and ecosystems, conduct evaluations and error analyses of the aquatic fate of chemicals. A recent upgrade of this model considers seasonal variations in transport and time-varying chemical loadings, making it quasi-dynamic. Users must specify transport fields to the model (Burns, 1982).

CORMIX

CORMIX is Cornell Mixing Zone Expert System. It is designed for mixing-zone analysis of aqueous conventional or toxic pollutant discharges into watercourse, with emphasis placed on the geometry and dilution characteristics of the initial mixing zone. The model uses a zone approach in which a flow classification scheme determines which near-field mixing processes to calculate. It can simulate single-port, submerged multi-port or buoyant surface discharges. The CORMIX model can not be calibrated in the classic sense since rates are fixed based on the built-in logic of the expert system (Doneker and Jirka, 1990). CORMIX was originally developed assuming steady ambient conditions; Version 3 allows for unsteady environment such as tidal reversal conditions, where transient recirculation and pollutant build-up can occur (CEAM, 1998).

SYMTOX3

SYMTOX3 is Simplified Method Program-Variable Complexity Stream Toxics Model. It is a one-dimensional steady-state model for simulating contaminants in the water column and bed sediments in the streams and non-tidal rivers. SYMTOX3 is an interactive computer program that uses an EPA technique for calculating concentrations of toxic substance in the water column and streambed as a result of a point source discharges to streams and rivers. The model predicts pollutant concentrations in dissolved and particulate phase for the water column and bed sediments, as well as total suspended solids (LimnoTech, 1992).

DYNTOX

DYNTOX is Dynamic Toxics Model. It is a one-dimensional, probabilistic toxicity dilution model for transport in rivers. It can provide either continuous, Monte Carlo or Lognormal probability simulations that can be used to analyze the frequency and duration of ambient toxic concentrations resulting from a waste discharge. The model considers dilution and net first-order loss, but no sorption and benthic exchange (LimnoTech, 1985).

CE-QUAL-W2

CE-QUAL-W2 has been developed by the Waterways Experiment Station of the U.S. Army Corps of Engineers (USACE) for nearly three decades. The model has been applied to over 400 systems, mostly reservoirs in 50 countries throughout the world (Cole, 2002). It is a water quality and dynamic 2-dimensional hydrodynamic model for stratified and non-stratified lakes, reservoirs, rivers and narrow estuaries. The density effects on flows as a function of the water temperature, salinity and suspended solids concentrations are considered. It can simulate up to 21 water quality parameters including one passive tracer (e.g., dye), total dissolved solids, coliform bacteria, inorganic suspended solids, algal/nutrient/DO dynamics (11 parameters), alkalinity, pH, and carbonate species (4 parameters) (Brown and Barnwell, 1987; Devris and Hromadka, 1992). The model's greatest strength is its ability to accurately simulate the hydrodynamics of the system (Cole, 2002). Its limitation is the hydrostatic assumption for vertical momentum equation.

AGNPS

AGNPS is the Agricultural Non-Point Source Pollution Model, developed by the Agriculture Research Service, U.S. Department of Agriculture, and the University of

Minnesota (Young *et al.*, 1989). It is an event-based and continuous model for non-point source pollution. It can simulate and predict runoff volume, peak rates, sediment load, soil erosion, and conventional pollutant concentrations after a single storm event. The watershed of interest is divided into square elements of about 100 m^2. Each element must be supplied with 22 input data values. The limitation of AGNPS is that it does not accommodate non-uniform storms because it uses a lumped modeling approach for its rainfall.

ANSWERS

ANSWERS is the Areal Non-Point Source Watershed Environmental Response Simulation. It is a continuous model for a non-point source pollution. It makes use of a grid-cell structure to represent the watershed information. Similar to AGNPS, the slope of the watershed is required in order to determine the erosion. The model can simulate hydrologic processes within each element including interception, infiltration, surface storage, surface flow, subsurface drainage, sediment drainage, and sediment attachment, transport, and deposit (City of Austin, 1992; Dillaha, 1998).

CREAMS

CREAMS is Chemicals, Runoff and Erosion from Agriculture Management Systems Model. It is a hydrology model which studies the agricultural pollution from data set of daily rainfall, erosion/sediment yield, and chemistry (nutrients and pesticides).

Its limitation is that the model is designed for small-scale field areas with a single land-use and homogenous soil and practices (Crowder *et al.*, 1984).

SWMM

SWMM is the Stormwater Management Model, developed by U.S. EPA. It is a comprehensive model for simulating urban runoff quantity and pollution from storm and combined sewer systems (James, 1992). In addition to urban hydrology, SWMM can simulate water quality processes such as rainfall, snowmelt, surface runoff, subsurface contribution to runoff, routing, storage, and the treatment of flows (DeVries and Hromadka, 1992; Huber, 1995). The limitation of SWMM is that it does not include modules to simulate water quality.

2.2.4 Criteria for Model Selection

In general, the selection of a water quality model depends on six criteria (U.S. EPA, 1987):

1) availability of pertinent documentation,
2) ease of application,
3) available time and resources,
4) applicability of model processes and variables,
5) hydrodynamic model capabilities, and
6) evidence of demonstrated applicability to size and type of project (U.S. EPA, 1987).

Based on the criteria above and opinion of experts, WASP6.1 was selected for this study. Supporting arguments are given as follows:

1) The availability of documented data for the river segment under study is very important in selecting the model. In this study, the 1999 and 2000 weekly monitoring data of

water quality in the Pong River from the Department of Industries, water releases from the Electricity-Generating Authority of Thailand (EGAT) and the Department of Royal Irrigation (RID) were used to construct the water-quality model for two reasons. First, the use of the available 1999 and 2000 weekly water quality data could save cost and time. Two, there was a fish-kill incident in 1999, but none in 2000; the comparison of water quality data between these two years could unravel why there was a fish kill.

With the availability of the weekly data mentioned above, WASP 6.1 seemed to be the most appropriate choice of model. WASP 6.1 can simulate under both dynamic and steady-state conditions. The dynamic simulation should provide very useful information about why the fish died in 1999, but none in 2000. If a more complicated model than WASP 6.1, with elaborate spatial and temporal domains, is selected, it would require detailed data which are not available and too costly for this study.

2) WASP 6.1 has high flexibility in both temporal and spatial options. It can simulate under both steady and dynamic conditions, and as one, two or three-dimensional systems. In this study, a dynamic model will be simulated to determine the cause of the fish kill in the summer.

3) WASP 6.1 is a free model and is available to the public.

4) WASP 6.1 can simulate most water quality variables in almost any water bodies.

5) WASP 6.1 has the hydrodynamic capability called DYNHYD5 which can be coupled to the water quality module.

6) WASP 6.1 is widely used around the world, especially in North America.

Many versions of WASP have been used to study Tampa Bay (Martin *et al.*, 1996), Lake Okeechobee (James *et al.*, 1998), Neuse River and estuary (Lung and Pearl, 1988), Black River

(Picket, 1997), Upper Mississippi River and Lake Pepin (Lung and Larson, 1995), Great Lakes (Thomann, 1975; Thomann *et al.*, 1976; Thomann *et al.*, 1979; Di Toro and Connolly, 1980), Potomac Estuary (Thomann and Fitzpatrick, 1982), and James River Estuary (Ambrose, 1987), and Deep River, NC (JRB, 1984).

Table 2.1 US EPA CEAM-Supported Models

Applicability to Hydraulic Regimes and Pollutant Type										Key Characteristics and References		
Model	Rivers & Streams			Lakes & Impoundments			Estuaries			Pollutant Loading Type	Transport Dimen-sionality	Key Reference
	Nutrients	Oxygen	Others	Nutrients	Oxygen	Others	Nutrients	Oxygen	Others			
QUAL2EU	X	X	X							Steady	1-D	Brown & Barnwell, 1987
WASP6.1	X	X	X	X	X	X	X	X	X	Dynamic	Quasi-2/3-D	Wool *et al.*, 2000
HSPF	X	X	X	X	X	X				Dynamic	1-D	Johnson *et al.*, 1984
MIKE11	X	X	X				X	X	X	Dynamic	1-D	DHI, 1994
EXAMSII			X			X			X	Dynamic	User Input	Burns, 1982
CORMIX	Near-field mixing model for all water body types									Steady	Quasi-3-D	Doneker & Jirka, 1990
MINTEQ	Equilibrium Metal Speciation Model									Steady	None	Brown & Allison, 1987
SYMTOX3			X							Steady	1-D	Limno Tech, 1992

2.3 FISH KILL

"Fish kill" occurs when a number of fish in a specific water body die from a specific cause. Only a fraction of dead fish is ever observed because many decompose on the bottom or are eaten by scavengers such as turtles and crayfish. Fish kills may be due to three main factors: infectious diseases, poor water quality and toxic substance (Pierce *et al.*, 1994).

Diseases are caused by pathogens such as bacteria, virus and parasites under stressful conditions. These conditions include a rapid change in water temperature, pollution, unfavorable water chemistry (especially low DO), algal bloom die-off and a possible drop in pH after a heavy rain. Other adverse conditions that may trigger a disease outbreak include overstocking, poor handling procedures, overfeeding or underfeeding and poor food quality (Pierce *et al.*, 1994). Open soars as shown in Figure 2.1 are the typical characteristics of fish kill from diseases. The behavioral and physical signs of fish suffering from disease outbreaks are shown in Table 2.2.

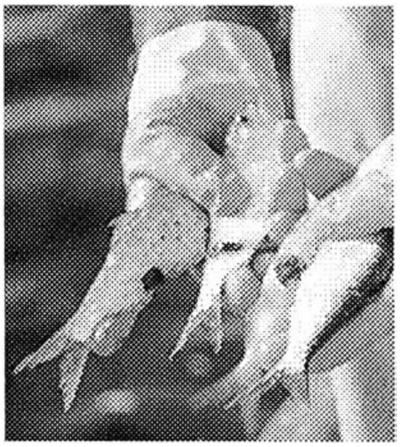


Figure 2.1 Open soars due to infectious diseases.

Table 2.2. Behavioral and chemical signs of fish suffering from diseases. (Source: Pierce *et al.*, 1994).

Behavioral signs	Physical signs
Failure to feed properly	Blistered areas
Flashing (turning on their sides)	Swollen bellies
Rubbing on the bottom	Open sores (may be bloody)
Lying listlessly in shallow water	Popped-out eyes
Gathering around the water inflow	Bloody (hemorrhaged) areas on fins
Reduced vitality	Discoloration or erosion of body parts
Gasping at the surface	Excessive mucus
Swimming erratically	Growths on the body

In addition to diseases, poor water quality can also cause massive fish kills. In fact, it is often a major factor contributing to fish disease and parasite infection. Water quality does not remain constant. If fish are stressed or dying, DO, CO_2, conductivity, pH, temperature, ammonia nitrogen, nitrite nitrogen, alkalinity and hardness should be immediately measured, besides the usual water quality parameters of color, BOD, calcium, iron, manganese, nitrate nitrogen, total suspended solids, turbidity, sulfate, chloride and phosphate (Pierce *et al.*, 1994).

Finally, lethal doses of toxic substances such as organic chemicals and heavy metals may also kill fish. At sub-lethal doses, they kill fish by weakening the fish's immune system and making the fish susceptible to diseases. "At the first sign of a fish kill, poor water quality should be eliminated as a potential cause," and if the stressful condition could not be identified, toxic chemicals should be suspected (Pierce *et al.*, 1994). Table 2.3 shows the clinical signs of fish when exposed to toxic substances.

Table 2.3 Clinical signs of toxic substances (Source: Pierce *et al.*, 1994).

Sign	Possible cause
White film on gills or skin	Acid, heavy metals or trinitrophenols
Sloughing of gill epithelium	Copper, zinc, lead, ammonia, detergents or quinoline
Clogged gills	Turbidity or ferric hydroxide
Bright red gills	Cyanide
Dark gills	Phenol, naphthalene, nitrite, H_2S or low DO
Hemorrhagic gills	Detergents
Distended opercles	Phenols, cresol, ammonia, or cyanide
Blue stomach	Molybdenum
Pectoral fins moved to extreme forward position	Organophosphate or carbamates
Lip papilomas or skin tumors	Polynuclear aromatic carbons

Among three factors of infectious diseases, poor water quality and toxic substances, aquaculturalists must investigate the fish kill problem by going through a process of elimination. Since poor water quality is usually the main factor contributing to diseases, it deserves more attention and elaboration. The following paragraphs describe the water quality parameters and stress which often cause the fish kill.

2.3.1 Low DO

Low DO can be caused by high BOD and nitrogen-containing materials from both urban and agricultural runoff, and the bloom die-off. As bacteria begin to decompose BOD and nitrogen materials, oxygen is depleted at a faster rate than normal. Warm water fish generally require DO of at least 5 mg/L. If DO levels drop below 2 mg/L, the fish aren't always able to recover. When concentrations fall to about 1 mg/L, fish begin to die (Saiki et al., 1999). If it is a DO-related fish kill, large fish tend to be affected first and more severely than other fish; small fish can be seen gulping or gasping for air at the surface just before a fish kill occurs. Heavy thunderstorm and sediment scouring can also have an adverse effect on oxygen levels, especially after extended periods of dry weather or during hot weather. This can be a problem during hot weather as there is less oxygen in the water. A combination of hot weather and cloudy skies can be particularly deadly for fish, as the decrease in sunlight (i.e., from cloud cover) makes it difficult for algae and plants to photosynthesize. The reduction in photosynthesis results in a decrease of oxygen being released into the water column. When overcast skies persist for several days, oxygen levels can become severely depleted.

2.3.2 High ammonia

Agricultural runoff and fish feed contribute ammonia to the water. Unbalanced equilibrium of the aquatic microorganisms particularly during the rapid temperature change can also cause high ammonia levels. The toxicity of NH_3 on fish depends on concurrent conditions of DO, temperature, pH, carbon dioxide, and other pollutants. The limit of 0.01 mg/L is reported by determining the 95th percentile protection level from a cumulative probability distribution of all of the chronic ammonia toxicity values reported in the literature (Dyer *et al.*, 2003). According to US EPA (1985), the lethal NH_3 level for most freshwater fish varies between 0.2 to 2.0 mg/L. High NH_3 concentration can cause fish to experience loss of equilibrium, hyperexcitability, increased heart and respiratory rates leading to coma and death (Bowie *et al.*, 1985; North Carolina Agricultural Research Service, 1997). For Nile tilapia, NH_3-N between 0.14 - 0.43 mg/L did not cause fish death (El-Shafai, *et al.,* 2004).

2.3.3 High nitrite

High levels of nitrite come from nitrifying bacteria, nitrosomonas which converts the toxic ammonia into nitrite – before it gets converted to less toxic nitrate by nitrobacter. As the conversion of ammonia to nitrite begins, the cycle is at its most toxic level. High levels of nitrite in fish's blood, often called the brown blood disease, can lead to fish kill. Nitrite enters the bloodstream through the gills and turns the blood to a chocolate-brown color. Hemoglobin, when combined with nitrite to form methemoglobin, becomes incapable of oxygen transport (Lewis *et al.*, 1986). This explains the gasping behavior in fish with brown blood disease, even when oxygen levels are relatively high (Jensen, 1985; Williams and Eddy, 1986). Warmwater fish apparently concentrate nitrite in the blood. Catfish and tilapia, for example, are fairly sensitive to nitrite. In tambaqui fish, *C. macropomum*, the first 24-h of NO_2^- exposure was critical for the fish's survival, since most of the deaths occurred during this period. Its 96-h median lethal concentration (LC_{50}) of nitrite was 1.82 ± 0.98 mg NO_2-N/L (Ferreira da Costa et al., 2004). In blue tilapia, the 96-h LC_{50} of nitrite was 16.2 ± 2.3 mg NO_2-N/L (Palachek and Tomasso, 1984). Small Nile tilapia were more tolerant of nitrite than large fish. The 96-h LC_{50} of nitrite for small and large Nile tilapias were reported to be 81 and 8 mg NO_2-N/L, respectively (Atwood *et al.*, 2000).

2.3.4 Toxic chemicals

Toxic chemicals such as pesticides in runoff, heavy metals, and chemical spills can also cause fish kills. Sixteen fish kills around Prince Edward Island that were either known or suspected to have been caused by pesticides, particularly endosulfan, occurred between 1994 and 2000 (DFO, 2000). Large fish kills were observed after the spraying of NaPCP for the purpose of killing snails in the rice fields of Surinam (Vermeer *et al.*, 1974). In South

Carolina, uncontrolled runoff with insecticides from tomato fields has been reported to cause fish kills in adjacent coastal waters (Scott *et al.*, 1990).

Heavy metals such as cadmium and mercury caused fish-kill occurrences in Japan (Kimura, 1988). When the contaminated sediment from Udono Harbor and Shingu River Estuary was removed, the tumor incidence in fish reduced from 40–50% prior to 1983 to about 20% in 1984–1985. In Bolivia, there was a report of massive fish kill hundreds of kilometers downstream from the metal spill from a mining industry (Macklin *et al.*, 1996).

Numerous chemical spills, particularly large oil spills, have been responsible for fish kill incidents (Marty *et al.*, 1999, 2003; Hower *et al.*, 2000; Crunkilton, 1984; Green and Trett, 1989). There was only one report of fish kill as the result of direct exposure to chlorophenols from a spill near Highland Creek in 1984 (Ministry of Environment and Parks, 1988). The 1984 spill was an isolated incident and there was no lasting impact on the Serpentine River system.

As toxic phenols and chlorophenols were found in the effluent of the pulp and paper mill at the ppb level (Palm *et al.*, 1995; Kemeny and Banerjee, 1997; Kringstad and Lindstrom, 1984), many studies had been funded to study their effect on fish. Chlorophenolic acid compounds were detected in the bile of both mountain whitefish and longnose sucker, but were rarely detected in fillets. (Owens *et al.*, 1994). In another study, chlorophenols were found in Juvenile fish living below the mill discharge (Merriman, 1991). Although these studies indicated the bioaccumulation of chlorophenols in fish, there was no fish kill associated with the bioaccumulation.

The literature review of toxic chemicals is limited to only pesticides and phenols because they were the most like chemicals associated with the fish kills. This watershed was mainly used for agriculture which the use of pesticides and fertilizers might be associated with; and in the river segment under study, there was mainly one industry of pulp and paper processing and its effluent was found to contain phenols at the concentration of 0.045 mg/L (CMS Engineering & Management, 1995). Although its concentration in the effluent did not exceed the industrial effluent standard of 1.0 mg/L (Appendix B), researchers still suspected that this class could cause the fish kill. NEB has established the water quality standard of phenol at 5 ppb (Appendix C).

2.3.5 Algal blooms and its toxins.

Place and Time of Bloom

Massive fish kills in estuaries of the East Coast of North America, Indo-Pacific, other coastal waters, freshwater ponds and lakes were related to blooms of cyanobacteria or blue-green algae (Burkholder *et al.*, 2001; Burkholder *et al.*, 1992; Glasgow *et al.* 2001; Magnien, 2001; Paerl, 1983; Maclean, 1989; and Yang and Hodgkiss, (in press), Sevrin-Reyssac and Pletikosic, 1990). In the coastal water of south China including Hong Kong, the fish-killing bloom lasted between March and April of 1998 (Yang and Hodgkiss, (in press)). A picture of a fish kill in Florida is shown in Figure 2.2.

Australia in November 1991 holds the history record of the largest toxic algal bloom; an estimated 1000-kilometre stretch of the Barwon and Darling rivers in New South Wales looked like a long ribbon of pea soup from air (Water Audit, 1995). There have been several reports of blooms in the Neuse River Estuary, North Carolina in the summer (Paerl, 1987). In fish ponds, the blooms also peaked in the summer (Sevrin-Reyssac and Pletikosic, 1990). In Colgate Creek, Baltimore City on July 23rd, 2002, the largest kill of approximately 60,000

Atlantic menhaden and a small number of bay anchovy, gizzard shad, pumpkinseed sunfish, and white perch died.

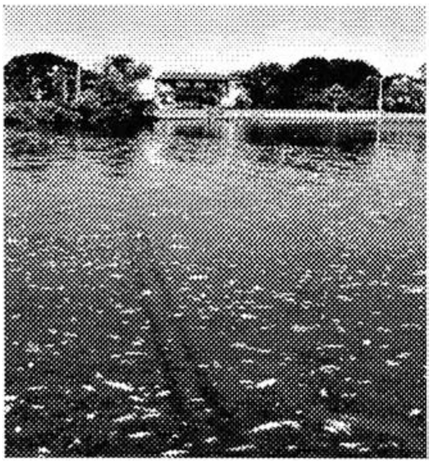


Figure 2.2 Fish kill on the west coast of Florida by the toxic dinoflagellate *Gymnodinium breve* (Photo Courtesy of the Florida Department of Environmental Protection.)

The bloom is often in the summer; therefore it is called the "summer kill." The conditions which most fish kills have in common were high temperature, no sunshine for a long period, rain, and algae die-off. The algal bloom is a natural component of nutrient-rich lakes and rivers, with high levels of nitrogen and phosphorus from both urban and agricultural runoff (Glandon *et al.,* 2003); and the contribution from the agricultural runoff is increasing every year (Vezjak *et al.*, 1998). Ammonia and phosphate are the most preferred forms of nutrients for cyanobacteria. When ammonia is not available, cyanobacteria can take up nitrate or urea (Shehawy and Kleiner, 2001).

The most studied river relating to eutrophication and the algal bloom was the Potomac Estuary in U.S. In the summer of 1983 from July through September, *Microcystis* sp. reportedly reached approximately 300 μg chl /L in the river, while in the embayments, the level reached almost 800 μg chl /L (MWCOG, 1984). The initial computer simulation predicted only about 100 μg chl/L because it did not include the nutrients source of about 4000-8000 lb/day.

General Characteristics of Bloom

The bloom is characterized by a significantly increased reproductive rate and total population biomass of blue-green algae or cyanobacteria. Blue-green algae are photoautotrophic prokaryotes which exist along with other eukaryotic algae as the phytoplankton community. A significant bloom is usually observed as scum floating on the surface of the smell and unsightly water; dead fish may be floating in the area also. Marine algal blooms are called red tides because the blue-green algae were red-colored *Pfiesteria piscicida* dinoflagellates.

Freshwater algal blooms are more difficult to spot as they are fluorescent light green color, typical of hypertrophic rivers and ponds (Figure 2.3). Hypertrophic aquaculture ponds develop a number of characteristic conditions that promote the dominance of cyanobacteria. These include warm water temperature (15–30 °C), pH>6 a dim underwater light climate, calm poorly-mixed conditions, high total phosphorus concentration, and low carbon dioxide concentration. (Hargreaves, 2003)

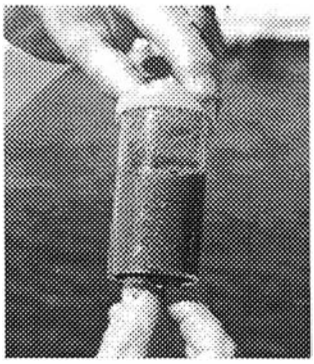


Figure 2.3 Microcystis bloom (Photo Courtesy of Swan River Trust, 2004)

Effect of Bloom and Its Die-Off on Fish

Mortalities of fish, crabs, clams, etc. are due to the significant decrease in oxygen in the water via bloom respiration or degradation (Fleming, 2002). A bloom is associated with toxins if the algal species are the blue-green algae *Microcystis*, *Cylindrospermopsis*, *Anabaena* and *Aphanizomenon*, as well as the microflagellate *Prymnesiam* (Carmichael *et al.*, 1983, Fastner, 1995; Fastner, 2003; Landsberg, 2002).

There is no field evidence on how the toxins cause the mass fish kill. There was one anecdotal reports describing the condition of the river water as "foaming and petroleum-smelling" before the fish kill in the presence of dinoflagellate *Pfiesteria piscicida* at the Hyrock fish farm in Princess Anne in 1996 (Terlizzi, 1997). While removing dead fish from the water, workers reported that the water felt "hot" (temperature was 28 ^{0}C), suggesting dermal irritation. When potassium permanganate (<4 mg/L), was used in a neighboring pond with similar mixed dinoflagellate populations, it appeared to arrest the bloom without fish mortality, possibly a result of permanganate oxidation of toxins.

The microcystis toxins called, microcystin-LR have been experimentally proved to affect the liver. They are highly toxic with intra-peritoneal mouse LD50s between 50-200 µg/Kg body weight. Microcystins inhibit protein phosphatase 1 and 2A which can promote tumor in the liver. Animal and epidemiological studies suggest that low-level chronic exposure to microcystins increase human health risk of carcinogenesis and tumor growth promotion of the liver (US EPA, 2001). Cousins *et al.* (1996) demonstrated that the primary degradation of the Microcystis toxin, called microcystin-LR, occurred within less than a week in a reservoir.

The World Health Organization (WHO) guideline of 1 μg/L for microcystin is based on an adult's typical daily intake of water, the individual's body weight, and the toxicity.

With only laboratory proof of toxicity and "descriptive" anecdotal report of the fish kill, the cause-effect relationship between the fish kill and the cyanotoxins could not be established. It is thus generally accepted that the fish kill is the result of oxygen depletion, or "asphyxiation" (Hallegraeff, 1992; Lee, 1996).

There are, however, several laboratory experiments to suggest how the toxins may cause the fish kill. These toxins are shown to be toxic to the liver in particular, due to selective transport mechanisms that concentrate these toxins in liver cells. And, they damage the liver by altering the cytoskeletal architecture of the hepatocytes (Carmichael *et al.,* 1983; Humpage, 2000; MacKintosh *et al.,* 1995; Repavich *et al.*, 1990, Pflumacher *et al.*, 2000). Other experiments suggests that the abnormal biochemical responses such as inactivation of gill transport-related enzymes activities, the fall in blood pO_2 and abnormal secretion of gill mucus may be one of the principal causes of fish kill by dinoflagellate *Cochlodinium polykrikoides* (Kim et al., 2000).

Chemical Trace of Cyanobacteria

Heptadecane is a characteristic marker of most cyanobacteria (Walsh *et al.*, 1998) and an important constituent of their membrane. Production of long-chain alkanes occurs in higher plants, fungi, bacteria, algae, insects and animals, often as components of waxes (for a barrier against water-exchange) or as constituents in the myelin sheaths of peripheral nerves (Cheesbrough *et al.*, 1984; Cheesbrough *et al.*, 1988; Dennis *et al.*, 1991). Release of heptadecane by algae into the surrounding water may act as an allelopathic agent since the general bioaccumulation of aliphatic hydrocarbon is well known to be toxic (Walsh *et al.*, 1994; Livingstone, 1984; Walsh *et al.*, 1995). Heptadecane is believed to be derived during the enzymic decarbonylation of aldehydes generated from an even-chain, precursor fatty acid. Walsh *et al.* (1998) induced the production of volatile organic carbons (VOC), predominantly heptadecane from cyanobacteria, *M. aeruginosa* with irradiance and iron.

Characteristics of Fish Died From the Bloom

Skin lesions as shown in Figure 2.3 on Atlantic menhaden during blooms of *Pfiesteria* and *Pfiesteria*-like dinoflagellates, are typical. The lesions range from areas of redness to raised friable masses to penetrating ulcers affecting the dermis, underlying muscle and sometimes exposing viscera (Kane *et al*, 1998).

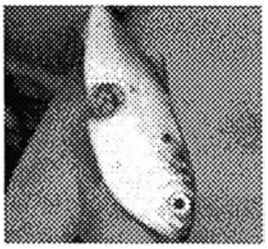


Figure 2.4 Skin lesion.