MODELING MERCURY IN THE EVERGLADES ECOSYSTEM

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MODELING MERCURY IN THE EVERGLADES ECOSYSTEM

by

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LIST OF SYMBOLS

C_o	Contaminant concentration in the organism (mass.mass^{-1})
C_s	Contaminant concentration in source (mass.mass^{-1} or mass.volume^{-1})
k_e	Elimination rate (time^{-1})
C_{hw}	Concentration of Hg (II) in water, ng / L (Nanogram per liter)
C_{hb}	Concentration of Hg(II) in bacteria (mg / kg)
C_b	Concentration of methylmercury in bacteria (mg / kg)
k_m	Methylation rate, d^{-1} (per day)
k_u	Uptake rate (L kg^{-1} d^{-1})
μ_b	Cell division rate for bacteria (d^{-1})
k_d	Depuration rate of MeHg (d^{-1})
P	Permeability coefficient (dm / day)
A_{cell}	Specific surface area of the cells (dm^2 kg-cell^{-1})
r_b	Radius of bacteria cell (μm)
k_x	Mass specific mercury uptake rate (L kg^{-1} d^{-1})
k_p	Uptake rate via passive diffusion (L kg^{-1} d^{-1})
k_f	Uptake rate via facilitated diffusion (L kg^{-1} d^{-1})
β_{HX}	Stability constant for the first order protonation reaction with membrane transport ligand
$[H^+]$	Concentration of the hydrogen ion H^+
C_w	Methylmercury concentration in water (mg / L)
C_{ph}	Methylmercury Concentration in phytoplankton (mg / kg)
μ_{ph}	Instantaneous rate of cell division for phytoplankton (d^{-1})
r_{ph}	Radius of phytoplankton cell (μm)
C_z	Methylmercury concentration in zooplankton (mg / kg)

C_f	Methylmercury concentration in food (mg / kg)
k_{uw}	Uptake rate from water (L kg-ww^{-1} d^{-1})
k_{uf}	Uptake rate from food (kg kg^{-1} d^{-1})
R	Respiration rate (d^{-1})
r_{oc}	Ratio of oxygen to carbon (kg O / kg C)
r_{cd}	Ratio of carbon to dry weight (kg C / kg-dw)
r_{wd}	Ratio of wet to dry weight (kg wet / kg dry)
C_{ow}	Concentration of dissolved oxygen in water (kg O / L)
E_m	Methylmercury transfer efficiency
E_o	Oxygen transfer efficiency
w	Weight of the organism (g)
T	Water temperature ^{o}C
C_d	Methylmercury concentration in detritus (mg / kg)
F_{zph}	Fraction of the consumption of zooplankton on phytoplankton (unit less)
F_{zd}	Fraction of the consumption of zooplankton on detritus (unit less)
G	Growth rate (d^{-1})
a	Food assimilation efficiency (unit less)
S	Food consumption rate (d^{-1})
β	Chemical assimilation efficiency (unit less)
$F_{i,j}$	Feeding preference of predator *i* for prey *j* (unit less)
C_j	Methylmercury concentration in prey *j* (mg / kg prey ww)
MF	Muscle fraction of fish
dw	Dry weight
ww	Wet weight

C_{xy} Pollutant concentration at downwind distance x and crosswind distance y (μg m^{-3})

Q Pollutant emission rate (g s^{-1})

K A scaling coefficient to convert calculated concentrations to desired units (default value of 1x 10^6 for Q in gs^{-1} and concentration in μg m^{-3})

V Vertical term

D Decay term

u_s Mean wind speed (m s^{-1}) at release height

σ_y Standard deviation of lateral concentration distribution (m)

σ_z Standard deviation of vertical concentration distribution (m)

z_r Receptor height above ground (m)

z_i Mixing height (m)

φ Decay coefficient, (s^{-1})

u_{ref} Observed wind speed (m s^{-1})

z_{ref} Anemometer height (m)

h_s Physical stack height (m)

h_e Effective stack height (m)

Λ Scavenging rate constant (s^{-1})

λ Scavenging coefficient $(\text{s-mm/hr})^{-1}$

ρ Precipitation rate (mm/hr)

F_d Deposition flux (μg m^{-2} s^{-1})

V_d Deposition velocity (m s^{-1})

d_s Inside stack top diameter (m)

v_s Stack gas exit velocity (ms^{-1})

T_a Ambient Temperature (K)

T_s Exit temperature (K)

LIST OF ABBREVIATION

BAF	Bioaccumulation Factor
BCF	Bioconcentration Factor
CSA	Canadian Standards Association
FDEP	Florida Department of Environmental Protection
FSU	Florida State University
FWC	Florida Fish and Wildlife Conservation Commission
GDNR	Georgia Department of Natural Resources
IDNR	Iowa Department of National Resources
NJDEP	New Jersey Department of Environmental Protection
NRC	National Research Council
PCB	Polychlorinated Biphenyl
PU	Purdue University
SA	Sensitivity Analysis
SFWMD	South Florida Water Management District
USEPA	U.S. Environmental Protection Agency
USFWS	U.S. Fish & Wildlife Service
USGS	U.S. Geological Survey
WBG	World Bank Group
WDNR	Wisconsin Department of Natural Resources

PEMODELAN RAKSA DALAM EKOSISTEM EVERGLADES

ABSTRAK

Raksa merupakan salah satu bahan pencemar utama kerana bentuk organiknya yang dikenali sebagai metilraksa boleh mengakumulasi sehingga ke tahap tinggi dalam rantai makanan akuatik. Metilraksa (MeHg) ialah sejenis bentuk organik raksa yang sangat toksik dan lipofilik. Bioakumulasi MeHg dalam rantai makanan akuatik di Florida Everglades telah mencapai tahap membimbangkan sejak beberapa dekad yang lalu. Bermula dari peringkat trofik yang rendah seperti periphyton, fitoplankton dan zooplankton, MeHg mengakumulasi sehingga ke tahap berbahaya dalam pelbagai organisma pada peringkat trofik akuatik yang tinggi seperti ikan. Faktor bioakumulasi MeHg untuk ikan dalam lingkungan 10 juta telah direkod. Sebab utama masalah raksa di Everglades ialah penurunan raksa tak organik kepada bentuk organik MeHg oleh bakteria penurunan sulfat (SRB). Beban raksa setinggi 2.5 mg/kg dalam largemouth bass di Everglades telah direkod oleh Florida Department of Health. Tahap ini dianggap tidak selamat berdasarkan semua standard kesihatan. Lebih 90 % bajet tahunan raksa di Everglades Protection Area berjumlah 35.3 $\mu g/m^2$/tahun disumbangkan oleh pengendapan atmosfera, di mana 50 % daripada amaun ini berasal dari punca tempatan. Dalam tesis ini, beberapa model bioakumulasi telah dibangunkan untuk menganggar kepekatan MeHg dalam SRB (suatu komponen periphyton), fitoplankton, zooplankton dan ikan. Pengendapan raksa di Everglades juga disimulasi dengan menggunakan model penyebaran dan pengendapan atmosfera ISCST3. Secara umumnya, keputusan yang diperolehi berada dalam lingkungan data yang ditinjau.

MODELING MERCURY IN THE EVERGLADES ECOSYSTEM

ABSTRACT

Mercury is recognized as one of the primary pollutants in the world mainly because its organic form known as methylmercury can accumulate to high levels in the food chain of many aquatic systems. Methylmercury (MeHg) is a highly toxic and lipophilic organic form of mercury. The bioaccumulation of methylmercury in the aquatic food chain in the Florida Everglades has been a concern for several decades. Beginning with lower trophic levels such as periphyton, phytoplankton and zooplankton, MeHg has been observed to accumulate to dangerously high levels in many types of organisms in the higher trophic levels of the aquatic food chains such as fish. The MeHg bioaccumulation factors for fish ranging up to 10 million have been recorded. Mercury problem in the Everglades is primarily due to the conversion of inorganic mercury to the organic MeHg by sulfate-reducing bacteria (SRB). High mercury burdens of 2.5 mg/kg have been recorded by the Florida Department of Health in the largemouth bass in the Everglades, a level that is deemed unsafe by all health-based standards. Over 90 % of the annual budget of mercury in the Everglades Protection Area is contributed from atmospheric deposition, amounting to 35.3 $\mu g/m^2/yr$, of which local emissions contribute some 50 % to this total. In this thesis, several bioaccumulation models are developed to predict MeHg concentrations in SRB (a component of periphyton), in phytoplankton, in zooplankton and in fish. Also, mercury deposition on the Everglades is simulated by using ISCST3 air dispersion and deposition model. In general, the obtained results are within the range of the observed data.

CHAPTER 1

INTRODUCTION

1.1 Mercury in the Environment

Mercury is known to be a toxic element. When released into the environment, it can take the inorganic and organic forms (USEPA, 2001a). Mercury is a well–documented killer to wildlife and human (FSU, 1997). In the natural environment, mercury is present in coal and mineral ores. Approximately 3×10^{-6} % of the crust of the earth is formed of mercury, mostly in combination with sulfur (USEPA, 2003). Over the last 100 years, global atmospheric mercury concentration increases from approximately 0.3 ng m^{-3} to an estimated global average of 1.5 ng m^{-3} (Sunderland and Chmura, 2000). According to Lin and Pehkonen (1999), approximately 6000 tons of mercury is present in the troposphere, while 10800 tons are available in the water bodies on earth. An estimated 66 percent of mercury in the environment is a result of man-made sources (PU, 2002).

Mercury is a concern to the world, because it can accumulate (especially the organic form known as Methylmercury) to high levels in the food chain in many aquatic systems (USEPA, 1997; NRC, 2000; USGS, 2000; Atkeson and Parks, 2001; FDEP, 2002; Lutter and Irwin, 2002; PU, 2002; Atkeson and Axelrad, 2003). The most well documented cases of severe methyl mercury poisoning among humans were recorded in Minamata Bay, Japan in 1956 and in Iraq in 1971. The occurrence of methyl mercury in Minamata was through industrial release of mercury into the bay, while in Iraq it was due to the

consumption of wheat treated with a methyl mercury fungicide (USGS, 1995; Bale, 2000). In each of the aforementioned cases, hundreds of people died, and thousands more were afflicted, with many suffering permanent neurological disorders due to mercury poisoning (USGS, 1995).

1.2 Atmospheric Mercury

Mercury (Hg) is present in the atmosphere in three forms, gaseous elemental mercury Hg(0), divalent mercury Hg(II), and particulate associated mercury Hg(p). Hg(0) is the dominant form in the atmosphere, Hg(II) is produced from the oxidation of Hg(0), and Hg(p) consists of Hg(II) and particulate matter (coarse and fine). Emissions of elemental mercury can remain for one year in the atmosphere (Atkeson and Parks, 2001; Seigneur et al., 2003) and can be transported over thousands of miles before being deposited (USEPA, 1997; Hanisch, 1998), while emissions of divalent mercury can remain in the atmosphere for hours to days. Mercury associated with fine particulate matters remains days to weeks in the atmosphere, while mercury associated with coarse particulate matters can be transported over a few miles before deposited, because it has high gravitational settling (Atkeson and Parks, 2001).

Mercury emissions come to the atmosphere from two main sources, natural sources such as volcanoes, soils, lakes, and oceans (Lee et al., 2001), and anthropogenic (human activities) sources, which include combustion and waste incineration (Hanisch, 1998; Lin and Penhkonen, 1999; PU, 2002) as well as burning of fossil fuels such as coal and oil (Atkeson and Parks, 2001;

Atkeson and Axelrad, 2003). According to USEPA (1997), atmospheric deposition of mercury to land or water at a location is the result of contributions from the following:

(i) Local emissions (within 100 km from the emission source);

(ii) Regional emissions;

(iii) Global emissions.

1.3 Mercury in the Everglades

The Everglades is chosen as a study site in this thesis for two reasons. First, mercury contamination in the Everglades is a serious problem, and hence deserves attention. Secondly data on various aspects of mercury pathways required in this study is available for the Everglades. The focus of this thesis relates to mercury transport, deposition and eventual bioaccumulation in the food chain of the Florida Everglades. A brief introduction to the Everglades ecosystem is provided in this section. Mercury begins its pathways into the Everglades via two ways. The first is from runoff from the watershed and the second is from atmospheric deposition (wet and dry depositions). Mercury loads from wet deposition (by rainfall) are about 50 times more than mercury loads from the inflows of surface water. Mercury dry deposition adds another 30% to rainfall deposition. Over 95% of the annual budget of mercury to the Everglades Protection Area EPA (Water Conservation Area WCA plus Everglades National Park ENP) is from the atmosphere (Atkeson and Parks, 2001; Atkeson and Axelrad, 2003). As a result, atmospheric deposition represents the dominant mercury source into the Everglades.

1.3.1 The Everglades

The Everglades is one of the wonderful regions in the world. It is located in the southern parts of Florida in the United States of America, bounded to the north by the southern edge of Lake Okeechobee, to the west by the Big Cypress Swamp, to the east by the Atlantic Ocean, and to the south by the Florida Bay (Figure. 1.1).

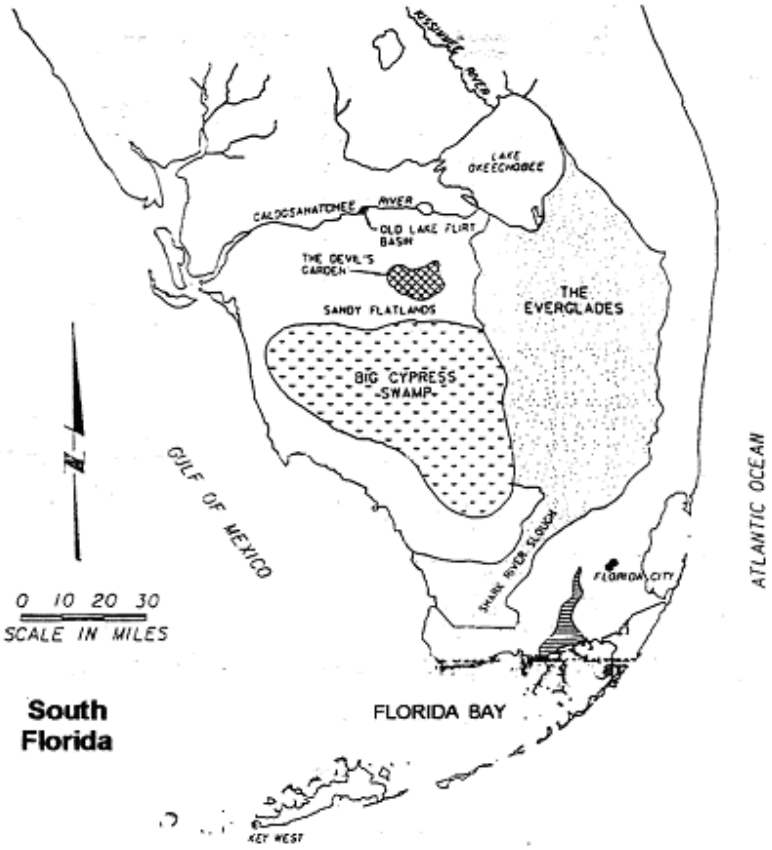

Figure 1.1. Location of Everglades in south Florida. From (Gleason and Stone, 1994).

The Everglades Ecosystem

An ecosystem is a geographic area including all the living organisms (people, plants, animals, and microorganisms), their physical surroundings (such as soil, water, and air) and the natural cycles that sustain them (USFWS,

2006). The Everglades ecosystem is an unparalleled natural resource. It serves as the home to millions of people and untold numbers of plant and animal species. Further, Everglades acts as a natural filter of industrial and agricultural runoff inland.

The historical Everglades covers an area of approximately 10,500 square kilometers (USEPA, 1996; DeAngelis et al., 2002). This area extends south from lake Okeechobee for over 200 km and from east to west for about 80 km. During the summer rainy seasons, water overflows from Lake Okeechobee along its southern shore line into the Everglades due to the gradual slope of the land of 3 cm / km. This flow continues until it reaches the waters of the Florida Bay or the Gulf of Mexico.

Climate

The Everglades has a tropical climate, with a summer wet season from May through October and a dry season from November until April (Schaffranek and Jenter, 2000). During summer, it rains on a daily basis, mostly in the afternoons. The Everglades rarely experience freezing temperatures associated with winter cold fronts. The average temperatures are warm all year in the upper 27° C to 32° C (Duever et al., 1994).

1.3.2 Mercury Problem in the Everglades

According to Atkeson and Axelrad (2003), mercury was first discovered in the Everglades fish in the late 1980s. In 1989, high levels of mercury in fish from the Everglades was recorded during a monitoring survey conducted jointly

by the Florida Fish and Wildlife Conservation (FWC), the Florida Department of Environmental Protection (DEP) and the Florida Department of Health (DOH). In the early 1990s, an extensive sampling was completed. The sampling revealed alarmingly high mercury burdens in the largemouth bass, averaged nearly 2.5 mg/kg mercury, which exceeded all health based-standards (FDEP, 2002). This undesirable situation regarding the state of mercury contamination in the Everglades motivates the selection of mercury contamination pathways in the Everglades as a research focus in this thesis.

1.3.3 Mercury Emissions to the Everglades

Local sources of mercury emissions in the neighbourhood of the Everglades are located in the heavily developed southeastern coast of Florida, where medical waste incinerators, municipal solid waste combustors, cement kilns and power plants are located. Mobile sources such as automobiles, ships and other engines powered by fossil fuels also contribute to mercury emissions. The global background mercury emission to the Everglades comes during the summer months, where approximately 85 % of rainfall mercury deposition into the Everglades occurs when the easterly trade winds blow from the Atlantic Ocean (Atkeson and Parks, 2001).

1.3.4 Deposition of Atmospheric Mercury on the Everglades

As was mentioned in section 1.3, atmospheric deposition represents the ultimate mercury source to the Everglades. The Florida Department of Environmental Protection (FDEP) has estimated the total deposition of mercury for the period June 1995 through June 1996. The result was 35.3 $\mu g / m^2 / yr$,

of which 23 μg / m^2 / yr was measured by Florida Atmospheric Mercury Study (FAMS) as wet deposition, and the remaining 12.2 μg / m^2 / yr was modelled as dry deposition (FDEP, 2002). According to FDEP (2002) and Atkeson and Axelrad (2003), the contributions of local, regional, and global mercury emissions to the total deposition of mercury on the Everglades (35.3 μg / m^2 / yr) are as follows:

(i) Local Emissions: 52 %;

(ii) Regional emissions: 29.1 %;

(iii) Global emissions: 18.4 %.

1.3.5 The Cycle of Mercury in the Everglades

Upon entering the water, mercury is subjected to transformation processes. During the transformation processes, inorganic mercury in the form of Hg (II) is converted into organic mercury in the form of methylmercury (MeHg) by bacteria. The bacteria themselves may excrete the methylmercury into the water where it is taken up by the planktons (USGS, 2000) and other aquatic organisms such as fish. Methylmercury can also be converted back by bacteria to Hg (II) (Bale, 2000; Krabbenhoft et al., 2000) or to the elemental mercury Hg(0) (USGS, 1996a). USGS (2000) suggests that sunlight may also breaks down organic methylmercury to inorganic Hg(II).

1.4 Mercury Bioaccumulation

Bioaccumulation refers to the accumulation in an organism of a substance that enters that organism through a combination of pathways such as respiration, food intake and skin contact (Jørgensen, 1990; Oost et al., 2003;

USGS, 2005). Hence, a chemical can accumulate in an organism such as fish by the direct uptake from the contaminated water through the gills and via the consumption of contaminated food through the gastrointestinal tract (Trudel and Rasmussen, 2001). Uptake via the skin is usually insignificant (Gobas, 1993). The accumulation of mercury in fish and other aquatic organisms in the Everglades begins with the uptake of foods consisting of the first trophic level comprising phytoplankton and periphyton. This follows the bacterial conversion of inorganic Hg(II) to the highly toxic organic methylmercury (MeHg), which is easily bioaccumulated in the food chain (King et al., 2001).

1.5 Study Sites

The current study focuses on two regions in the Everglades, named the Water Conservation Area 3A (WCA-3A), and Water Conservation Area 2A (WCA-2A). The Everglades Water Conservation Areas (Figure 1.2) are marshlands bordered by canals, where WCA-2A has 210 square miles of marsh, while WCA-3A is the largest WCAs, with an area approximately 915 square miles of marsh (FWC, 2005a).

Figure 1.2. Map of the Everglades sites. From (USEPA, 2001b).

1.6 Objectives, Scope and Organization of Thesis

It is noted that after emission to the atmosphere and before entering the fish body, mercury is subjected to the following processes based on its cycles mentioned in section 1.3.5:

(i) Atmospheric dispersion and deposition processes;

(ii) Transformation to its organic form (methylmercury) in the water by sulfate-reducing bacteria (SRB), and then bioaccumulation of methylmaercury in SRB;

(iii) Bioaccumulation in Plankton (phytoplankton and zooplankton);

(iv) Bioaccumulation in Fish.

Hence, the objectives of this thesis are:

1. To model the transport, dispersion and deposition of mercury into the Everglades due to the local emission sources;
2. To model bioaccumulation processes of methylmercury in the Everglades by Sulfate Reducing Bacteria SRB;
3. To model bioaccumulation processes of methylmercury in the Everglades through phytoplankton, and zooplankton and finally to fish.

This thesis consists of seven chapters. Background of mercury problem in the Everglades and the objectives of thesis are presented in chapter 1. In chapter 2, a general over view of some bioaccumulation models and air dispersion and deposition models is presented. In chapter 3, a new model is derived to predict mercury concentration in sulfate-reducing bacteria SRB after it is transformed from inorganic mercury Hg(II) to methylmercury MeHg by SRB. In chapter 4, two bioaccumulation models are developed to predict methylmercury concentrations in phytoplankton and in zooplankton, with the uptake of methylmercury by phytoplankton from water and the uptake of methylmercury by zooplankton from water and food. In chapter 5, an age structured bioaccumulation model is developed to predict methylmercury concentrations in each age class of two groups of the Everglades fishes, namely largemouth Bass and warmouth. The uptake of methylmercury from water and food into the fish is modeled by forming a set of initial value problems with the retained MeHg in a previous age class as the initial MeHg for the next age class. In chapter 6, simulation is conducted to predict the deposition of mercury on the Everglades due to the local emissions of mercury by using

ISCST3 air dispersion and deposition model. Finally, in chapter 7, general conclusions and recommendations for future studies are discussed.

CHAPTER 2

LITERATURE REVIEW

2.1 Previous Studies

For perspectives on modelling contamination in the Everglades food chain, it might be beneficial to relate a previous research performed on modelling polychlorinated biphenyls (PCB) bioaccumulation in fish and its effects on the Everglades fish ecology (Al-Rabai'ah, 2002). Several mathematical and simulation models were developed for the purpose of tracking the pathways of PCBs in the Everglades fish, including the effect that PCBs might have on the fish ecosystem in the Florida Everglades. A model was developed to predict the length and size of fishes in the Everglades subject to changes in temperature (Al-Rabai'ah and Koh, 2003). This model was then enhanced by extending the temperature dependence of growth in individual fish to cover other fish biological activities such as food consumption rate (Al-Rabai'ah et al., 2002b). Another model was developed to simulate the changes in water levels in the fresh water marshes and its effect on fish population dynamics subject to the impact of interactions with lower trophic communities. This hydrological-ecological model is useful as the Everglades is subject to regular changes in water levels in each year. In some of the models, a mass balance steady state bioaccumulation model was used to asses the fate and pathways of polychlorinated biphenyls (PCBs) in the aquatic food web, in particular in the graminoid-dominated areas of the Everglades, which include the areas of saw grass, peat and wet prairies. Finally, a time-concentration-response model was developed to predict the responses of fish exposed to different

levels of contaminant at different exposure durations (Al-Rabai'ah et al., 2002c). The results obtained from the models showed a general agreement with the observed data. Based upon the methodology developed in this previous research on modelling PCB contamination in the Everglades fish, this thesis will simulate the pathways of mercury, another major contaminant, in the Everglades fish ecosystem, following similar approach adapted for mercury. With this in mind, the subsequent literature review will begin with a brief exposition of general bioaccumulation models for aquatic organisms to provide a broad background.

2.2 Bioaccumulation Models

A bioaccumulation model simulates chemical accumulation in the food web in response to chemical exposure, based upon chemical mass balances for aquatic biota. The general form of the bioaccumulation equation is to equate the rate of change in chemical concentration within the aquatic organism, based upon the sum of chemical fluxes into and out of the organism. These fluxes include the direct uptake of chemical from water, the flux of chemical into the organism through feeding, and the loss of chemical due to elimination and dilution due to growth (USEPA, 2006a). There are many bioaccumulation models that are developed to predict the bioaccumulation of chemicals in the organism. Some of these bioaccumulation models that predict the concentration of xenobiotic organic chemicals in the organism are mentioned below.

Norstrom et al. (1976) developed a pollutant accumulation model to calculate the PCB concentration and methylmercury in Ottawa River Yellow

perch. In the model, the uptake of pollutant from water is proportional to the respiration rate and the uptake from food is proportional to the ingested ration, while the elimination rate is related to the body weight. The model simulated the concentrations of methyl mercury and PCB in body tissue as a function of the body weight. The predicted values of the concentrations of methylmercury and PCB in tissue fall within the natural scatter of the field data.

Thomann (1981) constructed a steady state compartment food chain model from a general mass balance equation of the chemicals transfer into the organism. The model is derived to estimate the relative effect of the uptake of three substances directly from water versus the uptake from the food. The model is based upon two equations, the first equation is for the organism, such as phytoplankton, in which the uptake of the substance occurs only via water and the second equation is for the organism, such as fish, in which the uptake of the substance occurs via water as well as via food. The first equation consists of two terms, one for the uptake from water and the other for the elimination rate, while the second equation, in addition to the two terms, contains a third term for the uptake from food. The model depends on many parameters such as the respiration rate, consumption rate, excretion rate, growth rate, and the chemical assimilation efficiency. Most of the parameters are related to the organism weight and the water temperature. Thomann (1981) concluded that this simple steady state model of the transfer of chemical in the food chain could help to understand the observed concentration factors for the chemical. The model highlighted the importance of parameters such as food assimilation, excretion rate and net weight. These observations will be

incorporated in this thesis in its selection of simulation methods, where simplicity and clarity will be preferred where appropriate.

To account for age dependency, Thomann and Connolly (1984) constructed an age-dependent food chain model of uptake and transfer for PCB in the Lake Michigan food chain. The model is based on the same mass balance equation that was used in the earlier paper (Thomann, 1981). The model used the parameters such as growth rate, respiration rate, and food assimilation efficiency to predict PCB concentrations that are obtained on a wet weight basis. The model consists of four species in the food chain: phytoplankton, Mysis relicta (zooplankton), alewife (small fish) and lake trout (big fish). The calibration of the model with the field data obtained from Lake Michigan showed that the transfer of PCB through the food chain is the major contributor to the observed concentrations of PCB in lake trout, accounting for more than 99% of the body burden in adult trout. The model was validated in the field with the two fish species, alewife and lake trout.

Based upon the success of the earlier research, Thomann (1989), Thomann et al. (1992) and Al-Rabai'ah et al. (2002a) developed improved steady state models for predicting the chemical concentration in aquatic food webs for various ecosystems. The enhancement includes additional mechanistic details for the organic chemicals, such as the inclusion of octanol-water partition coefficient (K_{ow}) as a parameter controlling the tendency of the chemicals to partition into the lipid of the organisms. Therefore, the predicted chemical concentration is obtained on a lipid basis. In these later types of

models, the chemical uptake efficiency, the chemical assimilation efficiency, and the excretion rate are related to the octanol-water partition coefficient (K_{ow}). The amount of chemical entering the organism due to the uptake from water depends on (K_{ow}), where the uptake efficiency increases as log K_{ow} increases up to a point. When stability is reached after a high value of log K_{ow} > 6.5 is achieved, the uptake efficiency begins to decrease. In addition, the model developed by Thomann (1989) consisted of four levels of food chain: phytoplankton, zooplankton, small fish, and top predator. The model was used to calculate the bioconcentration factors (BCF) and the bioaccumulation factors (BAF), as a function of K_{ow}, for many chemicals such as PCB. The model was applied mostly to Lake Michigan and Lake Ontario. The model results indicates that the food chain effects are not significant for chemicals with log K_{ow} up to ~ 5 (< 5), while the calculated and observed concentration factors in top predator are significantly above calculated BCF values for log K_{ow} of 5-7. Further, the model results indicate that for log K_{ow} of < 5, the decreased uptake and increased excretion inhibit food chain buildup. In Thomann et al. (1992), the model consists of five biological compartments: benthic invertebrates, phytoplankton-detritus, zooplankton, forage fish, and piscivorous fish. The model tested the relation between the product of food chain multiplier and food assimilation efficiency. The model calculations showed that the effect of the product of food chain multiplier and food assimilation efficiency is small for log K_{ow} of < 4-5 but the effect increases to reach a peak at log K_{ow} of 6-6.5 and then the effect decreases there after. This indicates that the food chain effects are generally insignificant for chemicals with log K_{ow} of < 4-5 while the food

chain effects may be significant for log K_{ow} of > 5 and < 7. In Al-Rabai'ah et al. (2002a), the model consists of five compartments: sedimented detritus, phytoplankton, zooplankton, macroinvertebrates, and fish. The model was applied to calculate total PCBs concentrations in all compartments. The model results showed that the model is successfully applied to predict the residue levels of total PCBs in fish species in graminoid-dominated areas in the Everglades National Park (ENP), where the results are within the range of the reported field data. Moreover, the results showed that there is an increase in contamination as we move up from the primary producers to the top predators level. It is also observed that the model is sensitive to the lipid content.

Connolly (1991) developed a food chain model to simulate PCB contamination in the lobster and winter flounder food chains in New Bedford Harbor. The model, based on the mass balance equation, is similar to that mentioned in Thomann and Connolly (1984). In the model, the lobster food chain consists of crabs, mussels, polychaetes, phytoplankton, and sediment detrital organic material. The winter flounder food chain consists of polychaetes, phytoplankton, and sediment detrital organic material. The model includes three specific parameters, chemical/oxygen transport efficiency ratio at the gill, assimilation efficiency of the ingested chemical and bioconcentration factor, where the last parameter is related to K_{ow} and the fraction of lipid of the organism. The results of the model indicate that most PCB concentration in the flounder is derived from the sediment and the whole body PCB concentration in flounder is more than that in lobster. Further, the dietary uptake appears to be the major source of contamination.

Gobas (1993) developed a steady-state model to estimate the transfer and bioaccumulation of hydrophobic organic chemicals (PCB is one of them) in single organisms and simple aquatic food web, using rate constants and chemical concentrations in sediment and water. The model consists of four compartments: phytoplankton, zooplankton, benthic invertebrate (two species), and fish (four species). The model requires basic data regarding the organisms of the food web such as the types of species and their weights, chemical properties such as chemical concentration in water and environmental conditions such as water temperature. The model was applied to Lake Ontario food web. The model results showed that the food-web model result is in good agreement with the observed data from Lake Ontario, despite or perhaps because of the simplicity of the model.

Loizeau et al. (2001) developed a bioaccumulation model to simulate the PCB contamination in the sea bass food web from the Seine Estuary. The model is based on equations similar to those described in the equilibrium model developed by Thomann (1989). In the model, seasonal variation is taken into account. The model consists of six biological compartments: zooplankton, shrimp (two species), mysidaceans, and fish (two species). These compartments were considered together with the contaminant concentration in water, in detritus, and in phytoplankton. In general, the growth rate, respiration rate, consumption rate and elimination rate are related to the weight and the water temperature. The model results obtained for PCB contamination are consistent with the observed data from Seine Estuary except for the oldest fish. Because of the relative success of these simple steady-state models to predict

contaminant concentrations in the aquatic food chain, this simple steady-state approach will be adopted in this thesis. When more refined field and lab data are available, they will be used to formulate more refined models.

2.3 Atmospheric Dispersion and Deposition Models

It is known that mercury in the Everglades wetlands are mainly derived from atmospheric deposition originating from sources in the neighbourhood. Hence it is important to predict the atmospheric transport and deposition of mercury from sources into the Everglades wetlands.

When a pollution source emits a chemical into the atmosphere at an initial concentration, the chemical does not remain at that initial concentration. Atmospheric processes act to disperse the emissions downwind into lesser concentrations. Therefore, the atmospheric dispersion models can be defined as a computation tool that uses mathematical equations to describe the dispersion process. If the initial concentration of the chemical is known, then one can use a dispersion model to predict the downwind concentration of pollutant emitted by various pollution sources (Westbrook, 1999). According to WBG (1998), the data required by the dispersion models fall into the following four categories:

(i) Emission Parameters, such as stack location, stack height and inside diameter;

(ii) Meteorological conditions, such as air temperature, Pasquill stability class;

(iii) Point source elevation and building dimensions;

(iv) Receptor data, usually receptors are specified by their coordinates and elevation.

The atmospheric dispersion models are also known as atmospheric diffusion models, air dispersion models, air quality models and air pollution dispersion models. According to USEPA (2006b), the following models are recommended.

AERMOD is a steady-state plume model that incorporates air dispersion based on planetary boundary layer turbulence structures and scaling concepts, including treatment of both surface and elevated sources, and both simple and complex terrains. AERMOD consists of 3 components, AERMOD (air dispersion model), AERMET (meteorological data preprocessor) and AERMAP (terrain preprocessor). The basic input files are the source locations (including point, volume and area source types), parameter data, receptor locations and meteorological data files that are provided by AERMET (meteorological data preprocessor). AERMOD does not distinguish between simple terrain and complex terrains as some models do. For applications concerning elevated terrains, AERMAP (terrain preprocessor) has been developed to facilitate the generation of hill heights scales for AERMOD (USEPA, 2004a).

CALPUFF is a non-steady-state puff dispersion model that contains modules for complex terrain effects, coastal interaction effects, building downwash, wet and dry depositions and simple chemical transformation. CALPUFF simulates the effects of time and space-varying meteorological

conditions on pollution transport, transformation and removal. CALPUFF can be applied on the scales of tens to hundreds of kilometres (Scire et al., 2000).

Other than the above models, there are also other commonly used models such as ISC3, CTDMPLUS and SCREEN3. The first two models are the most commonly used for the assessment of pollutant dispersion (WBG, 1998). These models are briefly discussed below.

ISC3 (Industrial Source Complex) is used for point, area and volume sources in a flat terrain or in a complex terrain. There are two versions of ISC3, the first is ISCST3 which is a steady state Gaussian plume model. It is used for estimating the near field (less than 50 km) downwind air dispersion and deposition rates of pollutant on receptors from a wide variety of sources. ISCST3 is used for shorter averaging periods of 24 hours or less. ISCST3 requires three main types of data: emission source parameters, meteorological information and receptor locations. The second version is ISCLT3, which is used for averaging longer periods of 30 days or more (WBG, 1998; Abbott et al., 2001; Schnelle and Brown, 2002).

CTDMPLUS (Complex Terrain Dispersion Model Plus Algorithms for Unstable Situations) is a refined air dispersion model. It is used in all stability conditions for complex terrain applications. CTDMPLUS requires five main input files: a general file containing source data, meteorological tower coordinates and hill surface roughness lengths, a terrain data file, a receptor file, a surface

meteorological data file and a user-created meteorological profile data file (USEPA, 1989).

SCREEN3 is a single source Gaussian plume model that provides maximum ground-level concentrations for point, area, flare and volume sources. It is designed to determine quickly and easily the impacts from a single source. This model requires no site-specific meteorological inputs.

Due to their reliability and simplicity, the popularly used models ISCST3 and its enhanced version AERMOD are used in this thesis to simulate the transport and deposition of mercury from sources into the Everglades wetlands.

CHAPTER 3

MODELING MERCURY IN BACTERIA

3.1 Introduction

As was mentioned in chapter 1, mercury problem in the Everglades is initiated primarily by the conversion of deposited inorganic Hg(II) to the organic methylmercury (MeHg) by bacteria in the Eveglades wetlands. Methylmercury is a highly toxic, lipophilic, organic form of mercury (King et al., 2001), and has been observed to accumulate to dangerously high levels in many types of organisms in numerous aquatic food chains (USEPA, 1997; NRC, 2000; USGS, 2000; Atkeson and Parks, 2001; FDEP, 2002; Lutter and Irwin, 2002; PU, 2002; Atkeson and Axelrad, 2003), beginning usually with the first trophic level such as periphyton. The mechanism for the transfer of MeHg from the lower trophic level to the higher trophic level in the food chain is now just beginning to be understood, with methylmercury being first synthesized by sulfate reducing bacteria (a component of periphyton) through an anerobic process (Krabbenhoft et al., 2004).

The earlier studies concerning methylmercury (MeHg) focused on modelling phytoplankton as the first trophic level of the food chain (Powell, 1997; Tetra Tech, 2001). However, methylmercury is first bio accumulated in Sulfate Reducing Bacteria (SRB) after the transformation from the inorganic Hg(II) to MeHg by SRB. Therefore in this chapter a new model is developed for the bioaccumulation of methylmercury in sulfate reducing bacteria by combining the processes of the uptake of inorganic Hg(II) and the transformation and

bioaccumulation of MeHg in SRB. The model is based on a single compartment model with first order uptake and elimination kinetics.

3.2 Methylation

The dominant form of deposited mercury in the Everglades is the inorganic mercury Hg (II). As was mentioned in chapter 1, this inorganic mercury Hg (II), upon entering the wetland, is converted into organic methyl mercury MeHg primarily by SRB (USGS, 1996a; Lutter and Irwin, 2002). This transformation process is known as methylation. Methylation may proceed in two different ways, either by biological methylation or by chemical methylation (Beijer and Jernelöv, 1979). However, in this study, only the biological methylation is considered, as it is the main methylation process reported in the Everglades. In addition, Krabbenhoft et al. (2004) has contended that methylation only occurs in the periphyton “mats”, through sulfate reducing bacteria in the absence of oxygen and in the presence of sulfate (Atkeson and Axelrad, 2003). The periphyton mats cover most submerged plants and form thick mats on the sediment surface in many locations in the Everglades (USGS, 1996b). Following SRB the next consumer in the food chain may consume the periphyton mats, which contain the bacteria with methylmercury (USGS, 1996a). Moreover, the bacteria themselves in these mats may excrete methylmercury into the water, after which it is taken up by the planktons (USGS, 2000). Methylmercury can also be converted back into inorganic Hg (II) or Hg(0) (Bale, 2000; Krabbenhoft et al., 2000; USGS, 2000), a process known as demethylation.