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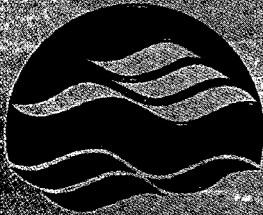
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**MODELLING OF NONYLPHENOLS AND ITS
ETHOXYLATES (NPE) FOR PULP AND PAPER
MILLS ACROSS CANADA**

Booty, W.G. and R.C. McCrimmon

NWRI Contribution No. 02-003

**Modelling of Nonylphenols and its Ethoxylates (NPE) for
Pulp and Paper Mills across Canada**

Final Report

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Management Perspective

As increasing pressure is applied to develop and enforce Canadian water quality guidelines under the Canadian Environmental Protection Act, for assuring water quality downstream of contaminant sources, greater emphasis is being placed on the application of toxic chemical water quality models. The models are used to optimize the competing demands of regulation, environmental protection, and cost of proposed control measures. This study presents the results of the application of two toxic chemical water quality models for various streamflow and effluent scenarios to examine the possible ranges of concentration of nonylphenols and its ethoxylates (NPEs) downstream of selected pulp and paper mills across Canada. The model predicted concentrations in water and sediments are examined with respect to the draft Canadian Environmental Quality Guidelines.

Abstract

This study was carried out to provide modelling support to the Toxics Pollution Prevention Directorate (TPPD), Renewable Resources Division (RRD), Pulp and Paper Sector on modelling the concentrations of NPE's directly downstream of selected pulp and paper mills across Canada. The model results are used to examine compliance of the mills with the new Canadian Environmental Quality Guidelines for nonylphenols and its ethoxylates. The models were applied for various streamflow and effluent load scenarios to examine downstream NPE concentrations with respect to the water quality guidelines.

Of the seven sites examined, only Thunder Bay, Grande Prairie and Dryden had river NPE concentrations that exceed the water guideline of 1 ug/L. The model results indicate that the Dryden site is approximately 1,000% above the guideline while Thunder Bay and Grande Prairie are 50% to 100% above the guideline. The Prince Albert and Temiscaming sites had NPE concentrations 30 to 40% below the guidelines while Gatineau and Masson-Angers sites were approximately 80% below the guidelines. None of the sites had sediment NPE concentrations predicted by the models above or even close to the guideline of 1,400 ug/kg.

Sommaire à l'intention de la direction

On note une pression croissante pour l'élaboration et l'application de lignes directrices canadiennes sur la qualité de l'eau destinées à assurer la qualité de l'eau en aval des sources de contaminants, en application de la *Loi canadienne sur la protection de l'environnement*, et on insiste davantage sur l'application de modèles de limitation des agents chimiques toxiques pour assurer la qualité de l'eau, qu'on utilise pour optimiser les demandes concurrentes de réglementation et les mesures de protection de l'environnement, ainsi que pour réduire les coûts des mesures de limitation proposées. Cette étude présente les résultats de l'application de deux modèles de limitation des agents chimiques toxiques pour assurer la qualité de l'eau, par rapport à divers scénarios d'écoulement et d'effluents, afin d'examiner les gammes possibles de concentrations des nonylphénols et de leurs éthoxylates (NPE) en aval d'usines de pâtes et papiers choisies dans l'ensemble du Canada. On étudie les concentrations dans l'eau et les sédiments prévues par le modèle en regard de la version préliminaire des Recommandations canadiennes pour la qualité de l'environnement.

Résumé

On a effectué cette étude pour faciliter les travaux de modélisation de la Direction générale de la prévention de la pollution par des toxiques (DGPPT), de la Division des ressources renouvelables (DRR) et du secteur des pâtes et papiers pour l'étude des concentrations de NPE directement en aval d'usines de pâtes et papiers choisies dans tout le Canada. On utilise les résultats de ce modèle pour examiner la conformité de ces usines aux nouvelles Recommandations canadiennes sur la qualité de l'environnement visant les nonylphénols et leurs éthoxylates. On a appliqué ces modèles à divers scénarios d'écoulement et de charges d'effluents pour l'étude des concentrations de NPE en aval, en regard des lignes directrices relatives à la qualité de l'eau.

Des sept sites examinés, seuls les cours d'eau de Thunder Bay, de Grande Prairie et de Dryden présentaient des concentrations de NPE dépassant la limite de 1 µg/L. Les résultats du modèle indiquent qu'au site de Dryden, les concentrations dépassaient la limite d'environ 1 000 %, contre 50 à 100 % pour Thunder Bay et Grande Prairie. Toutefois, les concentrations de NPE des sites de Prince-Albert et de Temiscaming étaient inférieures de 30 à 40 % à celles des limites, et celles des sites de Gatineau et de Masson-Angers, d'environ 80 %. Dans ces sites, les concentrations de NPE liés aux sédiments n'atteignait pas les valeurs prévues par les modèles, car aucune ne dépassait ni n'approchait la limite de 1 400 µg/kg.

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1 INTRODUCTION

1.1 Study Objectives

The purpose of this study is to model the concentrations of NPE's directly downstream of selected pulp and paper mills across Canada. The model results will be used to examine potential environmentally harmful concentrations of nonlyphenols and its ethoxylates as a result of mill discharges.

Deterministic 1-dimensional water quality models were to be applied to the following pulp and paper mill sites, wherever adequate data was available at the time of this study:

- 1) Bowater Pulp and Paper Canada Inc., Thunder Bay, Ontario
- 2) Bowater Pulp and Paper Canada Inc., Gatineau, Quebec
- 3) Weyerhaeuser Canada Ltd., Grande Prairie, Alberta
- 4) Weyerhaeuser Company Ltd., Dryden, Ontario
- 5) Weyerhaeuser Saskatchewan Ltd., Prince Albert, Saskatchewan
- 6) Papier Masson Limitee, Masson-Angers, Quebec
- 7) Tembec Inc., Temiscaming, Quebec
- 8) Crown Packaging Ltd., Burnaby, British Columbia.

The models were to be applied for various streamflow and effluent load scenarios to examine downstream NPE concentrations and compare these concentrations with the draft Canadian Environmental Quality Guidelines.

2 EXWAT

The EXWAT model was used to model NPE concentrations at each of the Study sites. **Section Error! Reference source not found**, provides documentation on the EXWAT model and was extracted from the original model documentation (Brüggemann et. al. 1996)

Steady-state model for the transport of chemicals in surface waters (rivers)

Surface water is the primary environmental aquatic medium receiving chemical input. Untreated and treated waste waters are routinely released into rivers and streams. Various processes determine the transport and fate of chemicals in this medium, which must be taken into account by the simulation model EXWAT. These are advection, dispersion, sorption to sediments and particles, sedimentation, volatilization and degradation.

2.1 Purpose and Scope

The model EXWAT (EXposure of surface WATers) was developed to evaluate the chemicals' fate in surface water bodies. The emphasis is put on comparative aspects. Apart from prediction or estimation of previously unmeasured concentrations, it also interprets the experimental results by chemodynamic arguments and identifies emission sites and the amounts released. Its results can be applied as fate and descriptors, e.g. % of released chemical that is accumulated, degraded, transported and bioconcentrated in the river compartments. It is intended as a generalized simple model requiring only a few parameters about the chemical and the river. Concerning applications of EXWAT for a comparative evaluation, a recent publication may be cited: Brüggerman et al. (1994).

2.2 Description of the Model

The structure of the EXWAT model is seen in Figure 2-1.

2.2.1 Compartment Structure

Similar to the fugacity model QWASI of Mackay (1983, 1991), the EXWAT model describes a river, or as limiting case a "river lake", using boxes consisting of two compartments: the water body compartment includes suspended particles (suspended sediments) and fishes whereas the sediment compartment includes the sediment matrix and water-filled pores (Figure 2-2). The depth of the sediment corresponds to the well-mixed upper layer of the sediment, which is in interaction with the advective energy of the water flow. Usually a river is modelled by 50 boxes, which may have different environmental parameters.

Neighbouring boxes with the same set of environmental parameters can be combined into segments.

If not explicitly stated, the geometry of a segment is given by default values.

L	Length of the river segment	100 km
W	Width of the box	300 m
D _w	Depth of the water compartment	3 m
D _s	Depth of the sediment compartment	0.05 m
N _B	Number of boxes	50
N _S	Number of segments	1

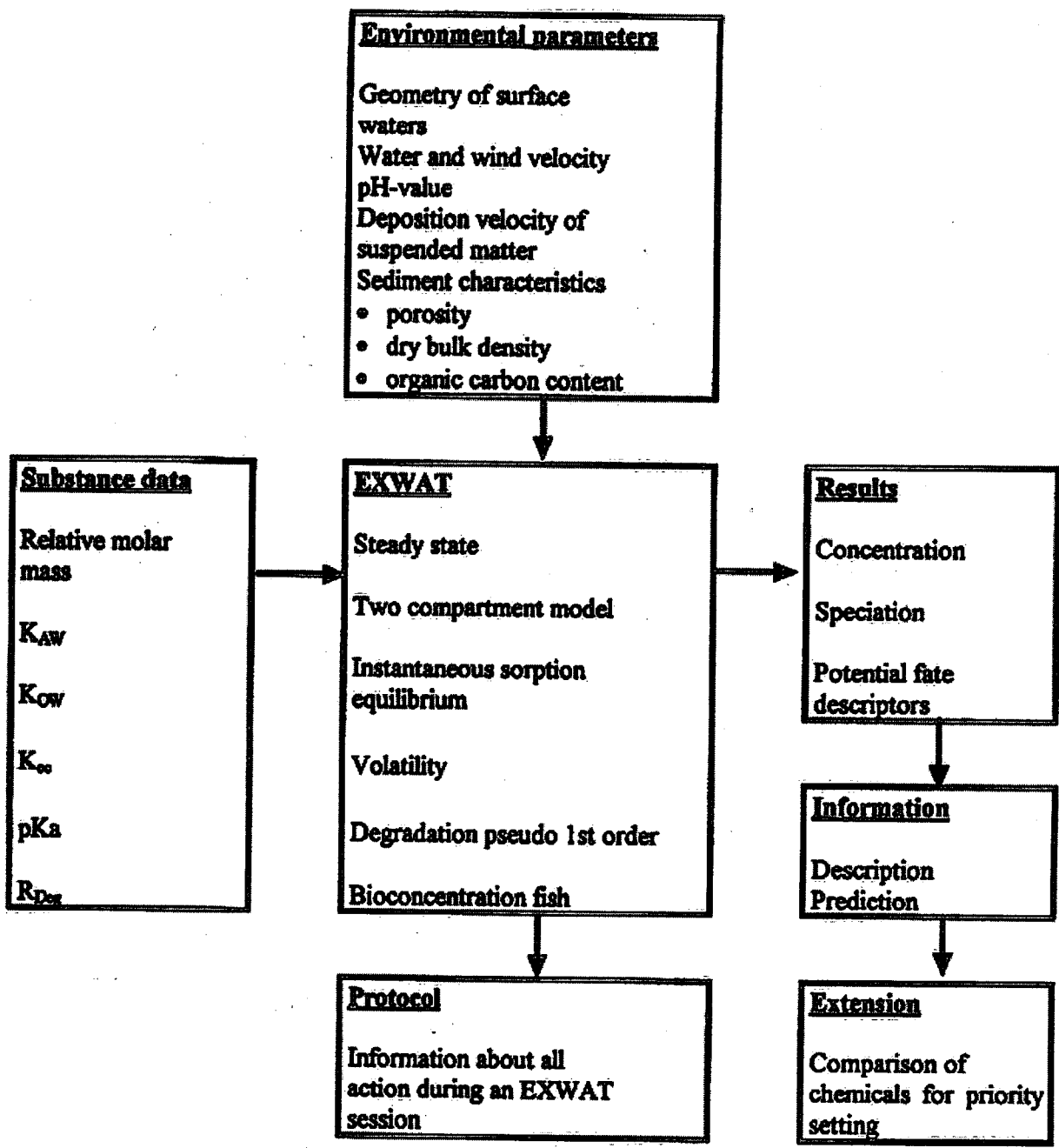


Figure 2-1 Flowchart of the EXWAT model

EXWAT can operate in two modes. The standard mode, Mode I, assumes two compartments – water and sediment – for each box. This mode is automatically used when the depth of the sediment is not equal to 0. The deposition velocity is interpreted as sink velocity (m/d). Mode II is used when the sediment depth is set to 0, assuming only one compartment per box. Then a net sedimentation rate is assumed, which results from deposition and resuspension processes. The advantage of the second mode is that many rarely available data are no longer required.

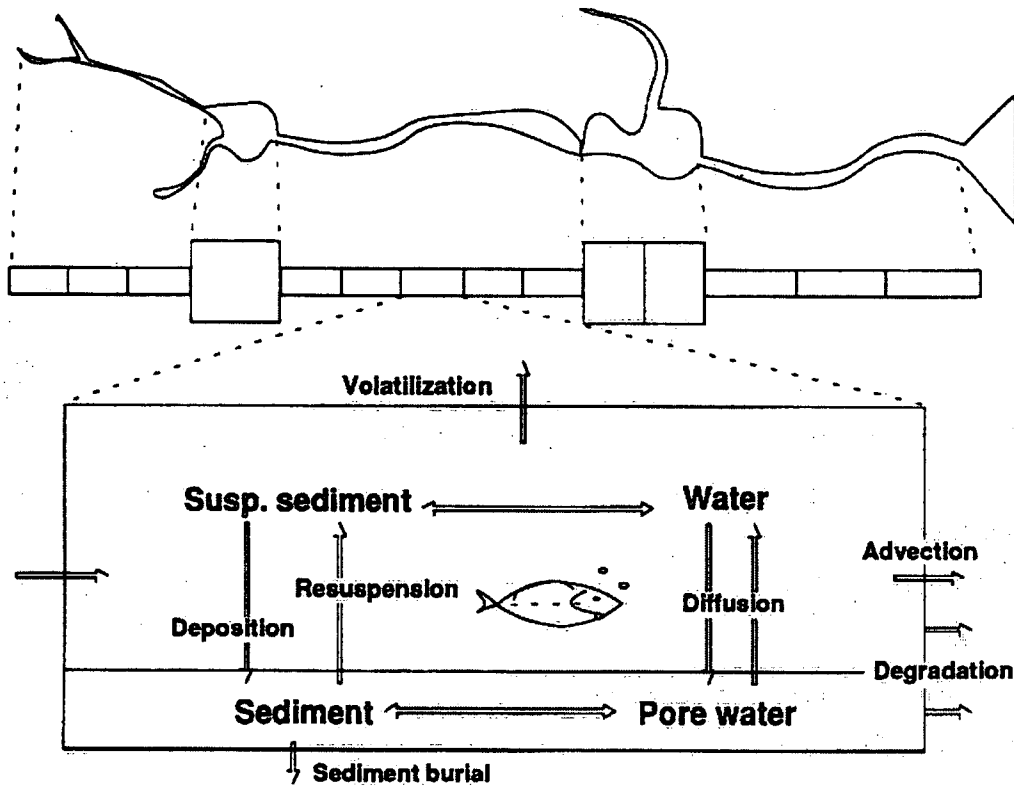


Figure 2-2 Unit box of the aquatic fate EXWAT model

2.2.2 Basic Equations (Mode I)

The relationships are described by two mass-balance equations related to each box, which are solved analytically to create steady-state concentrations in each box. Each box represents different hydrologic situations. By combining a number of (not necessarily identical) boxes, a concentration profile along rivers can be estimated.

The pair of equations for each box can be written as:

$$V_F * dC_F / dt = \text{Advection} + \text{Exchange} - \text{Sinks} \quad (2-1)$$

$$V_S * dC_S / dt = \text{Exchange} - \text{Sinks} \quad (2-2)$$

All right-hand terms may be different according to the different hydrologic properties of the boxes. With N boxes, 2 * N state equations result, which can be summarized by the matrix equation:

$$dC / dt = A * C + SO \quad (2-3)$$

The steady-state solution is given by:

$$dC / dt = 0 \quad (2-4)$$

As equation (2-3) is linear, the final expression for the state variables is easily written (provided the invertibility of A) as:

$$C = -A^{-1} * SO \quad (2-5)$$

The mathematically elegant formulation above is not the appropriate method to obtain the numerical solution. Instead of equation (2-5), the equations (2-1) and (2-2) are solved analytically and the state variables C_F and C_S are expressed for each box as functions of the hydrologic and chemical properties and the inputs. Then the freight of the i th box can be calculated and thought of as being a part of the input to the next downstream box $i+1$. Thus it is only necessary to discuss equation (2-1) and (2-2) in detail.

Explanations:

A	Matrix including coefficients for transport, exchange and degradation processes	(1/T)
C	Vector of concentrations in fluid and sediment (state variables)	(M/L ³)
C _F	Total concentration of the chemical in the fluid compartment	(M/L ³)
C _S	Total concentration of the chemical in the sediment compartment	(M/L ³)
DC/dt	Vector of time derivatives of the concentration in fluid and sediments	(M/L ³ T)
SO	Input vector (SOURCES), site specific release rates	(M/L ³ T)
t	Time	(T)
V _F	Volume of the fluid compartment	(L ³)
V _S	Volume of the sediment compartment	(L ³)

2.2.3 The Different Processes

In EXWAT, the following processes are considered:

Advection (mechanical transport of substances by the water flow¹):

- Input of chemicals by background concentrations
- Dilution by tributaries
- Freight at the end of the river

Exchange:

- Advective exchange processes between water and sediment by deposition of suspended matter and resuspension of sediments
- Exchange of chemicals between pore water of the sediment compartment and the fluid compartment driven by a concentration gradient
- Partitioning of chemicals between water and suspended matter in the fluid
- Partitioning of chemicals between pore water and benthic sediment solids
- Ionization equilibrium for acids and bases (only one – step dissociation)
- Partitioning of the chemicals between water and fish (biocentration)

Sinks:

- Sediment burial (net sedimentation if deposition processes exceed the resuspension processes)

¹ Sometimes also defined as convection

- Volatilization (note that EXWAT neglects the air as a compartment, thus volatilization is taken as a sink)
- Degradation in the water body and the benthic sediment
- Net sedimentation if EXWAT is run or segments are handled using Mode II

2.2.3.1 Advection

2.2.3.1.1 Inputs

The environmental chemicals may be released from many different sources:

Input "I" Inputs of the chemical by:
 Waste water treatment plants
 Deposition from air
 Runoff
 Other direct site specific releases

$$I = I_i + \text{DepAir} * L * B_F + \text{Runoff} * L \quad (2-6)$$

For each box a background input I_B has additionally to be considered:

$$I_B = Q_{i-1} * C_{i-1} = F_{i-1} \quad (2-7)$$

Explanations:

B_F	Width of the river	(L)
DepAir^2	Deposition from air	($M/L^2/T$)
F_{i-1}	Freight of upstream box	(M/T)
i	I refers to the i th box	(M/T)
I_B	Background input to the actual box	(M/T)
I_i	Box (site) specific release rates	(L)
L	Length of the box	(L)
Q_{i-1}	Advective flow from upstream	(L^3/T)
Runoff^2	Runoff from soil	($M/L/T$)

The total input I_{tot} is therefore given by $I_{\text{tot}} = I + I_B$

2.2.3.1.2 Advection between two boxes

Advection "A" Terms depending on the water flow:
 Inflow of the upstream part (Q_{i-1})
 Outflow to the next downstream box (Q_i)

The only connection between neighbouring boxes are the advective terms, "A". Note that in steady state it is not necessary to include longitudinal dispersion. However, exchange of the chemical into stagnant water zones may be described by dispersion terms.

According to the *i*th box:

$$A_i - Q_{i-1} * C_{F,i-1} - Q_i * C_{F,i} \quad (2-8)$$

Explanations

A_i	Advective transport	(M/T)
$C_{F,i}, C_{F,i-1}$	Total concentration of the chemical in the water body	(M/L ³)
$Q_{..}$	Advective flows	(L ³ /T)

2.2.3.2 Exchange processes

2.2.3.2.1 Exchange: water – sediment (Mode I)

General relation

Exchange "E" Terms describing dispersive and advective processes which govern the exchange of the chemical between the fluid and sediment compartments; they all have the dimension (L³/T), i.e. volumetric exchange.

As balanced for the fluid compartment:

$$E_i = \text{Advective Exchange} + \text{Diffusive Exchange} \quad (2-9)$$

$$\text{Advective Exchange} = \text{resuspension} - \text{deposition} = E_{i,S,F} * C_{S,sorb,i} - E_{i,S,F} * C_{F,sorb,i} \quad (2-10)$$

$$\text{Diffusive Exchange} = D_p * A_p * (C_{S,aq,i} - C_{F,aq,i}) \quad (2-11)$$

As balanced for the sediment compartment:

$$E'_i = \text{Advective Exchange}' + \text{Diffusive Exchange}' \quad (2-12)$$

$$\text{Advective Exchange}' = \text{resuspension} - \text{deposition} = E_{i,S,F} * C_{S,sorb,i} + E_{i,S,F} * C_{F,sorb,i} \quad (2-13)$$

$$\text{Diffusive Exchange}' = D_p * A_p * (C_{S,aq,i} - C_{F,aq,i}) \quad (2-14)$$

Explanations

A_p	Interface area of pores	(L ²)
$C_{F,aq}$	Concentration of the dissolved chemical in the fluid compartment	(M/L ³)
$C_{F,sorb}$	Concentration of the chemical sorbed to suspended particles	(M/L ³)
$C_{S,aq}$	Concentration of the dissolved chemical in the sediment compartment	(M/L ³)
$C_{S,sorb}$	Concentration of the chemical sorbed on the sediment matrix	(M/L ³)
D_p	Permeability	(L/T)
$E_{F,S}$	Deposition flowrate	(L ³ /T)
$E_{S,F}$	Resuspension flowrate	(L ³ /T)

Local equilibria

The relation between the above-mentioned state variables – species concentration [equations (2-10) – (2-14)] and the total concentration of each compartment of the *i*th box is given by the concept of local equilibria:

$$C_{F,sorb,i} = K_i^{(F)} * C_{F,aq,i} \quad (2-15)$$

and

$$C_{S,sorb,i} = K_i^{(S)} * C_{S,aq,i} \quad (2-16)$$

The concentrations $C_{F,sorb,i}$ and $C_{S,aq,i}$ are the mass of chemicals, sorbed and dissolved, related to the volume of the sediment compartment.

The dimensionless sorption coefficients $K_i^{(F)}$ and $K_i^{(S)}$ depend on the properties of the chemical and the environment. As shown in the literature, $K_i^{(\dots)}$ can be split into two factorial parts:

One that is purely dependent on environmental properties and the other that is a chemical-specific factor:

$$K_i^{(F)} = (\Xi_i * OrgC_i^{(F)}) * K_{oc} \quad (K_D = OrgC_i^{(F)} * K_{oc}) \quad (2-17)$$

$$K_i^{(S)} = [\rho_i * \{(1/\phi_i) - 1\} * OrgC_i^{(S)}] * K_{oc} \quad (K_{DS} = OrgC_i^{(S)} * K_{oc}) \quad (2-18)$$

The factors Ξ_i and $\rho_i \{(1/\phi_i) - 1\}$ come from the definition of K_{oc} , where the mass of the chemicals is related to the mass of particulate matter. K_D and K_{DS} are intermediate results.

The K_{oc} can be estimated for the n-octanol-water partition coefficient K_{ow} (Karickhoff et al. 1979, Brüggemann and Altschuh 1991, Brüggemann et al. 1992).

Note that K_{oc} may be corrected due to ionic equilibria. It is assumed that only the neutral species is sorbed. Therefore K_{oc} has to be multiplied by the correction factor Φ .

$$1/\Phi = (1 + 10^{A(pH-pKa)}) \quad (2-19)$$

A is a flag for acids (1), bases (-1) or neutral compounds (0).

It is convenient to introduce the following terms (the indication of the *i*th box omitted):

$$\lambda_a = C_{F,aq} / C_F \quad (2-20)$$

$$\lambda_b = C_{F,sorb} / C_F \quad (2-21)$$

and

$$\lambda_{a^*} = C_{S,aq} / C_S \quad (2-22)$$

$$\lambda_{b^*} = C_{S,sorb} / C_S \quad (2-23)$$

All species concentrations in equations (2-10) – (2-14) can therefore be expressed in terms of C_F and C_S . The fractions λ_a , λ_b , λ_{a^*} , λ_{b^*} can be expressed by the $K_{i(\dots)}$:

$$\lambda_{a,i} = 1/(1 + K_i^{(F)}) \quad (2-24)$$

$$\lambda_{b,i} = K_i^{(F)} / (1 + K_i^{(F)}) \quad (2-25)$$

$$\lambda_{a,i^*} = 1/(1 + K_i^{(S)}) \quad (2-26)$$

$$\lambda_{b,i^*} = K_i^{(S)} / (1 + K_i^{(S)}) \quad (2-27)$$

Explanations:

ρ	Dry bulk density	(M/L ³)
Φ	Correction factor for pH	(-)
Ξ	Suspended matter concentration	(M/L ³)
φ	Porosity of sediment	(-)
λ_a	Fraction of the chemical dissolved in the water	(-)
λ_{a^*}	Fraction of the chemical dissolved in pore water	(-)
λ_b	Fraction of the chemical sorbed to suspended particles	(-)
λ_{b^*}	Fraction of the chemical sorbed to the sediment matrix	(-)
C_F	Chemical's concentration in fluid phase (water + suspended matter)	(M/L ³)
$C_{F,sorb}$	Chemical's concentration in suspended particles	(M/L ³)
C_S	Chemical's concentration in sediment	(M/L ³)
$C_{S,sorb}$	Chemical's concentration in sediment matrix	(M/L ³)
K_D	Chemical's partition coefficient sorbed to suspended particles / water	(L ³ /M)
K_{DS}	Chemical's partition coefficient sorbed to sediment matrix / pore water	(L ³ /M)
$K_i^{(F)}, K_i^{(S)}$	Dimensionless partition coefficient between different phases of fluid or sediment	(-)
K_{oc}	Partition coefficient organic carbon / water	(L ³ /M)
OrgC	Organic carbon content of suspended matter and sediment	(M/M)

2.2.3.2.2 Deposition and resuspension

The E... terms of equations (2-28) and (2-29) are related with more familiar quantities by the equations:

$$E_{S,F} = (R_S / D_S) * V_S * \lambda_{b^*} \quad (2-28)$$

and

$$E_{F,S} = (S / D_F) * V_F * \lambda_{b^*} \quad (2-29)$$

Assuming stationary suspended matter and no sediment burial, the rarely-known resuspension flowrate R_S can be related to the sink velocity S by:

$$R_S = S * (\Xi / \Xi_S) \quad (2-30)$$

In order to maintain the suspended matter concentration in the water compartment, the unfamiliar term Ξ_S , expressing the concentration of particles in the sediment compartment, is replaced by φ and ρ . Thus the final equation follows:

$$R_S = S * [\Xi / \{(1 - \varphi) * \rho\}] \quad (2-31)$$

Explanations:

Ξ	Suspended matter concentration	(M/L ³)
ρ	Density of the sediment	(M/L ³)
ϕ	Porosity of the suspended matter	(-)
λ_b, λ_b^*	Fraction of the chemical sorbed to the suspended matter and to the sediment matrix, respectively	(-)
Ξ_s	Concentration of particles in the sediment compartment	(M/L ³)
E_F, D_S	Depth of the fluid compartment and sediment compartment	(L)
$E_{F,S}$	Deposition flowrate	(L ³ /T)
$E_{S,F}$	Resuspension flowrate	(L ³ /T)
R_S	Resuspension velocity	(L/T)
S	Sink velocity	(L/T)
V_F, V_S	Volume of the fluid compartment and sediment compartment	(L ³)

2.2.3.2.3 Dispersive exchange

The interface area (A_p) of the pores within the sediment to the water body is approximately given by:

$$A_p = \phi * V_S / D_S \quad (2-32)$$

The permeability (D_p) is related with a diffusion constant $D_{W,eff}$ by:

$$D_p = D_{W,eff} / D_S \quad (2-33)$$

Explanations:

ϕ	Porosity of the sediment	(-)
A_p	Interface area	(L ²)
D_p	Permeability	(L/T)
D_S	Depth of the sediment	(L)
$D_{W,eff}$	Diffusion constant	(L ² /T)
V_S	Volume of the sediment	(L ³)

2.2.3.2.4 Sedimentation without a special sediment compartment (Mode II)

The exchange processes between water and sediment are quite complex, and the sediment data needed to compute them are often not easy to obtain.

For this reason, it is possible to "switch off" the sediment compartment altogether and view it simply as a sink for deposited suspended sediment. If D_S is entered as 0, the exchange between fluid and sediment will be reduced to a net sedimentation rate of chemicals $R_{S,ed}$ that can be combined with the volatilization and degradation rates into a total elimination rate, k , as follows:

$$k = k_{sed} * \lambda_b + (k_v / D_F) * (1 - \lambda_b) + R_{F,sorb} * \lambda_b + R_{F,aq} (1 - \lambda_b) \quad (2-34)$$

With the chemicals sedimentation rate:

$$k_{sed} = [S_{NR} * \rho * (1 - \phi)] / D_F * \Xi \quad (2-35)$$

S_{NR} is considered as the time averaged net sedimentation rate of particles, often expressed as mm/a. The fraction of the chemical sorbed to organic matter is then:

$$\lambda_b = (K_D * \Xi) / (1 + K_D * \Xi) \quad (2-36)$$

with

$$k_D = \text{OrgC}_i^{(F)} * K_{oc} \quad (2-37)$$

These three values are computed as intermediate results for each river segment. However, k_{sed} is only used for those segments with a zero value of D_S .

Explanations:

Ξ	Suspended matter concentration	(M/L ³)
ρ	Dry sediment density	(M/L ³)
ϕ	Porosity of the sediment ($\phi = V_{pore} / V_S$)	(-)
λ_b	Fraction of the chemical sorbed to the suspended matter	(-)
D_F	Depth of the water compartment	(L)
D_S	Depth of the sediment compartment (here set to 0)	(L)
k	Elimination rate	(1/T)
K_D	Partition coefficient of the chemical sorbed to suspended matter / water	(L ³ /M)
K_{oc}	Sorption coefficient related to organic carbon	(L ³ /M)
K_{sed}	Sedimentation rate	(1/T)
K_v	Volatilization rate	(1/T)
OrgC	Organic carbon content	(-)
$R_{F,sorb}, R_{F,aq}$	Degradation rates of sorbed or dissolved chemical	(1/T)
S	Sink velocity (Mode I)	(L/T)
SNR	"Sedrate", net particle sedimentation rate (Mode II)	(L/T)
V_{pore}	Pore volume	(L ³)

2.2.3.2.5 Bioconcentration

The steady-state concentration in fish in the river boxes is estimated from the bioconcentration factor BCF and the total concentration, C_F .

$$C_{fish} = BCF / \rho_{fish} * C_F \quad (2-38)$$

The density of fish ρ_{fish} is assumed to be ~ 1 kg/l (wet weight basis).

Explanations:

ρ_{fish}	Density of fish	(M/L ³)
BCF	Fish bioconcentration factor	(-)
C_F	Concentration of the chemical in the water	(M/L ³)
C_{fish}	Concentration of the chemical in fish	(M/M _{wet weight})

2.2.3.3 Sinks

Sink, "S", terms describe the losses (mass flows M/T) of the chemical by:

- Volatilization in the water compartment
- Degradation (biotic and abiotic) in the water and sediment compartments
- Sediment burial in the sediment compartment
- Chemical sedimentation rate if Mode II is used (see 2.3.3.1)

2.2.3.3.1 Water compartment

In the water compartment, the following processes are regarded as sinks (mass flows):

$$S_i = \text{Volat} + \text{Deg}_w \quad (2-39)$$

2.2.3.3.1.1 Volatilization

The volatilization (Volat) is calculated according to the equation:

$$\text{Volat} = - (k_v/D_F) * V_F * C_{F,aq,i} \quad (2-40)$$

The volatilization rate (k_v) is estimated by the two-film theory. It depends on the dimensionless Henry's Law coefficient (K_{AW}), current and wind velocities, depth of the water compartment and the resistance in the gas and water films.

For the two-film theory, the following expression can be drawn:

$$1/k_v = 1/k_l + 1/(K_{AW} * k_g) \quad (2-41)$$

$$K_{AW} = H/RT$$

K_{AW} is the dimensionless air-water partition coefficient.

Equation (2-41) corresponds to resistance equations by:

$$R_G = r_l + r_g \quad (2-42)$$

The quantities $r...$ are the total, liquid and gaseous film resistance while the overall volatilization rate, k_v , consists of k_l and k_g , the film (phase) specific transfer rates. Many different formulas exist to estimate k_l and k_g . For the EXWAT model, the relationships deduced by Southworth (1979) are preferred because they relate k_l to such important hydrologic parameters as $v_{w,0.1}$, the wind velocity (0.1 m above the water), v_{curr} , the current velocity and D_F , the depth of the water body. Furthermore, the validation studies (see Brüggemann et al. 1989) show that for the rivers the formulas of Southworth lead to acceptable results.

It was found that:

$$k_1 = 0.2351 * v_{curr}^{0.969} * D_F^{-0.0673} * F \sqrt{\frac{32}{MW}} \quad (2-43)$$

with:

$$F = \begin{cases} 1 & v_{W,0.1} < 1.9 \text{ m/s} \\ e^{0.526 * (v_{W,0.1} - 1.9)} & v_{W,0.1} \geq 1.9 \text{ m/s} \end{cases} \quad (2-44)$$

Furthermore, the transfer rate, k_g , through the gaseous film is given by:

$$k_g = 11.37 * (v_{W,0.1} + v_{curr}) * \sqrt{\frac{18}{MW}} \quad (2-45)$$

If the wind velocity is not measured at 0.1 m, then the extrapolation to this reference value from measured value $v_{W,h}$ at height h is given by:

$$v_{W,0.1} = v_{W,h} * [\log(h_{0.1}/Z_0) / \log(h/Z_0)] \quad (2-46)$$

The EXWAT input quantity is $v_{W,10}$, i.e. $v_{W,h}$ was measured at a height of 10 m. Therefore, the required $v_{W,0.1}$ is:

$$v_{W,0.1} = 0.5 * v_{W,10} \quad (2-47)$$

The current velocity, v_{curr} , can be estimated by:

$$V_{curr} = Q / (B_F * D_F) \quad (2-48)$$

With this final equation (2-48), all terms of equation (2-40) are explained or related to the input quantities. The lengthy expression is $k_v = \dots$ is suppressed here.

Explanations:

B_F, D_F	Width and depth of the water body, respectively	(L)
$C_{F,aq}$	Concentration of the chemical dissolved in the water body	(M/L ³)
D_F	Depth of the water body	(L)
D_S	Depth of the sediment compartment (here set to 0)	(L)
k_l, k_g	Phase-specific transfer rates	(L/T)
k_v	Volatilization rate	(L/T)
MW	Relative molar mass	(M/mol)
Q	Volume flow of the river	(L ³ /T)
r_G	Total resistance	(T/L)
r_l, r_g	Liquid -gaseous resistance	(T/L)
v_{curr}	Velocity of the river	(L/T)
V_F	Volume of the water body	(L ³)
Volat	Volatilization flow from the water compartment	(M/T)
v_w	Wind velocity	(L/T)

2.2.3.3.1.2 Degradation in the water compartment

The degradation in the water compartment is calculated according to:

$$\text{Deg}_w = - R_{F, \text{aq}, i} * V_F * C_{F, \text{aq}, i} - R_{F, \text{sorb}, i} * V_F * C_{F, \text{sorb}, i} \quad (2-49)$$

The degradation rates depend on the speciation and on the compartment.

Note that the degradation terms ($R_{F, \text{aq}, i}$, $R_{F, \text{sorb}, i}$, $R_{S, \text{aq}, i}$ and $R_{S, \text{sorb}, i}$) which include aquatic photolysis, hydrolysis and biotic transformations are written as pseudo 1st order reactions. Therefore it follows, for example, that varying microbial concentrations along the river need to be adjusted by hand. There is no support by the program.

Due to lack of data, it is assumed that:

$$R_{F, \text{aq}, i} \sim R_{F, \text{sorb}, i} \sim R_{\text{Water}} \quad (2-50)$$

The resulting equation is:

$$\text{Deg}_w = - R_{\text{Water}} * V_F * C_F \quad (2-51)$$

Explanations:

$C_{F, \text{aq}}$	Concentration of the chemical dissolved in the fluid compartment	(M/L ³)
$C_{F, \text{sorb}}$	Concentration of the chemical sorbed to the suspended matter	(M/L ³)
Deg_w	Degradation of the chemical in the fluid compartment	(M/T)
$R_{F, \text{aq}}$	Degradation rate of the chemical dissolved in the fluid compartment	(1/T)
$R_{F, \text{sorb}}$	Degradation rate of the chemical sorbed to suspended matter	(1/T)
R_{Water}	Overall degradation rate of the chemical in the fluid compartment	(1/T)
V_F	Volume of the fluid compartment	(L ³)

2.2.3.3.2 Sediment compartment

Within the sediment compartment, the following processes are regarded as sinks (mass flows):

$$S'_i = \text{Sedbur} + \text{Deg}_s \quad (2-52)$$

2.2.3.3.2.1 Sediment burial

The sediment burial may be calculated by hand according to the equation:

$$\text{Sedbur} = - (k_B / D_S) * V_S * C_{S, \text{sorb}, i} \quad (2-53)$$

The sediment burial rate, k_B , describes the process through which a chemical sorbed in the active zone of the sediment may be buried by newly deposited sediments, if the deposition processes exceed the resuspension processes in the considered scale of space and time. The chemical will therefore be prevented from participating in exchange processes. Only very high water discharges will bury the chemical load, thus creating a "chemical time bomb".

Explanations:

$C_{S, \text{sorb}}$	Concentration of the chemical sorbed to the sediment matrix	(M/L ³)
D_S	Depth of the active sediment zone	(L)

k_B	Sediment burial rate	(L/T)
Sedbur	Sediment burial flux	(M/T)
V_S	Volume of the sediment	(L ³)

The process of sediment burial determines, among other things, the concentrations of chemicals in the sediment [see section 2.2.4, equation (2-60)].

2.2.3.3.2.2 Degradation in the sediment

The degradation in the sediment compartment is calculated according to the equation:

$$\text{Deg}_S = -R_{S, \text{aq}, i} * V_S * C_{S, \text{aq}, i} - R_{S, \text{sorb}, i} * V_S * C_{S, \text{sorb}, i} \quad (2-54)$$

The degradation rates depend on the speciation and on the compartment. Note that the degradation terms ($R_{F, \text{aq}, i}$, $R_{F, \text{sorb}, i}$, $R_{S, \text{aq}, i}$ and $R_{S, \text{sorb}, i}$) which include aquatic photolysis, hydrolysis and biotic transformations are written as pseudo 1st order reactions. Therefore it follows, for example, that varying microbial concentrations along the river need to be adjusted by hand. There is no support by the program.

Due to lack of data, it is assumed that:

$$R_{S, \text{aq}, i} \sim R_{S, \text{sorb}, i} \sim R_{Sed} \quad (2-55)$$

The resulting equation is:

$$\text{Deg}_S = -R_{Sed} * V_S * C_S \quad (2-56)$$

In almost all real cases, even the difference between R_{Sed} and R_{Water} might not be known. Therefore, if R_{Water} is known from the input but R_{Sed} is unknown, then R_{Sed} is set equal to R_{Water} , although the type of degradation processes in the sediment may differ from those in the water body.

Explanations:

C_S	Concentration of the chemical dissolved in the sediment	(M/L ³)
$C_{S, \text{aq}}$	Concentration of the chemical dissolved in the sediment fluid	(M/L ³)
$C_{S, \text{sorb}}$	Concentration of the chemical in the sediment matrix	(M/L ³)
Deg_S	Degradation of the chemical in the sediment	(M/T)
$R_{S, \text{aq}}$	Degradation rate of the chemical in the sediment fluid	(1/T)
$R_{S, \text{sorb}}$	Degradation rate of the chemical in the sediment matrix	(1/T)
R_{Sed}	Degradation rate of the chemical in the sediment	(1/T)
V_S	Volume of the active sediment zone	(L ³)

2.2.4 Final Formulas

The terms of equations (2-1) and (2-2) were discussed in the preceding sections. The box-by-box algorithm requires some condensed formulas, which are given now. As mentioned above, a recursive box-by-box solution is faster and numerically more stable than the matrix inversion. Beginning with the first box, C_F and C_S can be calculated. The freight exiting the first box is F . With F and further site-specific inputs, the concentration of the next box can be calculated. Therefore the main task of this section is to derive explicit formulas for C_F and C_W .

$$F = Q * C_F \quad (2-57)$$

Together with the site-specific inputs of the second box, a new input will be calculated and the concentration of the second box is yielded. This procedure is repeated until the last box downstream is reached.

The mathematical expressions of the processes dealt with in section 2.2.2 are the basis for equations (2-1) and (2-2).

Solving them under stationary conditions results in the following two equations:

$$0 = \text{Advection} + \text{Exchange} - \text{Sinks} + \text{Inputs} \quad (2-58)$$

$$0 = \text{Exchange}' - \text{Sinks}' + \text{Inputs}' \quad (2-59)$$

Water compartment of the ith box (i>1)

$$\begin{aligned} V_F * (dC_F/dt) = & Q_{i-1} * C_{F,i-1} - Q_i * C_{F,i} + E_{i,S,F} * C_{S,sorb,i} && \text{(advection)} \\ & - E_{i,F,S} * C_{F,sorb,i} + D_P * A_P (C_{S,aq,i} - C_{F,aq,i}) && \text{(exchange)} \\ & - (k_V/D_F) * V_F * C_{F,aq,i} - R_{F,aq,i} * V_F * C_{F,aq,i} - R_{F,sorb,i} * V_F * C_{F,sorb,i} && \text{(sinks)} \\ & + I_i * Q_T + C_T && \text{(input)} \end{aligned} \quad (2-60)$$

Sediment compartment

$$\begin{aligned} V_S * (dC_S/dt) = & -E_{i,S,F} * C_{S,sorb,i} + E_{i,F,S} * C_{F,sorb,i} - D_P * A_P * (C_{S,aq,i} - C_{F,aq,i}) && \text{(advection)} \\ & - (k_B/D_S) * V_S * C_{S,sorb,i} - R_{S,aq,i} * V_S * C_{S,aq,i} - R_{S,sorb,i} * V_S * C_{S,sorb,i} && \text{(sinks)} \end{aligned} \quad (2-61)$$

The two unknowns of the ith box (the total concentration C_F and C_S) can now be expressed explicitly.

The pair of equations can be solved for C_F and C_S ; the mathematical expressions are given below:

$$C_F * V_F = [(EX_1 + W_S) / \{EX_1 * (Q/V_F + W_F) + W_S * (EX_2 + W_F + Q/V_F)\}] * I \quad (2-62)$$

and

$$C_S * V_S = (EX_2 * C_F * V_F) / (EX_1 + W_S) \quad (2-63)$$

The new terms EX_1 , EX_2 , W_F and W_S appear because of the rearrangements to solve the equations. They can be interpreted as follows:

EX_1	Total exchange sediment/fluid
EX_2	Total exchange fluid/sediment
W_S	Sum of elimination processes in the sediment compartment
W_F	Sum of elimination processes in the water compartment, including advective loss to the next box

$$EX_1 = D_P * (V_F/D_S) * \lambda_a * S * \Xi * \lambda_b * [(1 - \phi^{-1}) / (D_S * \rho)] \quad (2-64)$$

$$EX_2 = [(D_P * V_P) / (D_S * V_F)] * \lambda_a * S * (\lambda_b/D_F) \quad (2-65)$$

$$W_F = k_V * (\lambda_a/D_F) + R_{F,aq} * \lambda_a + R_{F,sorb} * \lambda_b + (Q/V_F) \quad (2-66)$$

$$W_S = k_B/D_S + R_{S,aq} * \lambda_a + R_{S,sorb} * \lambda_b \quad (2-67)$$

Note that again, the indices i, denoting the boxes, are omitted for the sake of simplicity.

Explanations:

Ξ	Suspended matter concentration	(M/L ³)
ρ	Dry sediment density	(M/L ³)
ϕ	Correction factor for pH	(-)
λ_a, λ_a^*	Fraction of the chemical related to the total in the fluid and the total in the sediment	(-)
λ_b, λ_b^*	Fraction of the chemical sorbed to suspended matter related to the total in the fluid and the total in the sediment, respectively	(-)
Ξ_S	Concentration of particles in the sediment compartment	(M/L ³)
A	Flag for acids or bases	(-)
A_P	Interface area of pores	(L ²)
$C_{F,aq}$	Concentration of the chemical dissolved in the water compartment	(M/L ³)
$C_{F,sorb}$	Concentration of the chemical sorbed to the suspended matter	(M/L ³)
$C_{S,aq}$	Concentration of the chemical dissolved in the sediment compartment	(M/L ³)
$C_{S,sorb}$	Concentration of the chemical sorbed to the sediment matrix	(M/L ³)
C_T	Concentration of the chemical in the tributary rivers	(M/L ³)
D_P	Permeability	(L ² /T)
$E_{F,S}$	Deposition flow rate	(L ³ /T)
$E_{S,F}$	Resuspension flow rate	(L ³ /T)
EX_1	Total exchange sediment - fluid	(1/T)
EX_2	Total exchange fluid - sediment	(1/T)
F	Freight outcome from the box under study	(M)
k_B	Burial velocity	(L/T)
$K_D, K_{D,S}$	Partition coefficients of the chemical sorbed to suspended matter -water body and sorbed to sediment matrix - pore water, respectively	(-)
$K_i^{(F)}, K_i^{(S)}$	Sorption coefficients	(-)
K_{oc}	Chemical specific sorption coefficient related to the organic C content	(L ³ /M)
k_V	Volatilization velocity	(L/T)
$OrgC^{(F)}, OrgC^{(S)}$	Organic carbon content in suspended matter and in the sediment	(-)
Q, Q_T	Volume flow of the river and tributaries	(L ³ /T)
V_F, V_S	Volume of the fluid and the sediment compartment	(L ³)
W_F	Sum of elimination processes in the fluid	(1/T)
W_S	Sum of elimination processes in the sediment	(1/T)

2.3 Data Needs (input)

Only input data needed directly for this model are listed in the following table. If essential data for running EXWAT are missing, the user will be asked to put them into the data sheet.

Symbol	Variable	Description	Unit	Default
Physico-chemical data				
Kaw	K_{AW}	Air-water partition coefficient (dimensionless Henry's Law coefficient)	(-)	
pKa	pKa	Protonic dissociation constant (-log)	(-)	
RSed	R_{Sed}	Pseudo 1st order degradation rate in sediment		
RWater	R_{Water}	Pseudo 1st order degradation rate in fluid	1/d	
Environmental parameters				
AirIn		Deposition rate from air	kg/m ² /d	0 (from EXIN1)
Boxes	N_B	Number of boxes	(-)	50
BurSed	k_B	Sediment burial rate	m/d	0.0001
ConcM		Measured concentrations	µg/l	0
Dens	ρ	Dry density of sediment	g/cm ³	1.309
Depos	S	Sink velocity	m/d	10
Depth	D_F	Depth of the water body	m	3
Dsed	D_S	Depth of the active sediment	m	0.05
Input	I	Substance input	kg/d	0
Length	L	Length of a segment	km	100
OrgC	$OrgC^{(F)}$	Organic carbon in suspended matter	-	0.04
OrgCS	$OrgC^{(S)}$	Organic carbon in sediment	-	0.04
Perm	D_p	Permeability	m/d	0.00025
pH	pH	pH value	-	6
Por	ϕ	Porosity	0..1	0.6
SedRate	S_{NR}	Net sedimentation rate (only if $D_S = 0$)	mm/a	10
Segmts.	Segmts.		(-)	1
SoilIn		Substance washed into river via surface water runoff from soil	kg/km/d	0 (from EXIN1)
Susp	Ξ	Suspended matter	g/m ³	100
Temp	T	Environmental temperature	°C	20
Volat	k_V	Volatilization rate	m/d	0
VolFlo	Q	Volume stream	m ³ /s	1000
VPTemp	p	Vapour pressure at water temperature	Pa	- ¹⁾
Width	B_F	Width	m	300
Wind	v_W	Wind velocity at 10 cm above water	m/s	4
¹⁾ Quantities depending on chemical and environment				

Table 2.1 EXWAT input data

2.4 Model Results (output)

Like other exposure models, EXWAT calculates concentrations and mass fluxes. An EXWAT-specific result is the estimation of profiles of the released chemical along a river. Additionally, sites of chemical input can be checked if measured concentrations along the river are available (see below). The following quantities are calculated in detail:

Concentrations:

Conc (C_F): Concentration in fluid phase (water + suspended matter)

ConcS (C_S): Concentration in sediment

ConcWa ($C_{F,aq,i}$): Concentration in water (not including suspended matter)

$$C_{F,aq,i} = \lambda_{a,i} * C_F \quad (2-68)$$

ConcSM ($C_{S,sorb,i}$): Concentration in sediment matrix

$$C_{S,sorb,i} = \lambda_{b,i} * C_S \quad (2-69)$$

ConcPW ($C_{S,aq,i}$): Concentration in pore water

$$C_{S,aq,i} = \lambda_{a,i} * C_S \quad (2-70)$$

ConcSS ($C_{F,sorb,i}$): Concentration in suspended sediment

$$C_{F,sorb,i} = \lambda_{b,i} * C_F \quad (2-71)$$

ConcBM ($C_{Bio,i}$): Concentration in biomass

$$C_{Bio,i} = BCF * C_{F,aq,i} \quad (2-72)$$

The EXWAT model can be used as a stand-alone program but can also be combined with other models of the model group E4CHEM.

From ConcM (measured concentrations), the release concentrations and freight can also be back-traced.

Descriptors

Results from EXWAT – as a percentage of the substance amount accumulated, degraded, transported and bioconcentrated – can easily be obtained by the user for setting appropriate priorities, but it is not supported by the program itself.

2.5 Limitations

- The conditions of steady-state must be fulfilled, therefore the transient behaviour cannot be studied.
- Stratified lakes or ponds cannot be considered.
- Sedimentation and resuspension are modelled by extremely simplified assumptions. The influence of water discharge, cohesiveness of sediments and distribution of particles' diameter are not taken into account.
- The influence of temperature is neglected.
- The fate of transformation products is not considered.
- The deposition of pollutants from air to water is neglected, because air is taken only as sink.
- Only the upper (well-mixed) zone of the benthic sediment is explicitly considered. Sediment burial is considered as a loss of chemicals.
- The program supports only sorption processes driven by hydrophobic forces.
- Only one stage acid-base-equilibrium is used.
- No exchange with groundwater is considered.
- The transport after short-term releases (e.g. after an incidental input) cannot be predicted due to the steady-state assumptions.

2.6 Validation

The sensitivity of different processes, especially the volatility as a function of environmental parameters and substance data, was carefully examined and can be found in the literature cited. Based on the results of EXWAT, chemicals were compared by cluster analysis due to their similarity. The consequences of a chemical spill which

took place in the Rhine in 1986 (see Brüggemann et al. 1987) were evaluated by the EXWAT model, in which eight spills were ranked according to their environmental hazard. EXWAT was also applied to monitoring studies of hazardous substances (e.g. dichloromethane) to estimate site-specific emissions from measured concentrations in the Rhine river (Brüggemann and Trapp, 1988)

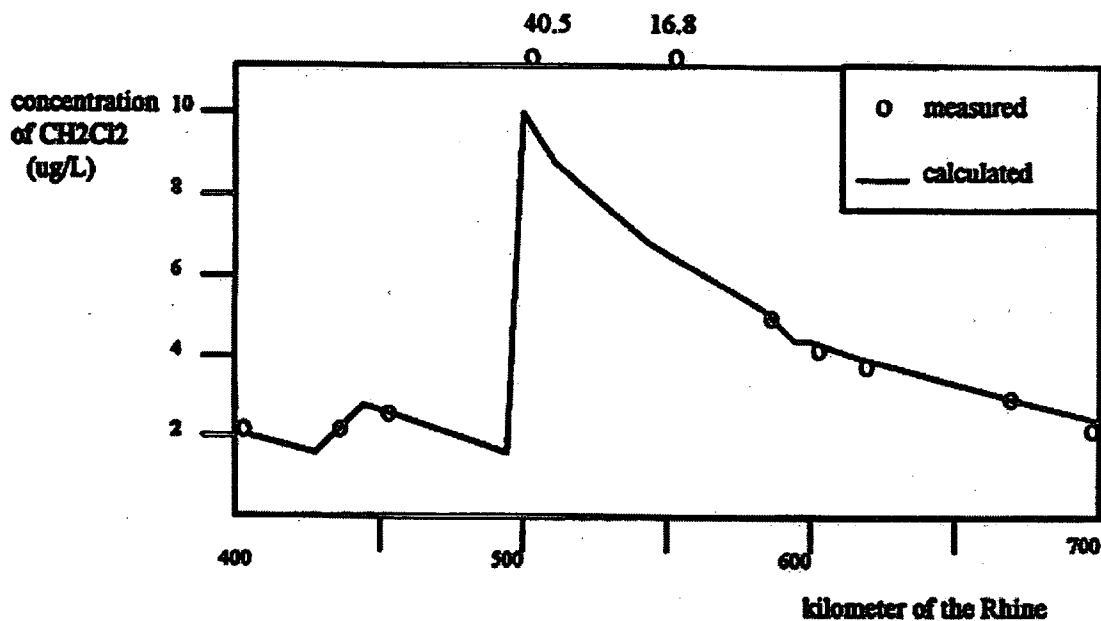


Figure 2-3 Actual and calculated concentration profile in the Rhine River

2.7 Check Procedure

EXWAT's check procedure estimates emissions into rivers in the following way. All known inputs and (measured) concentrations must be defined, together with additional sites where inputs are suspected. In the first step, the program computes concentrations from known inputs and compares them with measured values C_m . If the C_m exceeds the calculated values, the check is successful and the corresponding input at the last possible site can be estimated. If the check fails, other emission sites must be suspected and the procedure repeated. Figure 2-4 shows the results of the check procedure for the Rhine River.

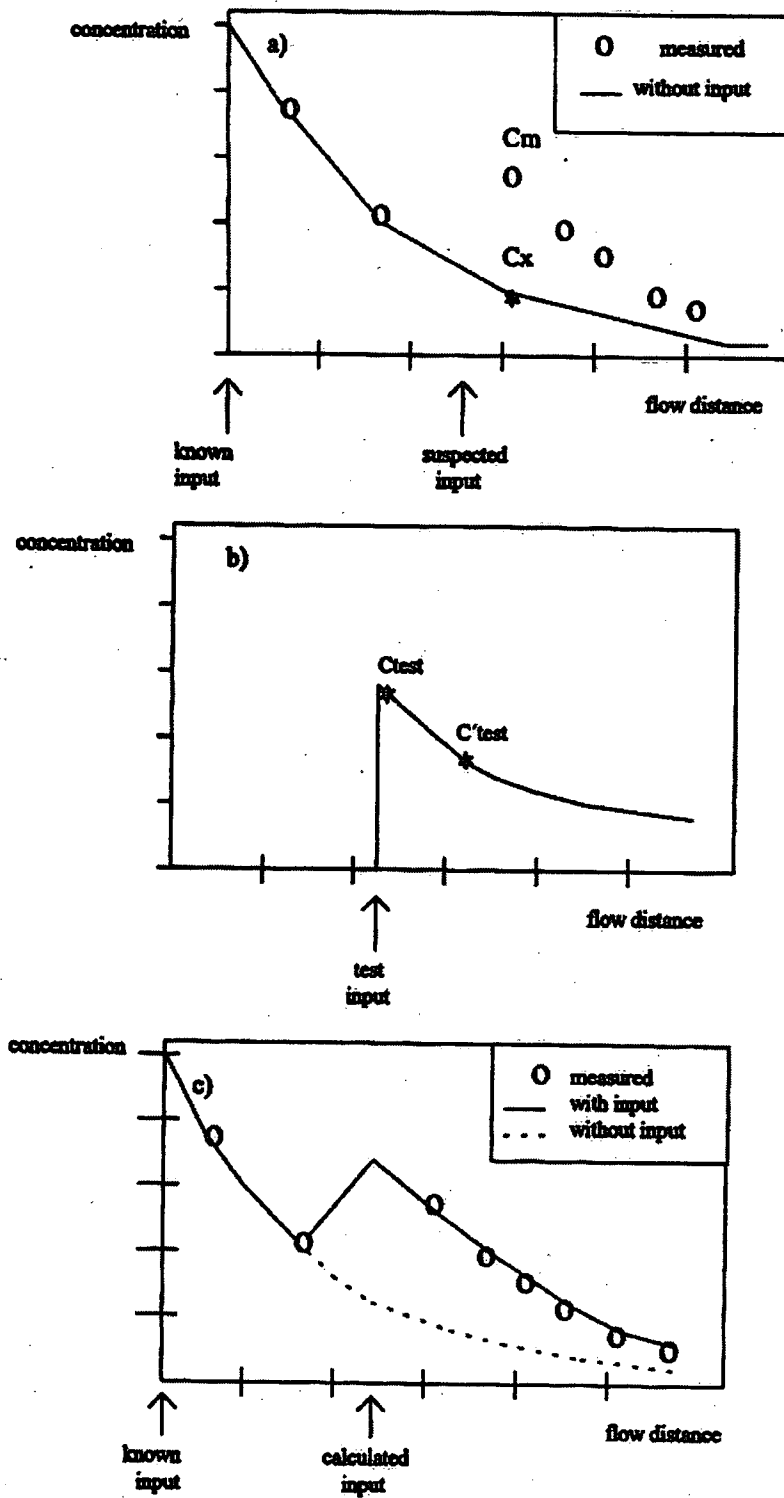


Figure 2-4 EXWAT check procedure

- a) First run of a check with known input
- b) Second run with test input at the suspected emission site
- c) Continuation of the simulation with calculated input

2.8 List of Symbols

In the following overview the symbols used in EXWAT are listed, along with the function in which they appear.

Symbol	Variable	Description	Dimension	Default (Units)	As ¹
Physico-chemical data					
Acid	A	Flag for acid (1) or base (-1)	-	1 or -1	I
BCF	BCF	Bioconcentration in fish	-	-	I
Kaw	K _{AW}	Air-water partition coefficient	-	-	I
Koc	K _{oc}	Sorption coefficient	L ³ /M	-	I
logKow	logK _{OW}	n-octanol-water partition coefficient	-	-	I
pKa	pKa	Acid-base dissociation constant	-	-	I
RSed	R _{Sed}	Lumped 1st order degradation rate in sediment	1/T	-	I
RWater	R _{Wat}	Lumped 1st order degradation rate in water	1/T	-	I
SolW	C _S	Water solubility	M/L ³	-	I
Environmental parameters					
	λ _a	Fraction of the chemical dissolved in the water body	-	-	C
	λ _{a*}	Fraction of the chemical dissolved in the sediment	-	-	C
	λ _{b*}	Fraction of the chemical sorbed to the sediment matrix	-	-	C
	A _p	Interface area of pores to sediment	L ²	-	C
	D _{w,eff}	Diffusion coefficient	L ² /T	-	C
	E _{F,S}	Deposition flow rate	L/T	-	C
	E _{S,F}	Resuspension flow rate	L/T	-	C
	EX ₁ , EX ₂	Total exchange sediment fluid, and vice versa	1/T	-	C
	h	Height at which wind velocity was measured	L	-	C
	K ^(f) , K ^(s)	Sorption coefficient	-	-	C
	k ₁ , k _g	Film-specific transfer rates	L/T	-	C
	k _{sed}	Net sedimentation rate	L/T	-	C
	Q _T	Sum of tributary flows	L ³ /T	-	C
	r _{..}	Total liquid and gaseous film resistance	-	-	C
	SO	Input vector	M/L ³ T	-	C
	v _{curr}	Current velocity	L/T	-	C
AirIn		Deposition of chemicals from air	M/L ² /T	0 (from EXINT)	C,I
Boxes	N _B	Number of boxes	(-)	50	D,I
BurSed	k _B	Sediment burial rate	L/T	0.0001 (m/d)	D,I
Conc	C _F	Concentration in the fluid phase (water + suspended matter)	M/L ³	- (µg/l)	O
ConcBM	C _{Bio,i}	Concentration in the biomass	M/M	- (µg/g)	O
ConcM	C _M	Measured concentrations	M/L ³	- (µg/l)	I
ConcPW	C _{S,sorb,i}	Concentration in pore water	M/L ³	- (µg/l)	O
ConcS	C _S	Concentration in the sediment	M/L ³	- (µg/l)	O
ConcSM	C _{S,sorb,i}	Concentration in the sediment matrix	M/L ³	- (µg/l)	O
ConcSS	C _{F,sorb,i}	Concentration in suspended sediment	M/L ³	- (µg/l)	O
ConcWa	C _w	Concentration in water (suspended matter not included)	M/L ³	- (µg/l)	O
Dens	ρ	Dry sediment density	M/L ³	1.309 (g/cm ³)	D,I

Symbol	Variable	Description	Dimension	Default (Units)	As ¹⁾
Depos	S	Deposition velocity of suspended matter	L/T	10 (m/d)	D,I
Depth	D _F	Depth of the water body	L	3 (m)	D,I
Dsed	D _S	Sediment depth	L	0.05 (m)	D,I
Elim	W _F , W _F	Total elimination rate	1/T	-	O
Input	I	Total input	M/T	- (kg/d)	I
Kaw _{Temp}		Air-water partition coefficient at water temp.	-	-	I ¹⁾ ,C
KD	K _D	Partition coefficient kg sorbed to suspended matter/kg in pore water	L ³ /M	cm ³ /g	C
KDS	K _{DS}	Partition coefficient kg sorbed to sediment matrix/kg in pore water	L ³ /M	cm ³ /g	C
Length	L	Length of the river segment	L	100 (km)	D,I
OrgC	OrgC ^(F)	Organic carbon in suspended matter	M/M	0.04 (-)	D,I
OrgCS	OrgC ^(S)	Organic carbon in sediment matrix	M/M	0.04 (-)	D,I
Perm	D _p	Permeability	L/T	0.00025 (m/d)	D,I
pH	pH	pH value of the river water	-	6 (-)	D,I
Por	φ	Sediment porosity	0..1	0.6 (-)	D,I
SedRate	S _{NR}	Sink velocity (net sedimentation)	L/T	10 (mm/a)	D,I
Segmts.	N _S	Number of river segments	-	1 (-)	D,I
SoilIn		Chemical as runoff from soil	M/L ² /T	0 (from EXINI)	C,I
SorbFrac	λ _b	Fraction in fluid sorbed to suspended sediment	-	-	O
Susp	Ξ	Concentration of suspended matter	M/L ³	100 (g/m ³)	D,I
Temp	T	Temperature of the river water	grad	20 (°C)	D,I
Volat	k _v	Overall volatilization rate	1/T	- (1/d)	C,I
VolFlo	Q	Volume flow of the river	L ³ /T	1000 (m ³ /s)	D,I
Width	B	Width of the river segment	L	300 (m)	D,I
Wind	v _w	Wind velocity	L/T	4 (m/s)	D,I

As¹⁾ : Appearance as I=Input, D=Default value, C=Internally calculated, intermediate figure or only in manual, O=Output
I¹⁾ Input value depending on chemical and environment

Table 2.2 List of Symbols for EXWAT

2.9 References

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3 Kaministiquia River Water Quality Model

The Kaministiquia River Water Quality Model was used to model NPE concentrations at the Thunder Bay site. Section 3 provides documentation on the model and was extracted from the original model documentation (McCrimmon et. al. 1990)

3.1 Purpose and Scope

The lower Kaministiquia River located near Thunder Bay, Ontario is subject to industrial pollutant loadings which often cause the river water quality to fall below desired levels (MOE 1972, 1988). The Canadian Pacific Forest Products Company operated the largest pulp and paper mill in Ontario, which discharged to the Kaministiquia River approximately 10 km. upstream of Lake Superior. Application of a riverine water quality model would normally be sufficient to determine viable solutions. However, the delta of the Kaministiquia River is unusual since cooler and cleaner Lake Superior water intrudes upstream along the river bottom, which creates a vertical thermal structure with a distinct thermocline similar to that observed in lakes. This phenomenon also results in both a horizontal and a vertical gradient of different contaminant concentrations since the polluted water is warmer and flows downstream nearer the surface. A general water quality model capable of simulating almost any contaminant that incorporates not only the multi-source, heated effluent conditions but also the modulations on parameter concentrations by the intrusion of the relatively cleaner, cooler and denser lake water was developed (McCrimmon et. al. 1988). The overall goal to develop and verify water quality models with predictive capability for the assessment of possible management strategies for the Municipal Industrial Strategy for Abatement (MISA) program on pollution control for rivers of the same type.

In a previous study (McCrimmon et. al. 1987), flow characteristics and water temperatures were determined for August 11-15, 1986 using a modified version of the one-dimensional dynamic reservoir simulation model, DYRESM. The river was divided into 16 connected segments, which were simulated in turn using DYRESM in six-hour time steps. In a subsequent study (McCrimmon et. al. 1988), a 3 layer 16 segment DO-BOD box model, which used the previously determined flows and water temperatures, was developed and calibrated for the 1986 data. In addition, data for June 15-21, 1987 was obtained and used to verify the DYRESM and DO-BOD models.

Subsequently, the DO-BOD model was modified and expanded into a general water quality model. This general model allows for the interactive input of kinetic reaction formulations and other required inputs so that almost any contaminant can be simulated. The model was tested for the 1986 period for 1) 2,4,6 Tri-chlorophenol (TCP) reacting with Suspended Sediments (SS) using equilibrium and non-equilibrium conditions, 2) Chloroform and 3) Aluminum. In this study, the water quality model was used to simulate NPE using the same set up used to model TCP.

3.2 Model Description

The method for predicting parameter concentrations involves a number of sequential steps, the results of which are used in ensuing steps. As outlined in previous reports (McCrimmon et. al. 1987, 1988) these steps involve predicting water temperatures and flow characteristics using DYRESM and then using these results in the 3 layer box model.

The general water quality model developed was basically a more flexible version of the previously developed DO-BOD model. The model is a 3 layer, 16 segment model and retains the transport and diffusion components of the DO-BOD model but the kinetic reactions of effluent parameters as well as initial conditions, loadings and observations can be inputted interactively.

One to four parameters can be simulated in the model though this number could be expanded if required. The differential equation for a parameter used in the model is

$$\frac{dVC_i}{dt} = -u \frac{dVC_i}{dx} + K_d V \frac{d^2C_i}{dz^2} + a_1 C_1 + a_2 C_2 + \dots + a_j C_j \quad (3-1)$$

flow
diffusion
kinetics

and for the middle layer add the following

$$+ K_{EX} V \frac{d^2C_i}{dx^2} \quad (3-2)$$

horizontal diffusion

where

- V = box volume (m³)
- t = time (d)
- x = horizontal distance (m)
- z = depth (m)
- i = index of parameters 1 to j
- j = number of parameters
- u = horizontal velocity (m/d)
- C = parameter concentration (mass/volume)
- a_j = relates changes of parameter C_j to parameter C_i
- K₂ = reaeration constant (d⁻¹)
- K_{EX} = horizontal diffusion rate (m²/d)
- K_d = vertical diffusion constant (m²/d)

Through experimentation of different model equation solutions, a predictor-corrector method using a 1/2 hour time step was selected for the DO-BOD model and was also used in the general model. It should be noted that to conserve mass the flow rates from the DYRESM results were used explicitly. In more detail, the model equations are solved as follows:

for time step 1: explicit solution (solve for C_iⁿ⁺¹)

$$V \frac{C_i^{n+1} - C_i^n}{\Delta t} = \text{flow} + \text{diffusion} + a_1 C_1^n + \dots + a_j C_j^n \quad (3-3)$$

for remaining time steps: 1) predictor (solve for C_i^{n+1})

$$V \frac{C_i^{n+1} - C_i^{n-1}}{2\Delta t} = \text{flow} + \text{diffusion} + a_1 C_1^n + \dots + a_j C_j^n \quad (3-4)$$

2) corrector (solve for C_i^{n+1})

$$V \frac{C_i^{n+1} - C_i^n}{\Delta t} = \text{flow} + \text{diffusion} + \frac{(a_1 C_1^n + a_1 C_1^{n+1})}{2} + \dots + \frac{(a_j C_j^n + a_j C_j^{n+1})}{2} \quad (3-5)$$

where Δt is the time step and n is the time step level. For each time step, the predictor calculation is performed for all boxes then the corrector is performed for all boxes to achieve the simulated value, C_i^{n+1} .

The $a_i C_i$ terms can be inputted interactively into the model in an explicit form for each parameter, C_i , of each layer. The model then automatically converts the explicit formulations into the predictor and corrector forms and creates the new model.

3.3 Model Data

Flow rates and water temperatures for August 11-15, 1986 were taken from previous studies (McCrimmon et. al. 1987, 1988). Other data required for calibration of the model, such as loadings and observations, were supplied by the Ontario Ministry of the Environment (MOE). In this section, the available data, calculated and estimated data and assumptions related to the data and model are presented.

The Kaministiquia River is located in northern Ontario near Thunder Bay. The stretch of river under investigation extended from the river outlet at Lake Superior to approximately 10 kilometres upstream, and included the McKellar and Mission River branches. The points A through P in Figure 4-1 indicate the cross-section locations at which parameter measurements were made by the MOE. By using these points and the added point Z, which is the location of the river's main pollutant source, as boundaries, 16 river sections were created for modelling purposes.

The general model was tested for TCP/SS, Chloroform and Aluminum over the period of August 11-15, 1986. Flow, water temperature and hypsometric data were taken from the DYRESM calibration data base and results. The parameter observations supplied by MOE included 1) 8 hourly surface values for 2 days at 3 cross-sections for TCP, at 11 cross-sections for Chloroform and at 12 cross-sections for Aluminum, and for 4 days at 15 cross-sections for SS, 2) a few isolated observations of each parameter in the top and bottom layers at cross-sections G, I, M and P and 3) diffuser loading concentrations for each parameter on a 4 hourly basis for one day and on a daily basis for the remainder of the period. The river segment values were then estimated as the average of the upstream and downstream cross-section values. The initial conditions were estimated using observations but the lack of lower layer observations led to the assumptions that the middle layer and the upper layer are initially the same and the lower layer, which is assumed to be cleaner due to the upstream flow of water from Lake Superior, was set to the low constant values of 1.0 ng/L for TCP, 1.0 mg/L for SS, 1.0 ug/L for Chloroform and 0.11 mg/L for Aluminum based on the minimum observed values of each parameter.

3.4 Results

The development of the general water quality model for the lower Kaministiquia River involved: 1) the simulation of flows and water temperatures using a modified version of DYRESM, 2) the calculation of vertical diffusions for temperature using the 3 layer box model, 3) the simulation of sodium to check the transport processes of the 3 layer box model, 4) the application of the 3 layer box model for DO-BOD, and 5) the testing of the general model which is a modified and more flexible version of the DO-BOD model. In this section, the results of the general model tests will be presented. The other steps, 1-4, were reported earlier.

3.4.1 2,4,6 Tri-Chlorophenol Simulation

The kinetic reactions used in creating the TCP model were based upon the assumption that only sorption, photolysis and possibly volatilization would be significant (National Research Council of Canada 1982). Suspended sediment (SS) can absorb TCP and, therefore, was also simulated in the TCP model. Settling of SS is considered in the kinetic reactions. The total quantity of TCP is taken as the amount of TCP dissolved in the water plus the particulate amount, which is the amount of TCP attached to the suspended sediments.

Two TCP-SS models were created to test the assumption of particulate and dissolved TCP always being in equilibrium, which has been used for chlorinated benzenes (e.g. Stepien et. al. 1987). The first model, the equilibrium model, forces the particulate and dissolved TCP to be in constant equilibrium. The second model, the non-equilibrium model, does not force instant equilibrium but instead uses absorption and desorption rate constants. For the equilibrium model the fraction of dissolved and particulate TCP was calculated using a partition coefficient, PI, as

$$C_p / C_d = PI * C_{ss} \quad (3-6)$$

where C_p is the particulate TCP concentration (ng/L), C_d is the dissolved TCP concentration (ng/L), PI is the partition coefficient (L/mg) and C_{ss} is the suspended sediment concentration (mg/L). To calculate the concentrations C_p and C_d the equation

$$C_T = C_p + C_d \quad (3-7)$$

can be combined with (6), where C_T is the total TCP concentration. Volatilization is not believed to have a significant effect upon TCP (NRCC 1982) but was placed in the model for testing purposes. The undissociated form of TCP, which is expected to be the only form affected by volatilization (NRCC 1982), was calculated as

$$\% \text{ Dissociated} = 100 \frac{10^{-pKa}}{10^{-pH} + 10^{-pKa}} \quad (3-8)$$

where $pKa = 5.99$ and the pH is approximately 7 in the Kaministiquia River. The resulting % undissociated is 8.9% so that the resulting model equations are

for TCP:

$$\frac{dVCT}{dt} = -u \frac{dVCT}{dx} + K_d V \frac{d^2CT}{dz^2} - W A C_p - D V C_d - .089 V K_v C_d \quad (3-9)$$

flow diffusion kinetics

for SS:

$$\frac{dVCss}{dt} = -u \frac{dVCss}{dx} + K_d V \frac{d^2C_{ss}}{dz^2} - W A C_{ss} \quad (3-10)$$

where W is the settling rate of SS (m/d), D is the decay rate (1/d) and K_v is the volatilization rate (1/d). A volatilization rate of 127.9 (cm/d) (NRCC 1982) was applied to the surface layer, which has a mean depth of 75 cm. The resulting K_v used in (8) for the surface layer is 1.7053 (1/d).

Suspended sediment concentrations were calibrated first since they are independent of TCP. The main source of SS loading was the Canadian Pacific Forest Products Company diffuser at segment ZB. Measurements of loadings as well as observations at most cross-sections were taken approximately every 8 hours. It was found that reducing the SS settling rate to zero from the original rate of 2.0 m/d resulted in reasonably good simulations of SS with a root mean square error of 24%.

For the simulation of TCP a partition coefficient of 0.00053 L/mg, which was estimated from Fraser River data, was used (J.H. Carey, Pers.comm. 1988). This value of PI is small and will result in TCP being mostly dissolved. The diffusion rates used were the same as those used in the DO-BOD model calibration of August 11-15, 1986. A decay value of .173 (1/s), which is equivalent to a 4 day half-life, resulted in an rms error of 160% for TCP. This rms error is large compared to the SS simulations but the relatively sparse input and observation data did not allow for a reasonable calibration. When the volatilization option was not used the surface layer values of TCP increased 10%, on average, by the end of August 15, 1986. Also, the rms error increased to 180% suggesting that volatilization is a significant factor on the TCP concentrations of the surface layer.

The simulated top layer TCP concentrations decrease downstream of the main diffuser at ZB due to photolysis and volatilization. In general, TCP diffuses into the ZB top layer segment from the lower layer and then is transported downstream.

The creation of the non-equilibrium TCP-SS model was similar to the equilibrium model except instant equilibrium is assumed to not occur so that an absorption rate, K_a, and a desorption rate, K_d, are used similar to Taylor (1987) as follows.

$$\text{if } C_d > C_{de} \text{ then } dC_p/dt = -dC_d/dt = -K_a (C_d - C_{de}) \quad (3-11)$$

$$\text{if } C_d < C_{de} \text{ then } dC_p/dt = -dC_d/dt = -K_d (C_d - C_{de}) \quad (3-12)$$

where C_{de} is the equilibrium value of C_d which is calculated using (3-6) and (3-7). Also, since C_p and C_d are not in equilibrium they were simulated separately as opposed to calculating them from (3-6), (3-7), and (3-9).

The results of the non-equilibrium model were very similar to those of the equilibrium model. This is due to the assumption that the diffuser loadings of TCP were in equilibrium, which caused the concentrations in the river to be near equilibrium. Therefore, equations (3-10) and (3-11) had little effect even when K_a and K_d were set to zero.

In general, the SS concentrations were well simulated but the TCP concentrations were not simulated as well due to the lack of measured TCP loadings and observations. More data and a better understanding of 2,4,6 TCP kinetics were required to truly test the TCP-SS model.

3.5 Conclusions

A general water quality 3 layer box model utilizing a predictor-corrector solution method and a 1/2 hour time step was developed from the previously developed DO-BOD model (McCrimmon et. al. 1988). The general model was used to create models for simulating 2,4,6 Tri-chlorophenol/Suspended Sediments, Chloroform and Total Aluminum. Reasonably good results were achieved for all parameters (rms errors less than 30%) except for TCP, which had a rms error of 160%. The higher errors for TCP are due, likely, to the fact that chlorophenols and the associated kinetics are not as well understood as the other parameters and that the TCP concentrations are difficult to measure.

Reasonable simulations of different parameters using the general model indicate the model is useful. However, most parameter observations were for the surface layer so it would be desirable to further test the model for parameters which have observations below the surface layer. As also outlined previously (McCrimmon et. al. 1988), more detailed loading observations and possibly a better hydrodynamic model would likely improve the general models performance.

3.6 References

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4 RESULTS

4.1 General

The EXWAT model (Bruggemann 1996) was applied to all of the Study sites except for Crown Packaging Ltd., Burnaby, British Columbia. The Burnaby site has tidal affects, which can't be properly modelled using EXWAT. The Thunder Bay site, which experiences thermal stratification, was also modelled using the Kaministiquia River Water Quality Model (McCrimmon et. al. 1990).

4.2 EXWAT Common Input Coefficients

There are a number of input coefficients for the EXWAT model that are based on the properties of NPE which remain the same for each site, and include the following:

- Substance Name = Nonylphenol
- Molecular formula (SumFor) = C₁₅H₂₄O
- Molecular mass (MolW) = 220.3 [g/mol]
- SolW = 0.005 [g/l] Solubility in water
- VP = 0.005 [Pascal] Vapour pressure at 20 °C
- MP = 82 [°C] Melting point
- BP = 300 [°C] Boiling point at 100000 Pascal
- Koc = 13000 [cm³ H₂O/g] Partition coefficient organic carbon - water
- logKow = 4.5 Logarithm of the n-octanol - water - partition coefficient
- Kaw = 9.044e-005 Partition coefficient air-water (or dimensionless Henry's law coefficient)
- ThOD = 2.977 [g O₂/g] Theoretical oxygen demand
- BCF = 1202 Bioconcentration factor in fish
- VFSG = 260.1 [cm³/mol] Molecular volume according to Fuller, Schettler and Giddings
- VLeBas = 297.3 [cm³/mol] Molecular volume according to LeBas
- DW = 3.983e-005 [m²/day] Diffusion coefficient in water
- DG = 0.4276 [m²/day] Diffusion coefficient in air
- pKa = 10.7 Acid dissociation constant
- Rings = 2 Number of aromatic and heterocyclic rings
- RWater = 0.007 [1/day] Overall degradation rate in water
- RSed = 0.002 [1/day] Degradation rate in sediment
- RSoil = 0.001 [1/day] Overall degradation rate in soil

4.3 Bowater Pulp and Paper Canada Inc., Thunder Bay, Ontario

4.3.1 Site Description

The Bowater Mill discharges to the Kaministiquia River approximately 10 km. upstream of Lake Superior. The delta of the Kaministiquia River is unusual since cooler and cleaner Lake Superior water intrudes upstream along the river bottom, which creates a vertical thermal structure with a distinct thermocline similar to that observed in lakes. The water quality model developed previously (McCrimmon et. al. 1990) included the thermal stratification effects and is applied in this Study in addition to the EXWAT model.

A site plan is shown in Figure 4-1. For modelling purposes, the river is broken up into a number of segments and matches the segmentation used previously (McCrimmon et. al. 1990).

4.3.1.1 Mill Loadings

Bowater mill loadings were obtained from Environment Canada's National Pollutant Release Inventory (NPRI) for 1999 for nonylphenol polyethylene glycol ether. Total release for 1999 was 3.07 kg/d (1.12 tonnes) in 2.80 m³/s (88,191,757 m³).

4.3.1.2 Stream Flow

The 7Q20 flow rate is 15.5 m³/s (Klose 1988) but since Ontario Hydro maintains a minimum flow rate of 17 m³/s upstream, this value was used for modelling.

4.3.1.3 Stream Parameters

River geometry, pH, and TSS were extracted from McCrimmon et. al. (1990) and are shown in Table 4.1. Organic carbon content (OrgC, OrgCS) values were abstracted from data sheets (Maddison 2001). Upstream and Lake Superior NPE concentrations were unknown and set to zero in the models.

4.3.2 EXWAT Modelling

Inputs to the EXWAT model are presented in Table 4.1. The Mill loading is applied to segment ZB. EXWAT default values for DSed, Por, Dens, Depos, Perm, BurSed, Wind, Volat, SedRate, KD, and KDS were used (refer to Table 2.2 for symbol explanations).

Results from the EXWAT model are presented in Table 4.2. The NPE river concentration (Conc) is a maximum of 1.77 ug/L in reach ZB, which is the reach where the mill discharges, then slowly decreases downstream to 1.71 ug/L at the outlet to Lake Superior, as seen in Figure 4-2. These values of NPE are approximately 70% above the guideline of 1 ug/L. The sediment concentration maximum is 0.54 ug/L or 0.41 ug/kg based on the default sediment dry density (Dens) of 1.309 g/cm³. This sediment concentration is much less than the NPE guideline of 1,400 ug/kg.

Figure 4-1 Site Location - Bowater Pulp and Paper Canada Inc., Thunder Bay, Ontario

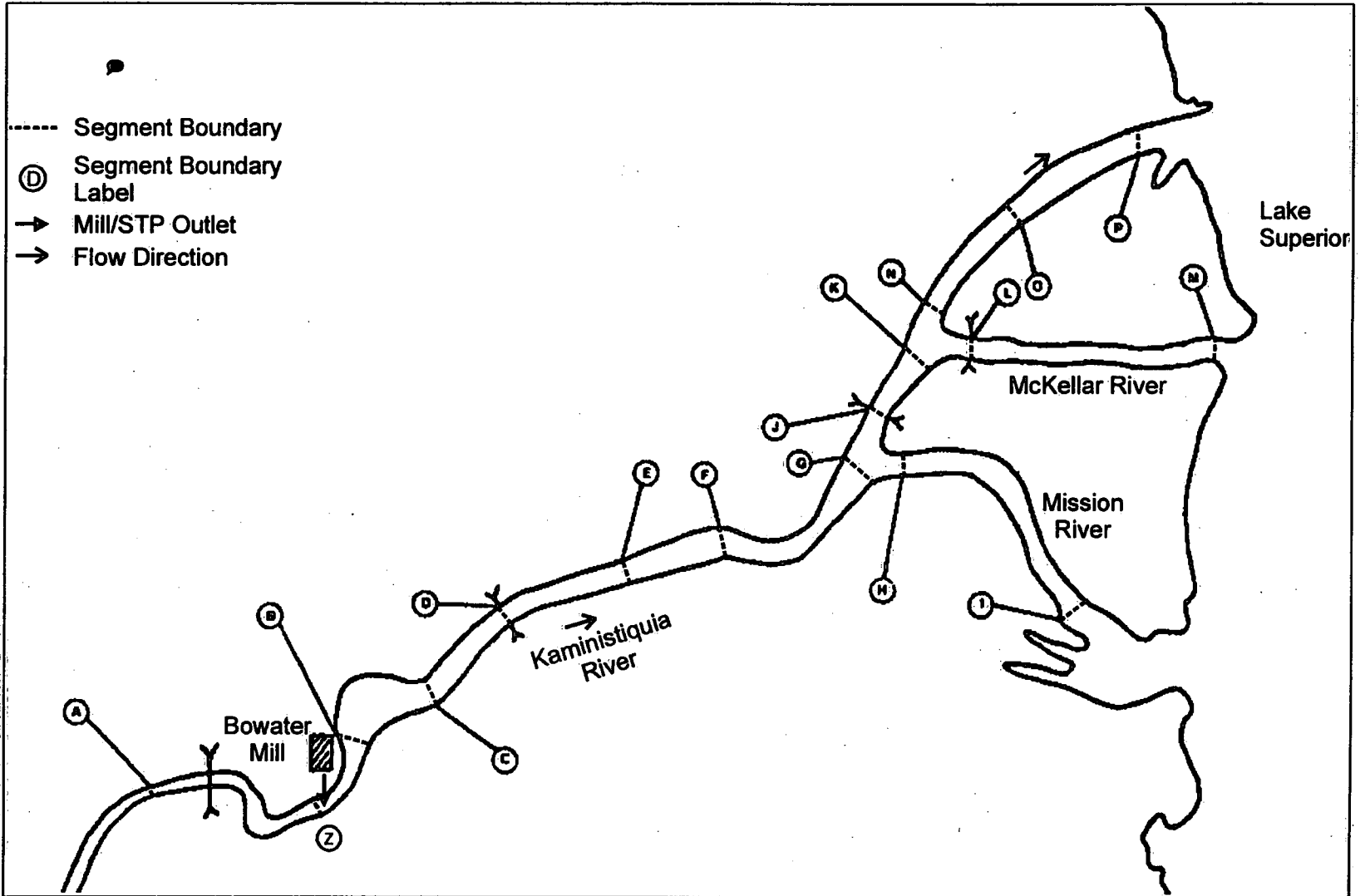


Table 4.1 EXWAT Input - Bowater Pulp and Paper Canada Inc., Thunder Bay, Ontario

Segment	Length km	Width m	Depth m	DSed m	VolFlo m3/s	Susp g/m3	Por 0..1	OrgC	OrgCS	Dens g/cm3
AZ	1.061	125	5.2	0.05	17	1.9	0.6	2E-06	2.4E-06	1.309
ZB	1.425	157	6.9	0.05	20	6.9	0.6	2E-06	2.4E-06	1.309
BC	2.425	167	7.3	0.05	20	6.9	0.6	2E-06	2.4E-06	1.309
CD	3.275	171	7.4	0.05	20	7.3	0.6	2E-06	2.4E-06	1.309
DE	4.115	162	7.3	0.05	20	7.6	0.6	2E-06	2.4E-06	1.309
EF	4.735	135	7.7	0.05	20	7.4	0.6	2E-06	2.4E-06	1.309
FG	5.945	100	8	0.05	20	7.1	0.6	2E-06	2.4E-06	1.309
GJ	6.895	102	7.7	0.05	20	6.8	0.6	2E-06	2.4E-06	1.309
JK	7.465	137	7.4	0.05	20	7.2	0.6	2E-06	2.4E-06	1.309
KN	7.94	150	7.3	0.05	20	7.3	0.6	2E-06	2.4E-06	1.309
NO	8.815	150	7.3	0.05	20	6.3	0.6	2E-06	2.4E-06	1.309
OP	9.945	150	7.3	0.05	20	5.2	0.6	2E-06	2.4E-06	1.309

Segment	Input kg/d	pH	Depos m/d	Perm m/d	BurSed m/d	Wind m/s	Volat 1/d	SedRate mm/a	KD cm3 H2O/g	KDS cm3 H2O/g
AZ	0	7.6	10	3E-04	1E-04	4	0	10	0.0312	0.0312
ZB	3.07	7.4	10	3E-04	1E-04	4	0	10	0.0312	0.0312
BC	0	7.2	10	3E-04	1E-04	4	0	10	0.0312	0.0312
CD	0	7.1	10	3E-04	1E-04	4	0	10	0.0312	0.0312
DE	0	7	10	3E-04	1E-04	4	0	10	0.0312	0.0312
EF	0	7	10	3E-04	1E-04	4	0	10	0.0312	0.0312
FG	0	7	10	3E-04	1E-04	4	0	10	0.0312	0.0312
GJ	0	7	10	3E-04	1E-04	4	0	10	0.0312	0.0312
JK	0	7	10	3E-04	1E-04	4	0	10	0.0312	0.0312
KN	0	7	10	3E-04	1E-04	4	0	10	0.0312	0.0312
NO	0	7.1	10	3E-04	1E-04	4	0	10	0.0312	0.0312
OP	0	7.1	10	3E-04	1E-04	4	0	10	0.0312	0.0312

Table 4.2 EXWAT Output - Bowater Pulp and Paper Canada Inc., Thunder Bay, Ontario

Segment	Conc ug/l	ConcS ug/l	ConcWa ug/l	ConcSM ug/l	ConcPW ug/l	ConcSS ug/l	ConcBM ug/g	SorbFra	Elim 1/d
AZ	0	0	0	0	0	0	0	5.9E-08	0.0070
ZB	1.77	0.54	1.77	0.014	0.88	3.8E-07	2.13	2.2E-07	0.0070
BC	1.77	0.54	1.77	0.014	0.87	3.8E-07	2.12	2.2E-07	0.0070
CD	1.76	0.54	1.76	0.014	0.87	4.0E-07	2.11	2.3E-07	0.0070
DE	1.75	0.53	1.75	0.014	0.86	4.2E-07	2.10	2.4E-07	0.0070
EF	1.75	0.53	1.75	0.014	0.86	4.0E-07	2.10	2.3E-07	0.0070
FG	1.74	0.53	1.74	0.014	0.86	3.9E-07	2.09	2.2E-07	0.0070
GJ	1.73	0.53	1.73	0.014	0.86	3.7E-07	2.08	2.1E-07	0.0070
JK	1.73	0.53	1.73	0.014	0.85	3.9E-07	2.08	2.2E-07	0.0070
KN	1.73	0.53	1.73	0.014	0.85	3.9E-07	2.08	2.3E-07	0.0070
NO	1.72	0.52	1.72	0.014	0.85	3.4E-07	2.07	2.0E-07	0.0070
OP	1.71	0.52	1.71	0.014	0.85	2.8E-07	2.06	1.6E-07	0.0070

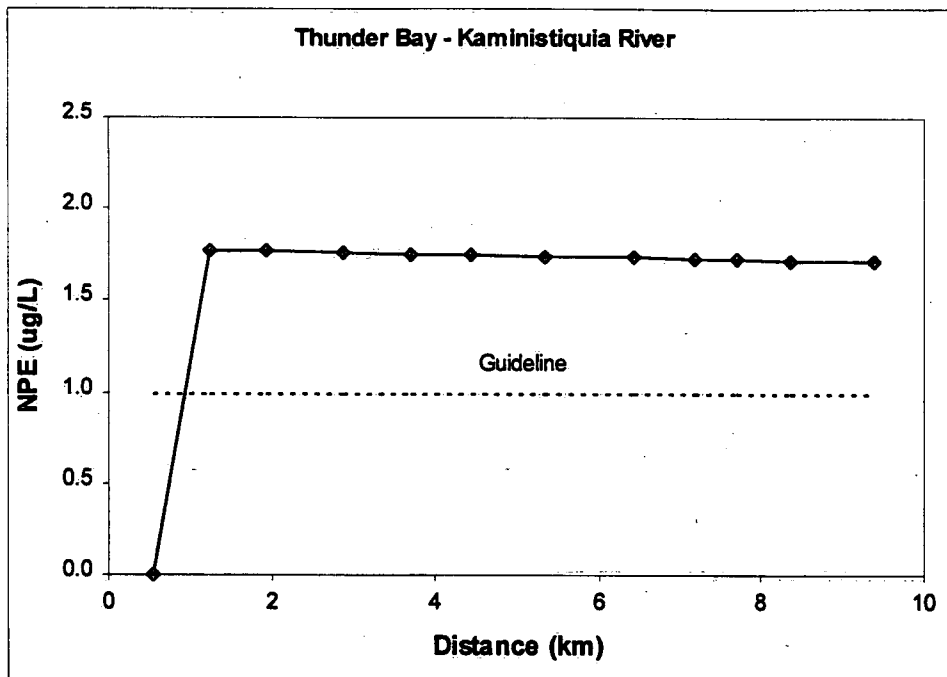


Figure 4-2 EXWAT Model NPE Concentration – Kaministiquia River, Thunder Bay, Ontario

4.3.3 Kaministiquia River Water Quality Model Results

The Kaministiquia general water quality model was modified to model NPE in the Kaministiquia River. The model uses actual flow data for the 5 day period of August 11-15, 1986. The daily flow rates for these 5 days are 47, 22, 20, 20, and 20 m³/s. The daily flow rate during the last 3 days is approximately the 7Q20 flow rate used in the EXWAT model.

As discussed in section 3, this model has 3 layers. The same mill loading used in the EXWAT model is inserted in the bottom layer of segment ZB. Additional inputs required for the model include:

- Percent undissociated = 0.0199% (equation 3-8 and pKa and pH used in the EXWAT)
- Decay rate = 0.007 (1/day) (same as EXWAT RWater coefficient)
- Partition coefficient = 3.12e-8 (L/mg) (same as EXWAT KD coefficient)
- Volatization = 0 (same as EXWAT Volat coefficient)

The maximum calculated NPE concentrations, which occur at the end of the simulation period (August 15, 1986), are shown for each layer in Figure 4-3 and Figure 4-4. The maximum concentration is 2.0 ug/L for the bottom layer at the site of the mill outlet (segment BZ). This value is twice the guideline value. As the warmer effluent rises to the upper layers and is transported downstream, the concentrations decrease. Upper layer concentrations are approximately 1.2 ug/L in the upstream segments, which are approximately 20% higher than the NPE guideline. The NPE sediment guideline could not be checked with the Kaministiquia water quality model since it does not calculate sediment concentrations.

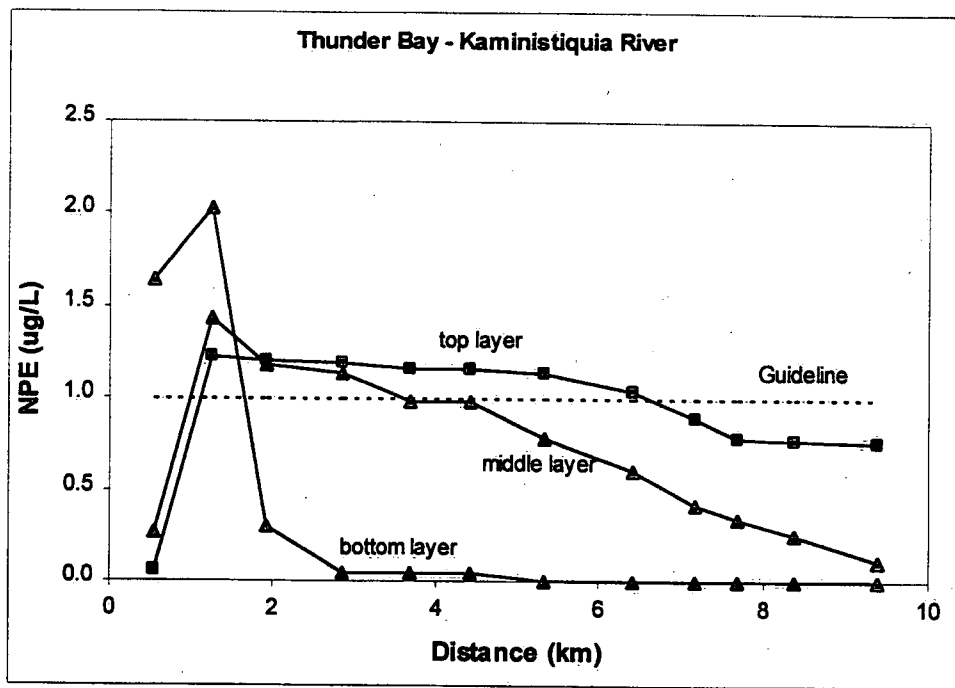


Figure 4-3 Kaministiquia Water Quality Model NPE Concentration – Kaministiquia River, Thunder Bay, Ontario

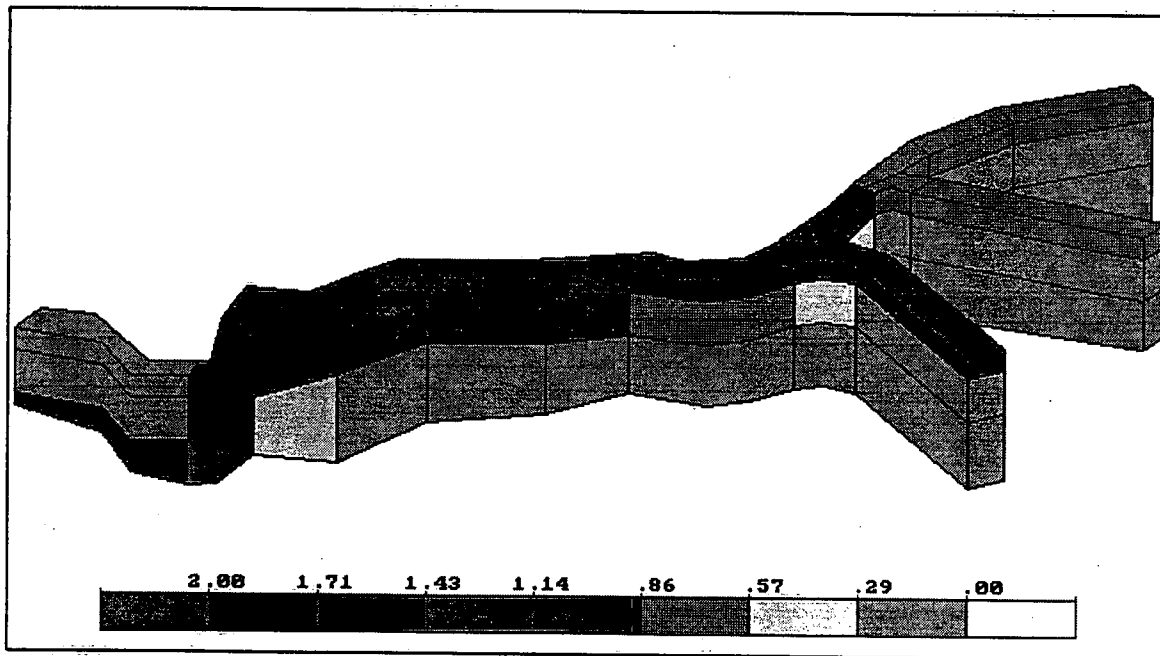


Figure 4-4 NPE Concentration (ug/L) - Kaministiquia Water Quality Model

4.4 Bowater Pulp and Paper Canada Inc., Gatineau, Quebec

4.4.1 Site Description

The Bowater Mill discharges to the Ottawa River north of Ile Kettle as shown in Figure 4-5. Approximately 4 km downstream of the Mill a sewage treatment plant also discharges to the river. For modelling purposes, the river is broken up into a number of segments.

4.4.1.1 Mill Loadings

Bowater mill loadings were obtained from Environment Canada's National Pollutant Release Inventory (NPRI) for 1999 for nonylphenol polyethylene glycol ether. Total release for 1999 was 0.67 kg/d (0.243 tonnes) in 0.83 m³/s (26,175,894 m³). Mill pH was 6.4 and suspended sediment 16.7 (ppm) for 1999 (Table 4.2 in Beak 2000). Mill loadings are inserted at segment BC.

4.4.1.2 Stream Flow

The 7Q20 flow rate for the Ottawa River at Britannia is 302 m³/s and was calculated using the Low Flow Frequency Analysis Package Version 2.0 (Environment Canada, 1993) and data available for 1961-1999 from Environment Canada's database HYDAT. The portion of flow north of Ile Kettle was estimated to be 60m³/s or 20% of the total flow based on river top-width north and south of the island. Downstream of the island, the total 7Q20 flow of 302 m³/s is used in the model, starting at segment DE.

4.4.1.3 Stream Parameters

Site specific stream model inputs include the following (refer to Table 4.3 for values):

- Segment length and width from Figure 4-5
- Segment depth estimated as 1/2 maximum depth (Figure 6.1 in Beak 2000)
- Suspended sediment 13 g/m³ (Ottawa River at Britannia average 1971-1976, Environment Canada HYDAT database)
- Organic carbon content 0.04 (EXWAT default)
- Upstream NPE concentrations were unknown and set to zero

4.4.2 EXWAT Model Results

Inputs to the EXWAT model are presented in Table 4.3. The Mill loading is applied to segment BC. EXWAT default values for DSed, Por, Dens, Depos, Perm, BurSed, Wind, Volat, SedRate, KD, and KDS were used (refer to Table 2.2 for symbol explanations).

Results from the EXWAT model are presented in Table 4.4 and Figure 4-6. The NPE river concentration (Conc) is a maximum of 0.128 ug/L in reach BC, which is the reach where the mill discharges. NPE then decreases downstream of Ile Kettle to 0.026 ug/L due to dilution from the rest of the Ottawa River. These values of NPE are below the guideline of 1 ug/L. The sediment concentration maximum is 1.03 ug/L or 0.78 ug/kg based on the default sediment dry density (Dens) of 1.309 g/cm³. This sediment concentration is much less than the NPE guideline of 1,400 ug/kg.

Figure 4-5 Bowater Pulp and Paper Canada Inc., Gatineau, Quebec

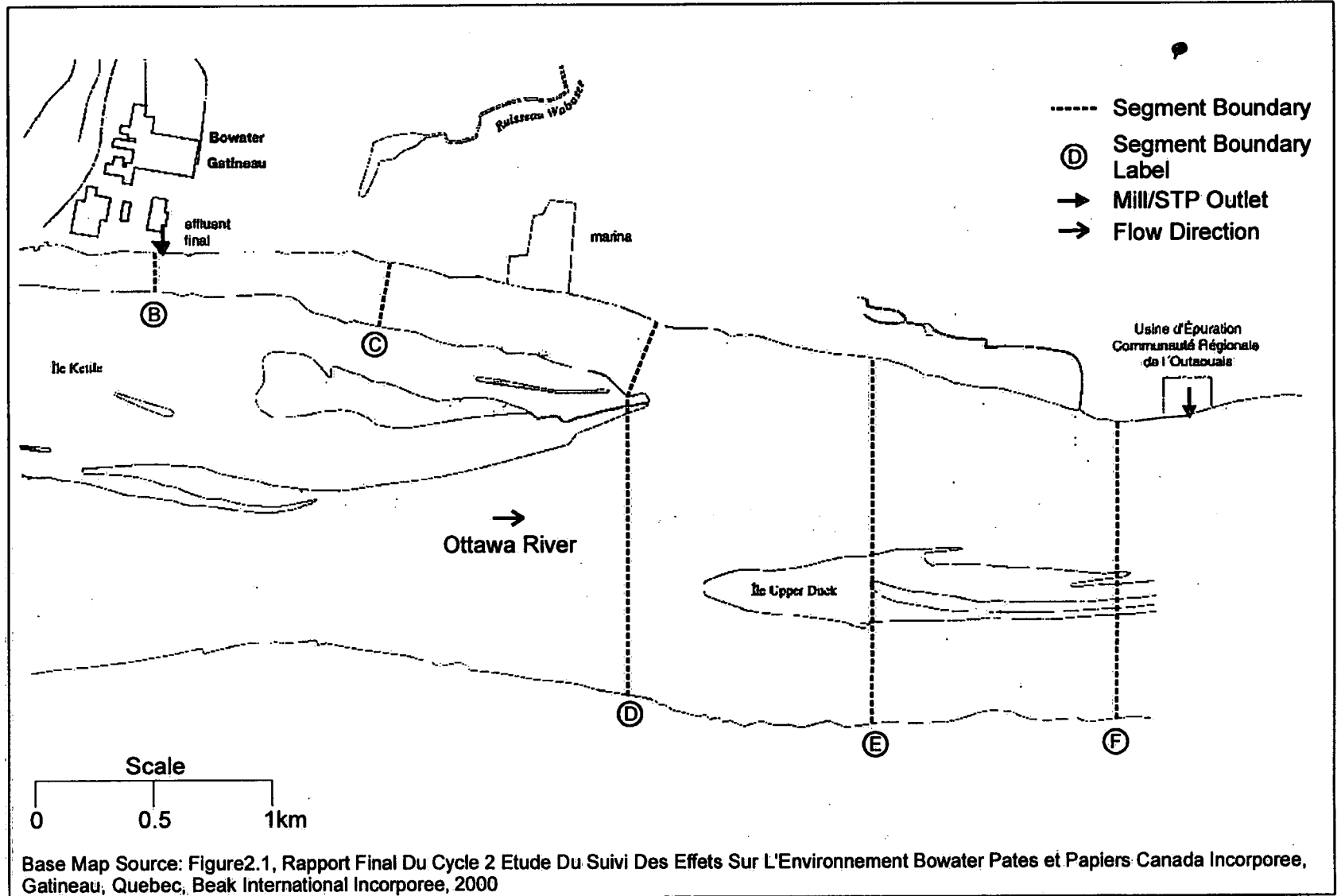


Table 4.3 EXWAT Input - Bowater Pulp and Paper Canada Inc., Gatineau, Quebec

Segment	Length km	Width m	Depth m	DSed m	VolFlo m3/s	Susp g/m3	Por 0..1	OrgC	OrgCS	Dens g/cm3
AB	1	170	2.25	0.05	60	13	0.6	0.04	0.04	1.309
BC	2	170	2.25	0.05	60.8	13.2	0.6	0.04	0.04	1.309
CD	3	260	2.25	0.05	60.8	13.2	0.6	0.04	0.04	1.309
DE	4	1200	2.25	0.05	302.8	13.2	0.6	0.04	0.04	1.309
EF	5	1200	2.25	0.05	302.8	13.2	0.6	0.04	0.04	1.309
FG	6	1200	2.25	0.05	302.8	13.2	0.6	0.04	0.04	1.309
GH	7	1200	2.25	0.05	302.8	13.2	0.6	0.04	0.04	1.309
HI	8	1200	2.25	0.05	302.8	13.2	0.6	0.04	0.04	1.309
IJ	9	1200	2.25	0.05	302.8	13.2	0.6	0.04	0.04	1.309
JK	10	1200	2.25	0.05	302.8	13.2	0.6	0.04	0.04	1.309
KL	11	1200	2.25	0.05	302.8	13.2	0.6	0.04	0.04	1.309
LM	12	1200	2.25	0.05	302.8	13.2	0.6	0.04	0.04	1.309

Segment	Input kg/d	pH	Depos m/d	Perm m/d	BurSed m/d	Wind m/s	Volat 1/d	SedRate mm/a	KD cm3 H2O/g	KDS cm3 H2O/g
AB	0	7.2	10	0.00025	0.0001	4	0	10	520	520
BC	0.67	7.2	10	0.00025	0.0001	4	0	10	520	520
CD	0	7.2	10	0.00025	0.0001	4	0	10	520	520
DE	0	7.2	10	0.00025	0.0001	4	0	10	520	520
EF	0	7.2	10	0.00025	0.0001	4	0	10	520	520
FG	0	7.2	10	0.00025	0.0001	4	0	10	520	520
GH	0	7.2	10	0.00025	0.0001	4	0	10	520	520
HI	0	7.2	10	0.00025	0.0001	4	0	10	520	520
IJ	0	7.2	10	0.00025	0.0001	4	0	10	520	520
JK	0	7.2	10	0.00025	0.0001	4	0	10	520	520
KL	0	7.2	10	0.00025	0.0001	4	0	10	520	520
LM	0	7.2	10	0.00025	0.0001	4	0	10	520	520

Table 4.4 EXWAT Output - Bowater Pulp and Paper Canada Inc., Gatineau, Quebec

Segment	Conc ug/l	ConcS ug/l	ConcWa ug/l	ConcSM ug/l	ConcPW ug/l	ConcSS ug/l	ConcBM ug/l	SorbFrac	Elim 1/d
AB	0	0	0	0	0	0	0	0.007	0.0103
BC	0.128	1.03	0.127	1.02	0.0038	0.0009	0.1522	0.007	0.0103
CD	0.127	1.03	0.127	1.02	0.0038	0.0009	0.1521	0.007	0.0103
DE	0.026	0.21	0.025	0.21	0.0008	0.0002	0.0305	0.007	0.0103
EF	0.026	0.21	0.025	0.21	0.0008	0.0002	0.0305	0.007	0.0103
FG	0.026	0.21	0.025	0.20	0.0008	0.0002	0.0305	0.007	0.0103
GH	0.026	0.21	0.025	0.20	0.0008	0.0002	0.0304	0.007	0.0103
HI	0.025	0.21	0.025	0.20	0.0008	0.0002	0.0304	0.007	0.0103
IJ	0.025	0.20	0.025	0.20	0.0008	0.0002	0.0304	0.007	0.0103
JK	0.025	0.20	0.025	0.20	0.0008	0.0002	0.0304	0.007	0.0103
KL	0.025	0.20	0.025	0.20	0.0007	0.0002	0.0304	0.007	0.0103
LM	0.025	0.20	0.025	0.20	0.0007	0.0002	0.0303	0.007	0.0103

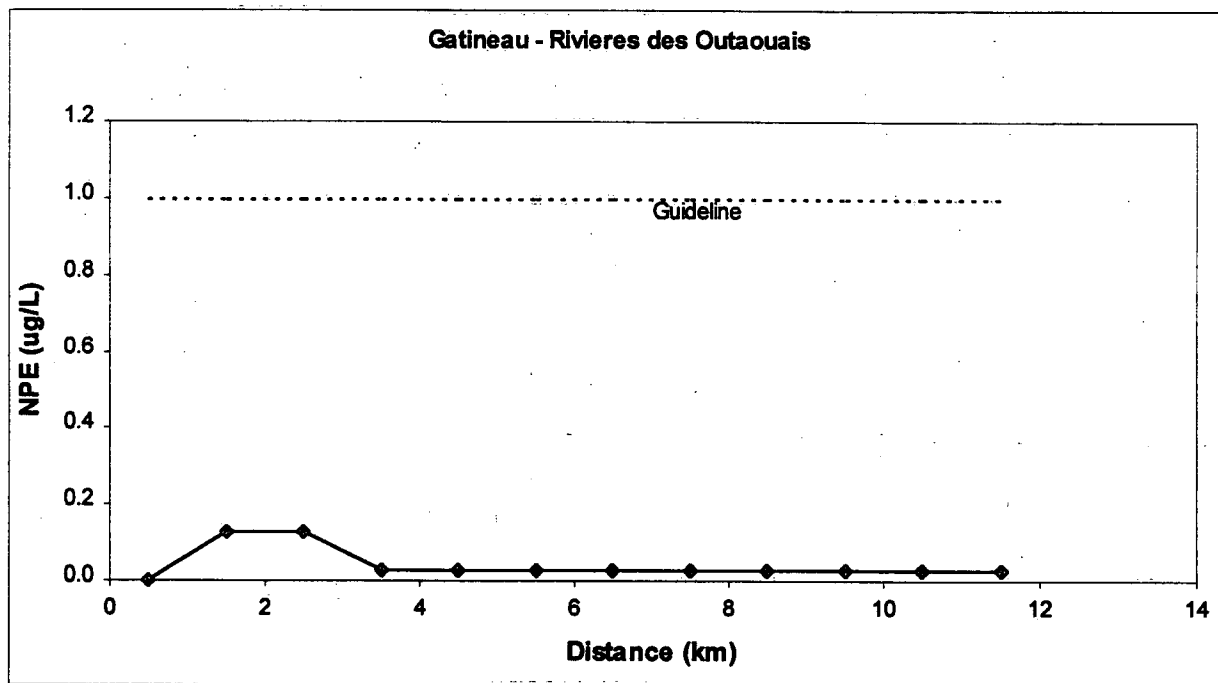


Figure 4-6 NPE Concentration – Ottawa River, Gatineau, Quebec

4.5 Weyerhaeuser Canada Ltd., Grande Prairie, Alberta

4.5.1 Site Description

Weyerhaeuser discharges to the Wapiti River near Grande Prairie as shown in Figure 4-7. Approximately 9 km upstream of the Mill a sewage treatment plant also discharges to the River. Approximately 8 km downstream, the Wapiti River empties into the Smoky River. For modelling purposes, the river system is broken up into a number of segments.

4.5.1.1 Mill and STP Loadings

Mill loadings were obtained from Environment Canada's National Pollutant Release Inventory (NPRI) for 1999 for nonylphenol polyethylene glycol ether. Total release for 1999 was 0.929 kg/d (0.339 tonnes) in 0.67 m³/s (21,043,934 m³). Mill pH and suspended sediment were unknown and assumed to have no affect on the river. Mill loadings are inserted at segment DE.

The STP mean flow rate is 0.23 m³/s and mean TSS is 5.06 mg/L (Golder Associates 2000). Mill pH and NPE concentration were unknown and assumed to have no affect on the river. The STP loadings are inserted at segment BC.

4.5.1.2 Stream Flow

The 7Q20 flow rates for the rivers in this system were calculated using the Low Flow Frequency Analysis Package Version 2.0 (Environment Canada, 1993) and data available from Environment Canada's database HYDAT as follows:

- Wapiti River at Grande Prairie 7Q20 = 6.18 m³/s (data available for 1961-1999)
- Smoky River at Wapiti River confluence 7Q20 = 8.58 m³/s estimated as the sum of Smoky River above Hells Creek (7.24 m³/s, 1969-1999) + Cutbank River near Grande Prairie (0.08 m³/s, 1970-1999) + Kakwa River near Grande Prairie (1.26 m³/s, 1977-1994)
- Simonette River near Goodwin 7Q20 = 0.89 m³/s (1970-1999)
- Puskwaskau River used January to March average flow 0.09 m³/s (Figure 2-5 in Golder Associates 2000)

The Cumulative flow rate (VolFlo) for the river system is shown in Table 4.5.

4.5.1.3 Stream Parameters

Site specific stream model inputs include the following (refer to Table 4.5 for values):

- Segment length from Figure 4-7
- Segment width and depth were unknown and assumed to be 6 m and 1 m so that stream velocity would be a typical 1m/s
- Suspended sediment was unknown and set to 1 g/m³
- Organic carbon content 0.04 (EXWAT default)
- pH was unknown and set to 7
- Upstream NPE concentrations were unknown and set to zero

4.5.2 EXWAT Model Results

Inputs to the EXWAT model are presented in Table 4.5. The Mill loading is applied to segment DE. EXWAT default values for DSed, Por, Dens, Depos, Perm, BurSed, Wind, Volat, SedRate, KD, and KDS were used (refer to Table 2.2 for symbol explanations).

Figure 4-7 Site Location - Weyerhaeuser Canada Ltd., Grande Prairie, Alberta

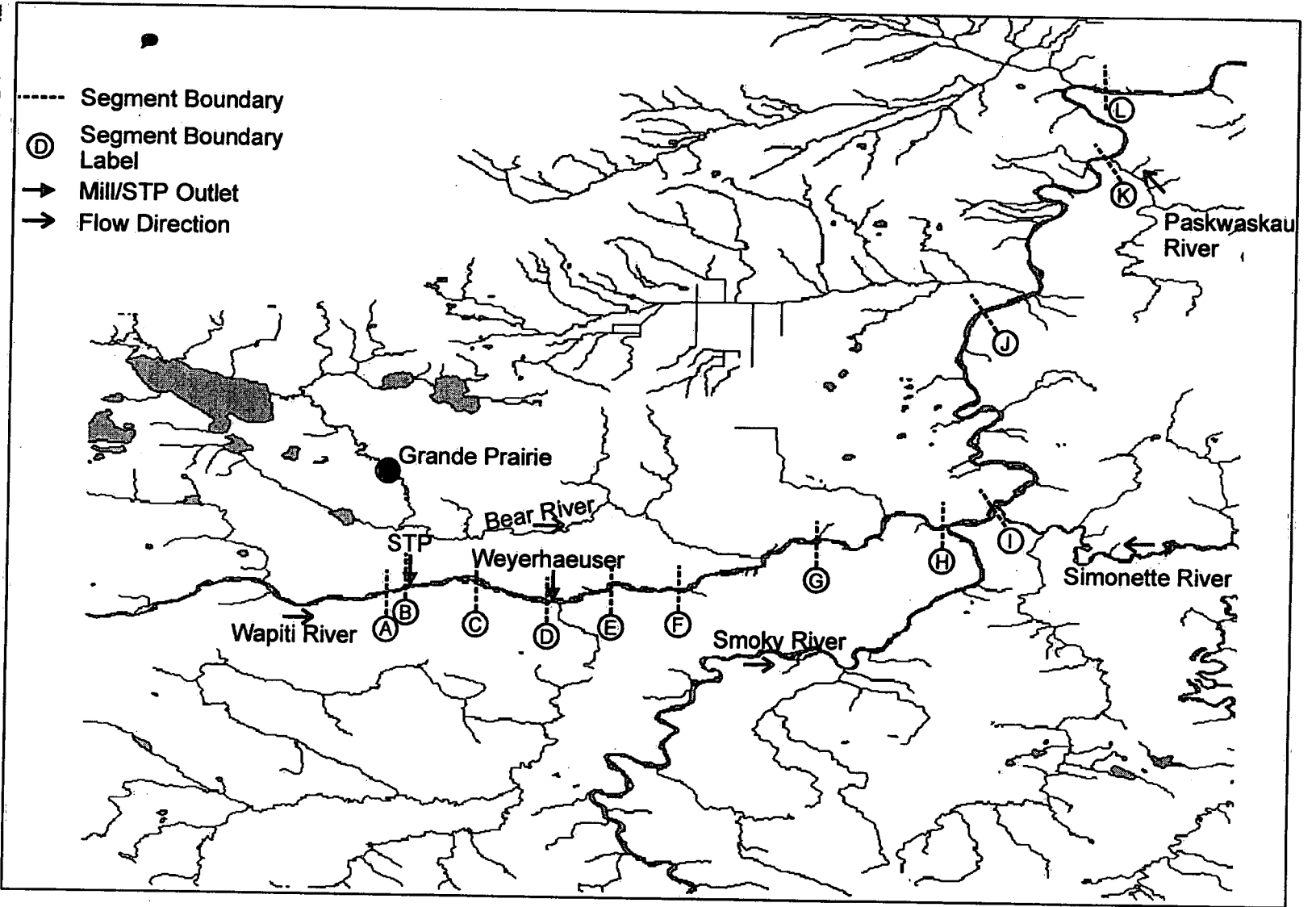


Table 4.5 EXWAT Input - Weyerhaeuser Canada Ltd., Grande Prairie, Alberta

Segment	Length km	Width m	Depth m	DSed m	VolFlo m3/s	Susp g/m3	Por 0..1	OrgC	OrgCS	Dens g/cm3
AB	1	6	1	0.05	6.18	1	0.6	0.04	0.04	1.309
BC	5.6	6	1	0.05	6.41	1.2	0.6	0.04	0.04	1.309
CD	10.2	6	1	0.05	6.41	1.2	0.6	0.04	0.04	1.309
DE	15.2	6	1	0.05	7.08	1.2	0.6	0.04	0.04	1.309
EF	20.2	6	1	0.05	7.08	1.2	0.6	0.04	0.04	1.309
FG	30.2	6	1	0.05	7.08	1.2	0.6	0.04	0.04	1.309
GH	40.2	6	1	0.05	7.08	1.2	0.6	0.04	0.04	1.309
HI	44.2	6	2	0.05	15.66	82	0.6	0.04	0.04	1.309
IJ	64.2	6	2	0.05	16.55	124	0.6	0.04	0.04	1.309
JK	84.2	6	2	0.05	16.55	124	0.6	0.04	0.04	1.309
KL	94.2	6	2	0.05	16.64	124	0.6	0.04	0.04	1.309

Segment	Input kg/d	pH	Depos m/d	Perm m/d	BurSed m/d	Wind m/s	Volat 1/d	SedRate mm/a	KD cm3 H2O/g	KDS cm3 H2O/g
AB	0	7	10	0.00025	0.0001	4	0	10	520	520
BC	0	7	10	0.00025	0.0001	4	0	10	520	520
CD	0	7	10	0.00025	0.0001	4	0	10	520	520
DE	0.929	7	10	0.00025	0.0001	4	0	10	520	520
EF	0	7	10	0.00025	0.0001	4	0	10	520	520
FG	0	7	10	0.00025	0.0001	4	0	10	520	520
GH	0	7	10	0.00025	0.0001	4	0	10	520	520
HI	0	7	10	0.00025	0.0001	4	0	10	520	520
IJ	0	7	10	0.00025	0.0001	4	0	10	520	520
JK	0	7	10	0.00025	0.0001	4	0	10	520	520
KL	0	7	10	0.00025	0.0001	4	0	10	520	520

Table 4.6 EXWAT Output - Weyerhaeuser Canada Ltd., Grande Prairie, Alberta

Segment	Conc ug/l	ConcS ug/l	ConcWa ug/l	ConcSM ug/l	ConcPW ug/l	ConcSS ug/l	ConcBM ug/l	SorbFrac	Elim 1/d
AB	0	0	0	0	0	0	0	0.001	0.0145
BC	0	0	0	0	0	0	0	0.001	0.0145
CD	0	0	0	0	0	0	0	0.001	0.0145
DE	1.52	34	1.52	33.8	0.1241	0.001	1.82	0.001	0.0145
EF	1.52	34	1.52	33.8	0.1240	0.001	1.82	0.001	0.0145
FG	1.52	34	1.52	33.7	0.1239	0.001	1.82	0.001	0.0145
GH	1.52	34	1.51	33.7	0.1238	0.001	1.82	0.001	0.0145
HI	0.68	1.1	0.66	1.1	0.0041	0.028	0.79	0.041	0.0106
IJ	0.65	0.7	0.61	0.7	0.0026	0.039	0.73	0.061	0.0105
JK	0.65	0.7	0.61	0.7	0.0026	0.039	0.73	0.061	0.0105
KL	0.64	0.7	0.60	0.7	0.0026	0.039	0.73	0.061	0.0105

Results from the EXWAT model are presented in Table 4.6 and Figure 4-8. The NPE river concentration (Conc) is a maximum of 1.5 ug/L in reach DE, which is the reach where the mill discharges. This value of NPE is above the guideline of 1 ug/L. NPE decreases below the guideline to 0.68 ug/L due to dilution from the Smoky River. The sediment concentration maximum is 34 ug/L or 26 ug/kg based on the default sediment dry density (Dens) of 1.309 g/cm³. This sediment concentration is much less than the NPE guideline of 1,400 ug/kg.

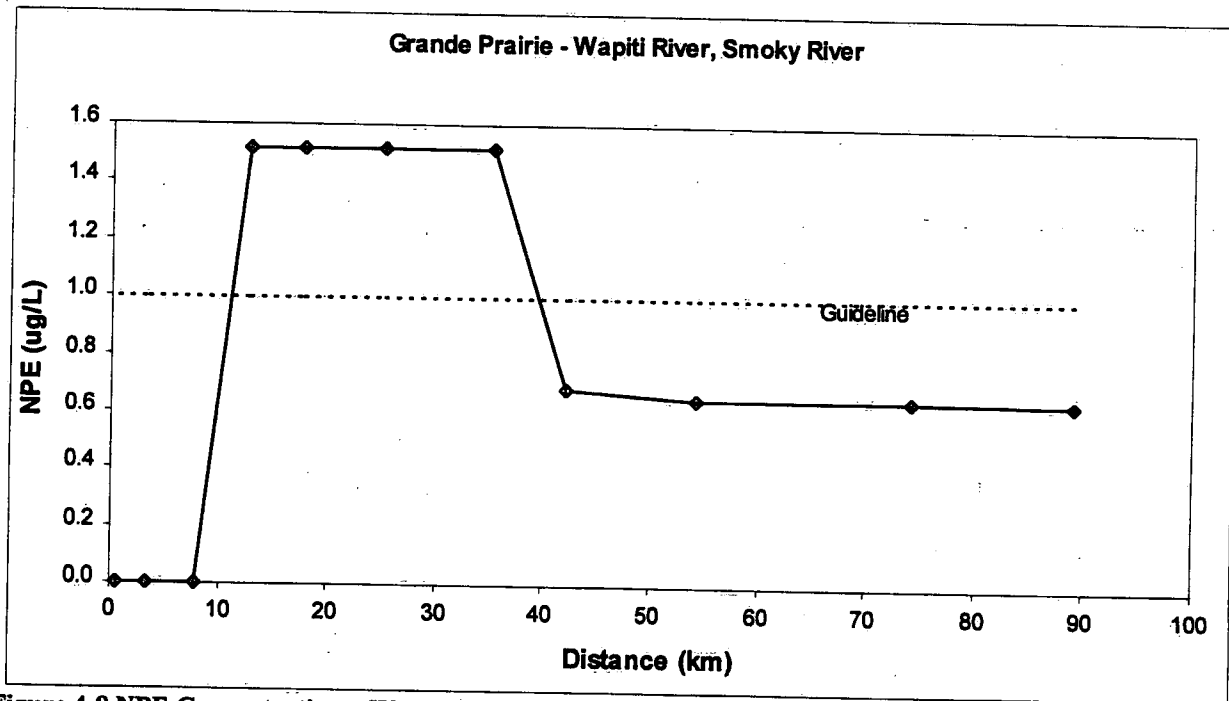


Figure 4-8 NPE Concentration – Wapiti River and Smoky River, Grande Prairie, Alberta

4.6 Weyerhaeuser Company Ltd., Dryden, Ontario

4.6.1 Site Description

Weyerhaeuser discharges to the Wabigoon River near Dryden, Ontario as shown in Figure 4-9. Approximately 1 km downstream of the Mill a sewage treatment plant also discharges to the river. For modelling purposes, the river system is broken up into a number of segments.

4.6.1.1 Mill and STP Loadings

Mill loadings were obtained from Environment Canada's National Pollutant Release Inventory (NPRI) for 1999 for nonylphenol polyethylene glycol ether. Total release for 1999 was 1.797 kg/d (0.656 tonnes) in 1.34 m³/s (42,266,922 m³). Mill pH was approximately 7.7 in 1998-1999 and suspended sediment was 32 mg/L in 1997 (Beak 2000). These values were used in the model. Mill loadings are inserted at segment BC.

The STP flow rate was estimated at 0.053 m³/s (1 million gallon/day) (www.cityofdryden.on.ca/profile). STP pH, TSS and NPE concentrations were unknown and assumed to have no affect on the river. The STP loadings are inserted at segment DE.

4.6.1.2 Stream Flow

The 7Q20 flow rate for the Wabigoon River is 0.789 m³/s (Beak 2000). The Cumulative flow rate (VolFlo) for the river system is shown in Table 4.7.

4.6.1.3 Stream Parameters

Site specific stream model inputs include the following (refer to Table 4.7 for values):

- Segment length and width from Figure 4-9
- Segment depth was unknown and set to 1 m so that stream velocity of 0.08 m/s (Beak 2000) would result.
- Suspended sediment = 19 mg/L and pH = 7.4 (averages of 1983, 1984 and 1987 values at federal flow gauge at Golf Course Bridge Dryden)
- Organic carbon content = 5.2mg/kg (Maddison per. comm..)
- Upstream NPE concentrations were unknown and set to zero

4.6.2 EXWAT Model Results

Inputs to the EXWAT model are presented in Table 4.7. The Mill loading is applied to segment BC. EXWAT default values for DSed, Por, Dens, Depos, Perm, BurSed, Wind, Volat, SedRate, KD, and KDS were used (refer to Table 2.2 for symbol explanations).

Results from the EXWAT model are presented in Table 4.8 and Figure 4-10. The NPE river concentration (Conc) is a maximum of 9.8 ug/L in reach BC, which is the reach where the mill discharges. This value of NPE is above the guideline of 1 ug/L. The sediment concentration maximum is 2.95 ug/L or 2.3 ug/kg based on the default sediment dry density (Dens) of 1.309 g/cm³. This sediment concentration is much less than the NPE guideline of 1,400 ug/kg.

Figure 4-9 Site Location - Weyerhaeuser Company Ltd., Dryden, Ontario

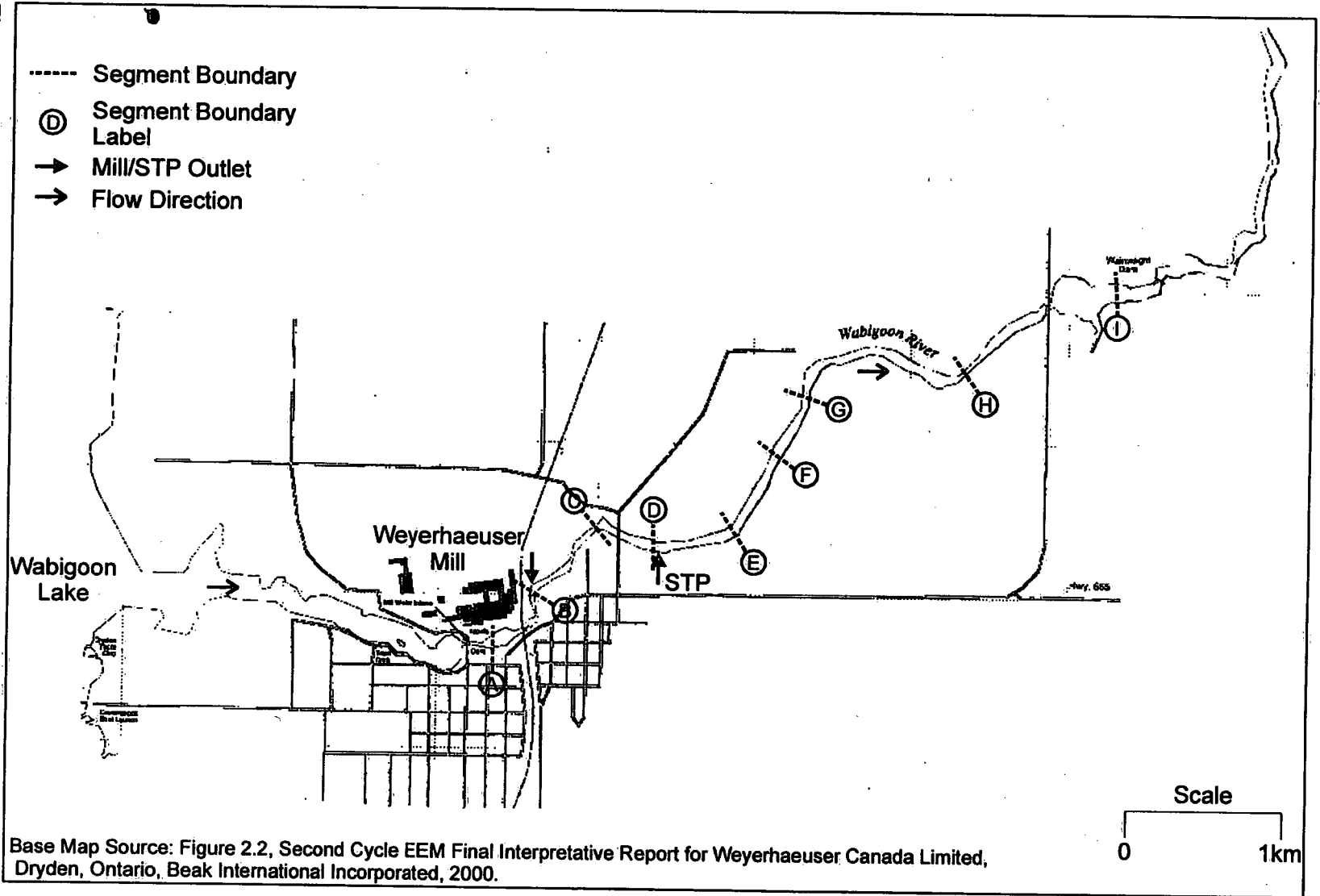


Table 4.7 EXWAT Input - Weyerhaeuser Company Ltd., Dryden, Ontario

Segment	Length km	Width m	Depth m	DSed m	VolFlo m3/s	Susp g/m3	Por 0.1	OrgC	OrgCS	Dens g/cm3
AB	0.5	30	1	0.05	0.789	19	0.6	5.2E-06	5.2E-06	1.309
BC	1.0	30	1	0.05	2.129	19	0.6	5.2E-06	5.2E-06	1.309
CD	1.5	30	1	0.05	2.129	19	0.6	5.2E-06	5.2E-06	1.309
DE	2.0	30	1	0.05	2.182	19	0.6	5.2E-06	5.2E-06	1.309
EF	2.5	30	1	0.05	2.182	19	0.6	5.2E-06	5.2E-06	1.309
FG	3.0	30	1	0.05	2.182	19	0.6	5.2E-06	5.2E-06	1.309
GH	4.0	30	1	0.05	2.182	19	0.6	5.2E-06	5.2E-06	1.309
HI	5.0	30	1	0.05	2.182	19	0.6	5.2E-06	5.2E-06	1.309
IJ	10.0	30	1	0.05	2.182	19	0.6	5.2E-06	5.2E-06	1.309
JK	15.0	30	1	0.05	2.182	19	0.6	5.2E-06	5.2E-06	1.309
KL	20.0	30	1	0.05	2.182	19	0.6	5.2E-06	5.2E-06	1.309
LM	25.0	30	1	0.05	2.182	19	0.6	5.2E-06	5.2E-06	1.309

Segment	Input kg/d	pH	Depos m/d	Perm m/d	BurSed m/d	Wind m/s	Volat 1/d	SedRate mm/a	KD cm3 H2O/g	KDS cm3 H2O/g
AB	0	7.4	10	0.00025	0.0001	4	0	10	0.0676	0.0676
BC	1.797	7.4	10	0.00025	0.0001	4	0	10	0.0676	0.0676
CD	0	7.4	10	0.00025	0.0001	4	0	10	0.0676	0.0676
DE	0	7.4	10	0.00025	0.0001	4	0	10	0.0676	0.0676
EF	0	7.4	10	0.00025	0.0001	4	0	10	0.0676	0.0676
FG	0	7.4	10	0.00025	0.0001	4	0	10	0.0676	0.0676
GH	0	7.4	10	0.00025	0.0001	4	0	10	0.0676	0.0676
HI	0	7.4	10	0.00025	0.0001	4	0	10	0.0676	0.0676
IJ	0	7.4	10	0.00025	0.0001	4	0	10	0.0676	0.0676
JK	0	7.4	10	0.00025	0.0001	4	0	10	0.0676	0.0676
KL	0	7.4	10	0.00025	0.0001	4	0	10	0.0676	0.0676
LM	0	7.4	10	0.00025	0.0001	4	0	10	0.0676	0.0676

Table 4.8 EXWAT Output - Weyerhaeuser Company Ltd., Dryden, Ontario

Segment	Conc ug/l	ConcS ug/l	ConcWa ug/l	ConcSM ug/l	ConcPW ug/l	ConcSS ug/l	ConcBM ug/l	SorbFrac	Elim 1/d
AB	0	0	0	0	0	0	0	1.3E-06	0.007
BC	9.76	2.95	9.76	0.16	4.64	1.3E-05	11.74	1.3E-06	0.007
CD	9.76	2.95	9.76	0.16	4.64	1.3E-05	11.73	1.3E-06	0.007
DE	9.52	2.87	9.52	0.16	4.52	1.2E-05	11.44	1.3E-06	0.007
EF	9.51	2.87	9.51	0.16	4.52	1.2E-05	11.43	1.3E-06	0.007
FG	9.51	2.87	9.51	0.16	4.51	1.2E-05	11.42	1.3E-06	0.007
GH	9.49	2.87	9.49	0.16	4.51	1.2E-05	11.41	1.3E-06	0.007
HI	9.48	2.86	9.48	0.16	4.50	1.2E-05	11.40	1.3E-06	0.007
IJ	9.43	2.85	9.43	0.16	4.48	1.2E-05	11.33	1.3E-06	0.007
JK	9.38	2.83	9.38	0.16	4.45	1.2E-05	11.27	1.3E-06	0.007
KL	9.32	2.81	9.32	0.16	4.43	1.2E-05	11.21	1.3E-06	0.007
LM	9.27	2.80	9.27	0.16	4.40	1.2E-05	11.14	1.3E-06	0.007

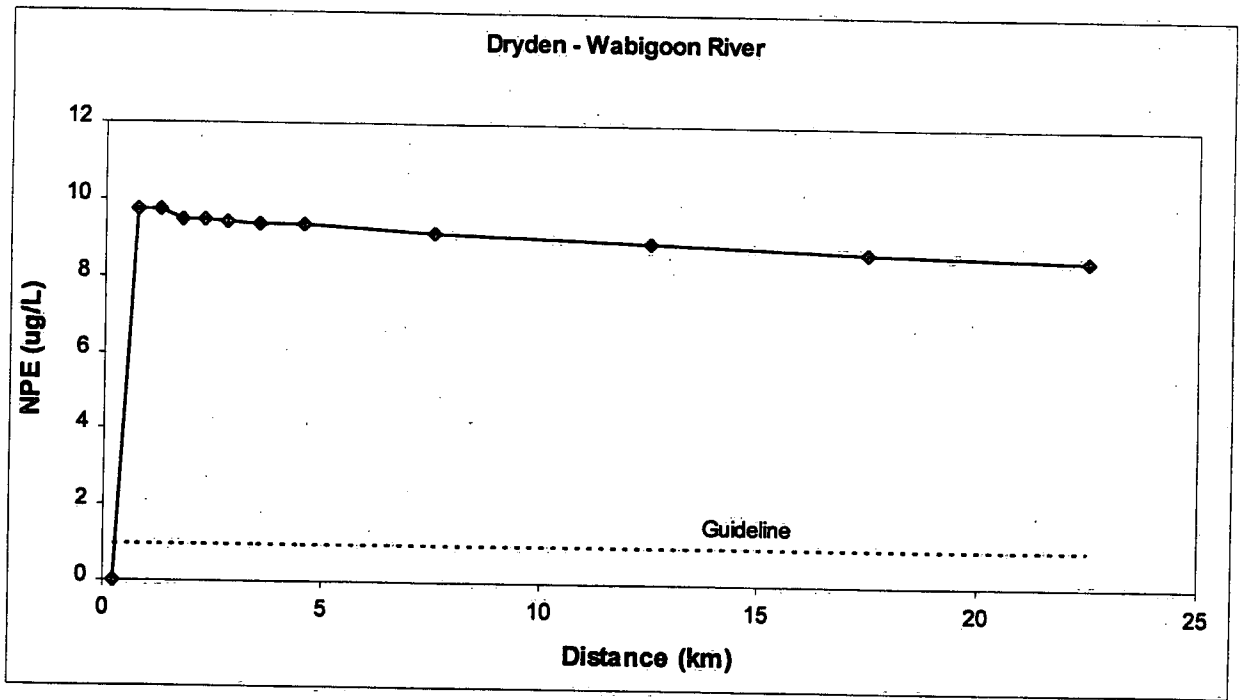


Figure 4-10 NPE Concentration – Wabigoon River, Dryden, Ontario

4.7 Weyerhaeuser Saskatchewan Ltd., Prince Albert, Saskatchewan

4.7.1 Site Description

Weyerhaeuser discharges to the North Saskatchewan River near Prince Albert, Saskatchewan as shown in Figure 4-11. A STP also discharges to the River approximately 12 km upstream of the mill. For modelling purposes, the river system is broken up into a number of segments.

4.7.1.1 Mill and STP Loadings

Mill loadings were obtained from Environment Canada's National Pollutant Release Inventory (NPRI) for 1999 for nonylphenol polyethylene glycol ether. Total release for 1999 was 0.82 kg/d (0.3 tonnes) in 1.07 m³/s (33,673,200 m³). Mill pH was approximately 7.6 and suspended sediment was 23 mg/L in 1999 (Table II-4 in Golder Associates 2000). These values were used in the model. Mill loadings are inserted at segment GH.

The STP flow rate was 0.17 m³/s in 1997 (Table III-1 in Golder Associates 2000). STP pH was 7.7 and TSS was 133 mg/L in 1997 (Table III-2 in Golder Associates 2000). These values were used in the model. NPE concentrations were unknown and assumed to have no affect on the river. The STP loadings are inserted at segment BC.

4.7.1.2 Stream Flow

The 7Q20 flow rate for the river is 14.7 m³/s and was calculated using the Low Flow Frequency Analysis Package Version 2.0 (Environment Canada, 1993) and data available from Environment Canada's database HYDAT for North Saskatchewan River at Prince Albert gauge using data for 1912-1999. The Garden River empties into the North Saskatchewan River downstream of the Mill but the 7Q20 is 0 m³/s

4.7.1.3 Stream Parameters

Site specific stream model inputs include the following (refer to Table 4.9 for values):

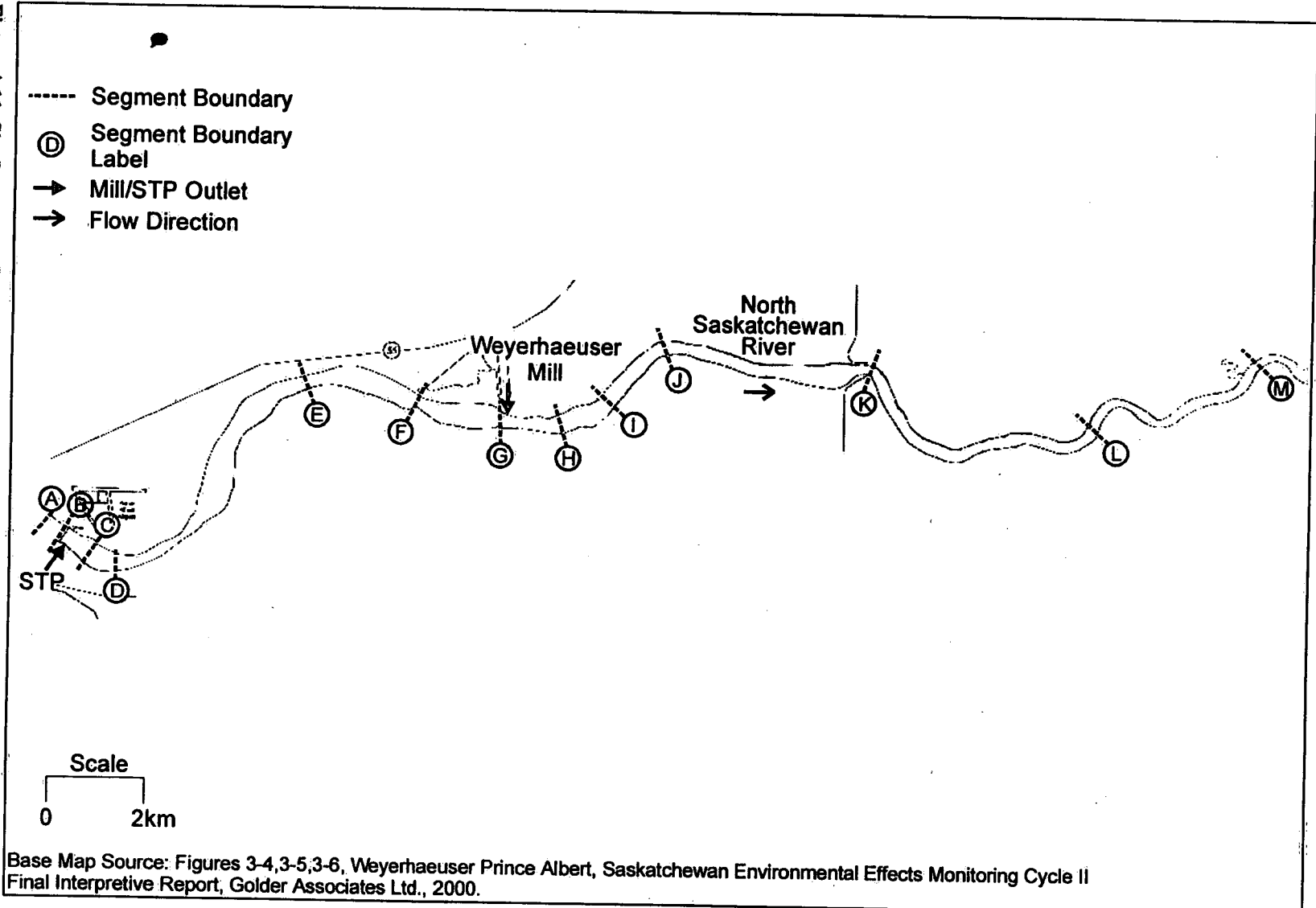
- Segment length and width based on transects (Tables 3-2 and 3-3 in Golder Associates 2000)
- Segment depth was unknown and estimated using survey data (Golder Associates 2000) adjusted for 7Q20 reduced flow
- Suspended sediment = 141 mg/L on average for 1962-1965 at gauge North Saskatchewan River at Prince Albert
- pH = 7.9 (average in 1998-1999, Table III-5 in Golder Associates 2000)
- Organic carbon content = 1.63e-7 (Maddison per. comm.)
- Upstream NPE concentrations were unknown and set to zero

4.7.2 EXWAT Model Results

Inputs to the EXWAT model are presented in Table 4.9. The Mill loading is applied to segment GH. EXWAT default values for DSed, Por, Dens, Depos, Perm, BurSed, Wind, Volat, SedRate, KD, and KDS were used (refer to Table 2.2 for symbol explanations).

Results from the EXWAT model are presented in Table 4.10 and Figure 4-12. The NPE river concentration (Conc) is a maximum of 0.59 ug/L in reach GH, which is the reach where the mill discharges. This value of NPE is below the guideline of 1 ug/L. The sediment concentration maximum is 0.18 ug/L or 0.13 ug/kg based on the default sediment dry density (Dens) of 1.309 g/cm³. This sediment concentration is much less than the NPE guideline of 1,400 ug/kg.

Figure 4-11 Site Location - Weyerhaeuser Saskatchewan Ltd., Prince Albert, Saskatchewan



Base Map Source: Figures 3-4,3-5,3-6, Weyerhaeuser Prince Albert, Saskatchewan Environmental Effects Monitoring Cycle II Final Interpretive Report, Golder Associates Ltd., 2000.

Table 4.9 EXWAT Input - Weyerhaeuser Saskatchewan Ltd., Prince Albert, Saskatchewan

Segment	Length km	Width m	Depth m	DSed m	VolFlo m3/s	Susp g/m3	Por 0.1	OrgC	OrgCS	Dens g/cm3
AB	1.0	110	0.7	0.05	14.7	141	0.6	1.63E-07	1.63E-07	1.309
BC	2.0	110	0.7	0.05	14.9	141	0.6	1.63E-07	1.63E-07	1.309
CD	3.4	110	0.7	0.05	14.9	141	0.6	1.63E-07	1.63E-07	1.309
DE	5.9	100	0.8	0.05	14.9	141	0.6	1.63E-07	1.63E-07	1.309
EF	10.5	85	0.8	0.05	14.9	141	0.6	1.63E-07	1.63E-07	1.309
FG	13.0	80	0.9	0.05	14.9	141	0.6	1.63E-07	1.63E-07	1.309
GH	14.0	100	0.8	0.05	16.0	133	0.6	1.63E-07	1.63E-07	1.309
HI	15.0	120	0.7	0.05	16.0	133	0.6	1.63E-07	1.63E-07	1.309
IJ	17.5	110	0.8	0.05	16.0	133	0.6	1.63E-07	1.63E-07	1.309
JK	21.0	90	0.9	0.05	16.0	133	0.6	1.63E-07	1.63E-07	1.309
KL	26.0	70	0.9	0.05	16.0	133	0.6	1.63E-07	1.63E-07	1.309
LM	30.0	60	1.1	0.05	16.0	133	0.6	1.63E-07	1.63E-07	1.309
MN	37.0	50	0.7	0.05	16.0	133	0.6	1.63E-07	1.63E-07	1.309
NO	42.0	60	0.6	0.05	16.0	133	0.6	1.63E-07	1.63E-07	1.309
OP	50.0	60	0.6	0.05	16.0	133	0.6	1.63E-07	1.63E-07	1.309
PQ	54.5	50	0.7	0.05	16.0	133	0.6	1.63E-07	1.63E-07	1.309

Segment	Input kg/d	pH	Depos m/d	Perm m/d	BurSed m/d	Wind m/s	Volat 1/d	SedRate mm/a	KD cm3 H2O/g	KDS cm3 H2O/g
AB	0	7.9	10	0.00025	0.0001	4	0	10	0.002119	0.002119
BC	0	7.9	10	0.00025	0.0001	4	0	10	0.002119	0.002119
CD	0	7.9	10	0.00025	0.0001	4	0	10	0.002119	0.002119
DE	0	7.9	10	0.00025	0.0001	4	0	10	0.002119	0.002119
EF	0	7.9	10	0.00025	0.0001	4	0	10	0.002119	0.002119
FG	0	7.9	10	0.00025	0.0001	4	0	10	0.002119	0.002119
GH	0.82	7.9	10	0.00025	0.0001	4	0	10	0.002119	0.002119
HI	0	7.9	10	0.00025	0.0001	4	0	10	0.002119	0.002119
IJ	0	7.9	10	0.00025	0.0001	4	0	10	0.002119	0.002119
JK	0	7.9	10	0.00025	0.0001	4	0	10	0.002119	0.002119
KL	0	7.9	10	0.00025	0.0001	4	0	10	0.002119	0.002119
LM	0	7.9	10	0.00025	0.0001	4	0	10	0.002119	0.002119
MN	0	7.9	10	0.00025	0.0001	4	0	10	0.002119	0.002119
NO	0	7.9	10	0.00025	0.0001	4	0	10	0.002119	0.002119
OP	0	7.9	10	0.00025	0.0001	4	0	10	0.002119	0.002119
PQ	0	7.9	10	0.00025	0.0001	4	0	10	0.002119	0.002119

Table 4.10 EXWAT Output - Weyerhaeuser Saskatchewan Ltd., Prince Albert, Saskatchewan

Segment	Conc ug/l	ConcS ug/l	ConcWa ug/l	ConcSM ug/l	ConcPW ug/l	ConcSS ug/l	ConcBM ug/l	SorbFrac	Elim 1/d
AB	0	0	0	0	0	0	0	3.0E-07	0.0070
BC	0	0	0	0	0	0	0	3.0E-07	0.0070
CD	0	0	0	0	0	0	0	3.0E-07	0.0070
DE	0	0	0	0	0	0	0	3.0E-07	0.0070
EF	0	0	0	0	0	0	0	3.0E-07	0.0070
FG	0	0	0	0	0	0	0	3.0E-07	0.0070
GH	0.59	0.18	0.59	0.00	0.29360	0.000	0.713	2.8E-07	0.0070
HI	0.59	0.18	0.59	0.00	0.29350	0.000	0.712	2.8E-07	0.0070
IJ	0.59	0.18	0.59	0.00	0.29320	0.000	0.712	2.8E-07	0.0070
JK	0.59	0.18	0.59	0.00	0.29270	0.000	0.711	2.8E-07	0.0070
KL	0.59	0.18	0.59	0.00	0.29230	0.000	0.709	2.8E-07	0.0070
LM	0.59	0.18	0.59	0.00	0.29190	0.000	0.708	2.8E-07	0.0070
MN	0.59	0.18	0.59	0.00	0.29150	0.000	0.708	2.8E-07	0.0070
NO	0.59	0.18	0.59	0.00	0.29120	0.000	0.707	2.8E-07	0.0070
OP	0.59	0.17	0.59	0.00	0.29080	0.000	0.706	2.8E-07	0.0070
PQ	0.59	0.17	0.59	0.00	0.29050	0.000	0.705	2.8E-07	0.0070

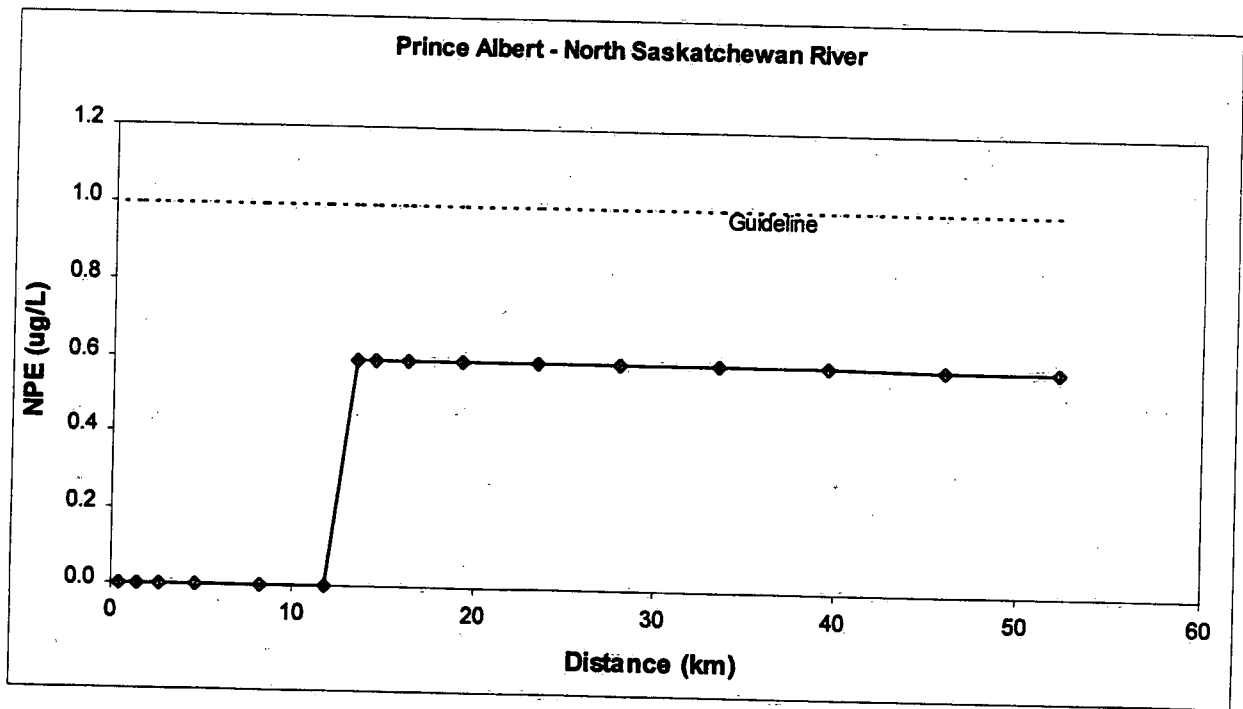


Figure 4-12 NPE Concentration – North Saskatchewan River, Prince Albert, Saskatchewan

4.8 Papier Masson Limitee, Masson-Angers, Quebec

4.8.1 Site Description

Papier Masson Limitee discharges to the Riviere du Lievre near Masson-Angers, Quebec as shown in Figure 4-13. The River empties into the Riviere des Outaouais approximately 1.5 km downstream. For modelling purposes, the river system is broken up into a number of segments.

4.8.1.1 Mill Loadings

Mill loadings were obtained from Environment Canada's National Pollutant Release Inventory (NPRI) for 1999 for nonylphenol polyethylene glycol ether. Total release for 1999 was 1.23 kg/d (0.45 tonnes) in 0.445 m³/s (14,029,236 m³). Mill pH was approximately 7.3 in 1996-1998 and suspended sediment was 38.6 mg/L in 1999 (ESG International 2000). These values were used in the model. Mill loadings are inserted at segment CD.

4.8.1.2 Stream Flow

The 7Q20 flow rates for the rivers in this system were calculated using the Low Flow Frequency Analysis Package Version 2.0 (Environment Canada, 1993) and data available from Environment Canada's database HYDAT as follows:

- Riviere du Lievre au Barrage de Masson 7Q20 = 81 m³/s (data available for 1957-1987)
- Ottawa River upstream of the confluence with Riviere du Lievre 7Q20 = 302 m³/s from gauge Ottawa River at Britannia for 1961-1999

The Cumulative flow rate (VolFlo) for the river system is shown in Table 4.11.

4.8.1.3 Stream Parameters

Site specific stream model inputs include the following (refer to Table 4.11 for values):

- Segment length and width based on Figure 4-13
- Segment depth from 1996 values (ESG International 2000)
- Suspended sediment was unknown for Riviere du Lievre and set to 1 mg/L; Ottawa River at Cumberland gauge TSS = 37 mg/l for 1977-1979 and was used for the Ottawa River
- pH was unknown at set to 7.2 as used in section 4.4.1.3 for Gatineau
- Organic carbon content = 0.04 (EXWAT default)
- Upstream NPE concentrations were unknown and set to zero

4.8.2 EXWAT Model Results

Inputs to the EXWAT model are presented in Table 4.11. The Mill loading is applied to segment CD. EXWAT default values for DSed, Por, Dens, Depos, Perm, BurSed, Wind, Volat, SedRate, KD, and KDS were used (refer to Table 2.2 for symbol explanations).

Results from the EXWAT model are presented in Table 4.12 and Figure 4-14. The NPE river concentration (Conc) is a maximum of 0.18 ug/L in reach CD, which is the reach where the mill discharges. This value of NPE is below the guideline of 1 ug/L. NPE concentration decreases downstream at the confluence with the Ottawa River due to dilution effects. The sediment concentration maximum is 4.0 ug/L or 3.1 ug/kg based on the default sediment dry density (Dens) of 1.309 g/cm³. This sediment concentration is much less than the NPE guideline of 1,400 ug/kg.

Figure 4-13 Site Location - Papier Masson Limitee, Masson-Angers, Quebec

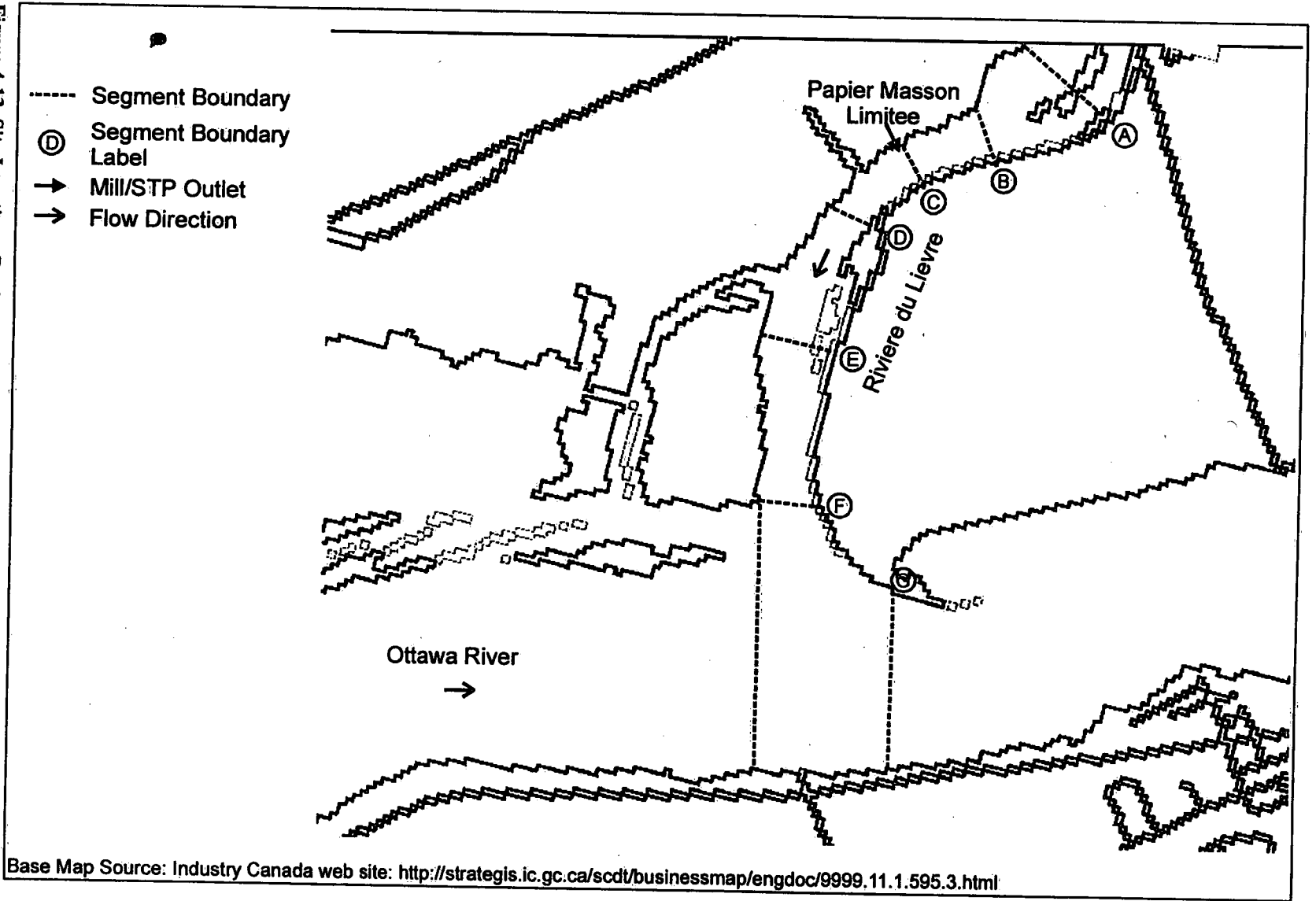


Table 4.11 EXWAT Input - Papier Masson Limitee, Masson-Angers, Quebec

Segment	Length km	Width m	Depth m	DSed m	VolFlo m ³ /s	Susp g/m ³	Por	OrgC	OrgCS	Dens g/cm ³
AB	0.69	250	3.6	0.05	81.0	1.0	0.6	0.04	0.04	1.309
BC	1.29	140	3.2	0.05	81.0	1.0	0.6	0.04	0.04	1.309
CD	1.47	140	3.5	0.05	81.5	1.2	0.6	0.04	0.04	1.309
DE	1.98	160	3.3	0.05	81.5	1.2	0.6	0.04	0.04	1.309
EF	2.56	160	6.1	0.05	81.5	1.2	0.6	0.04	0.04	1.309
FG	3.25	650	1.7	0.05	383.5	29.0	0.6	0.04	0.04	1.309

Segment	Input kg/d	pH	Depos m/d	Perm m/d	BurSed m/d	Wind m/s	Volat 1/d	SedRate mm/a	KD cm ³ H ₂ O/g	KDS cm ³ H ₂ O/g
AB	0	7.2	10	0.00025	0.0001	4	0	10	520	520
BC	0	7.2	10	0.00025	0.0001	4	0	10	520	520
CD	1.23	7.2	10	0.00025	0.0001	4	0	10	520	520
DE	0	7.2	10	0.00025	0.0001	4	0	10	520	520
EF	0	7.2	10	0.00025	0.0001	4	0	10	520	520
FG	0	7.2	10	0.00025	0.0001	4	0	10	520	520

Table 4.12 EXWAT Output - Papier Masson Limitee, Masson-Angers, Quebec

Segment	Conc ug/l	ConcS ug/l	ConcWa ug/l	ConcSM ug/l	ConcPW ug/l	ConcSS ug/l	ConcBM ug/l	SorbFrac	Elim 1/d
AB	0	0	0	0	0	0	0	0.001	0.009
BC	0	0	0	0	0	0	0	0.001	0.009
CD	0.18	4.0	0.17	4.0	0.01469	0.0001	0.210	0.001	0.009
DE	0.18	4.0	0.17	4.0	0.01468	0.0001	0.210	0.001	0.009
EF	0.18	4.0	0.17	4.0	0.01475	0.0001	0.210	0.001	0.008
FG	0.037	0.2	0.04	0.2	0.00059	0.0006	0.044	0.015	0.011

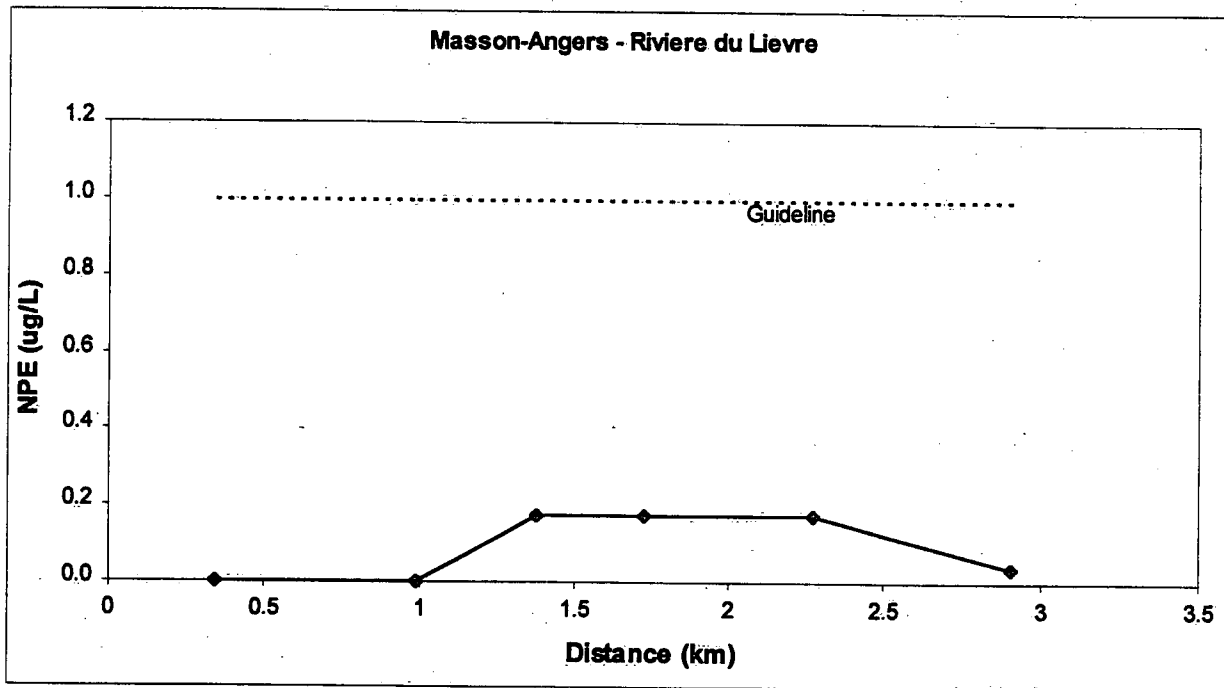


Figure 4-14 NPE Concentration – Riviere du Lievre and Riviere des Outaouais, Masson-Angers, Quebec

4.9 Tembec Inc., Temiscaming, Quebec

4.9.1 Site Description

Tembec Inc. discharges to the Ottawa River near Temiscaming, Quebec as shown in Figure 4-15. A STP also discharges on the opposite side of the River from the Mill. There was no data available for the STP so it was not included in the model. For modelling purposes, the river system is broken up into a number of segments.

4.9.1.1 Mill Loadings

Mill loadings were obtained from Environment Canada's National Pollutant Release Inventory (NPRI) for 1999 for nonylphenol polyethylene glycol ether. Total release for 1999 was 10.16 kg/d (3.71 tonnes) in 2.00 m³/s (63,118,411 m³). Mill pH was approximately 7.2 (August-November 1999 average, Table 1 in GDG Conseil 2000) and suspended sediment was 101 mg/L (1999 average, Maddison per. comm.). These values were used in the model. Mill loadings are inserted at segment DE.

4.9.1.2 Stream Flow

The 7Q20 flow rates for the river is 164 m³/s calculated using the Low Flow Frequency Analysis Package Version 2.0 (Environment Canada, 1993) and data available from Environment Canada's database HYDAT for gauge Ottawa River at Timiskaming for 1911-1951.

4.9.1.3 Stream Parameters

Site specific stream model inputs include the following (refer to Table 4.13 for values):

- Segment length, width and depth obtained from Figure 3 in GDG Conseil (2000)
- Suspended sediment was unknown and set to 10 mg/L (Ottawa River at Britannia gauge TSS = 13 mg/l)
- pH = 7.58 (GDG Conseil 2000)
- Organic carbon content = 0.496 (Maddison per. comm.)
- Upstream NPE concentrations were unknown and set to zero

4.9.2 EXWAT Model Results

Inputs to the EXWAT model are presented in Table 4.13. The Mill loading is applied to segment CD. EXWAT default values for DSed, Por, Dens, Depos, Perm, BurSed, Wind, Volat, SedRate, KD, and KDS were used (refer to Table 2.2 for symbol explanations).

Results from the EXWAT model are presented in Table 4.14 and Figure 4-16. The NPE river concentration (Conc) is a maximum of 0.71 ug/L in reach DE, which is the reach where the mill discharges. This value of NPE is below the guideline of 1 ug/L. The sediment concentration maximum is 71.7 ug/L or 55 ug/kg based on the default sediment dry density (Dens) of 1.309 g/cm³. This sediment concentration is much less than the NPE guideline of 1,400 ug/kg.

Figure 4-15 Site Location - Tembec Inc., Temiscaming, Quebec

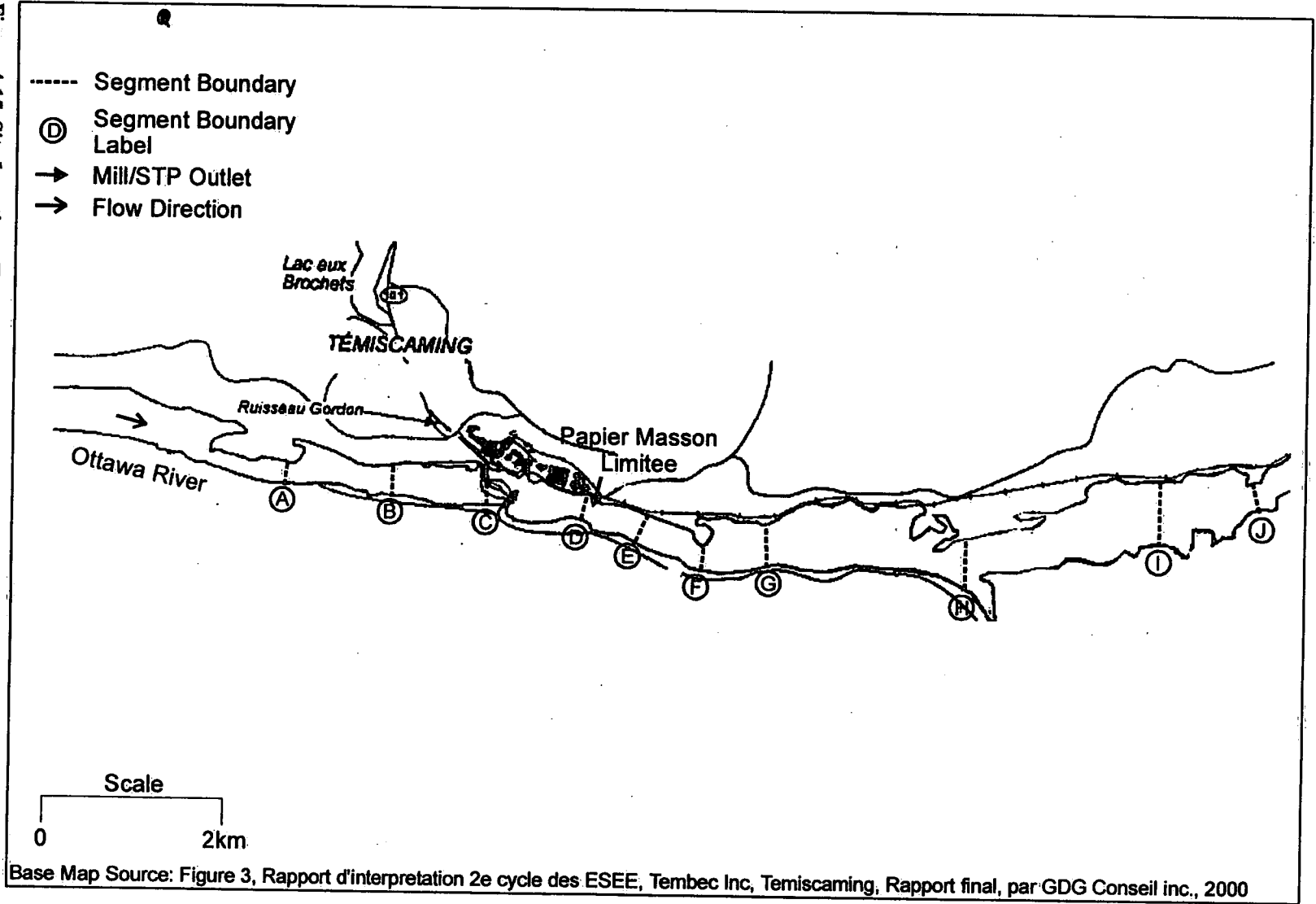


Table 4.13 EXWAT Input - Tembec Inc., Temiscaming, Quebec

Segment	Length km	Width m	Depth m	DSed m	VolFlo m3/s	Susp g/m3	Por 0..1	OrgC	OrgCS	Dens g/cm3
AB	1.20	310	15	0.05	164	10.0	0.6	0.496	0.496	1.309
BC	2.29	320	10	0.05	164	10.0	0.6	0.496	0.496	1.309
CD	3.39	320	10	0.05	164	10.0	0.6	0.496	0.496	1.309
DE	3.99	330	10	0.05	166	11.1	0.6	0.496	0.496	1.309
EF	4.85	375	10	0.05	166	11.1	0.6	0.496	0.496	1.309
FG	5.54	540	5	0.05	166	11.1	0.6	0.496	0.496	1.309
GH	7.82	730	10	0.05	166	11.1	0.6	0.496	0.496	1.309
HI	10.10	730	10	0.05	166	11.1	0.6	0.496	0.496	1.309
IJ	11.12	800	10	0.05	166	11.1	0.6	0.496	0.496	1.309

Segment	Input kg/d	pH	Depos m/d	Perm m/d	BurSed m/d	Wind m/s	Volat 1/d	SedRate mm/a	KD cm3 H2O/g	KDS cm3 H2O/g
AB	0	7.58	10	0.00025	0.0001	4	0	10	6448	6448
BC	0	7.58	10	0.00025	0.0001	4	0	10	6448	6448
CD	0	7.58	10	0.00025	0.0001	4	0	10	6448	6448
DE	10.16	7.58	10	0.00025	0.0001	4	0	10	6448	6448
EF	0	7.58	10	0.00025	0.0001	4	0	10	6448	6448
FG	0	7.58	10	0.00025	0.0001	4	0	10	6448	6448
GH	0	7.58	10	0.00025	0.0001	4	0	10	6448	6448
HI	0	7.58	10	0.00025	0.0001	4	0	10	6448	6448
IJ	0	7.58	10	0.00025	0.0001	4	0	10	6448	6448

Table 4.14 EXWAT Output - Tembec Inc., Temiscaming, Quebec

Segment	Conc ug/l	ConcS ug/l	ConcWa ug/l	ConcSM ug/l	ConcPW ug/l	ConcSS ug/l	ConcBM ug/l	SorbFrac	Elim 1/d
AB	0	0	0	0	0	0	0	0.061	0.0128
BC	0	0	0	0	0	0	0	0.061	0.0157
CD	0	0	0	0	0	0	0	0.061	0.0157
DE	0.71	71.7	0.660	72	0.0212	0.0473	0.7938	0.067	0.0156
EF	0.71	71.5	0.659	71.5	0.0212	0.0472	0.7924	0.067	0.0156
FG	0.71	71.3	0.659	71.3	0.0211	0.0471	0.7915	0.067	0.0243
GH	0.70	70.8	0.653	70.81	0.0210	0.0467	0.7845	0.067	0.0156
HI	0.69	70.2	0.647	70.18	0.0208	0.0463	0.7776	0.067	0.0156
IJ	0.69	69.9	0.644	69.88	0.0207	0.0461	0.7742	0.067	0.0156

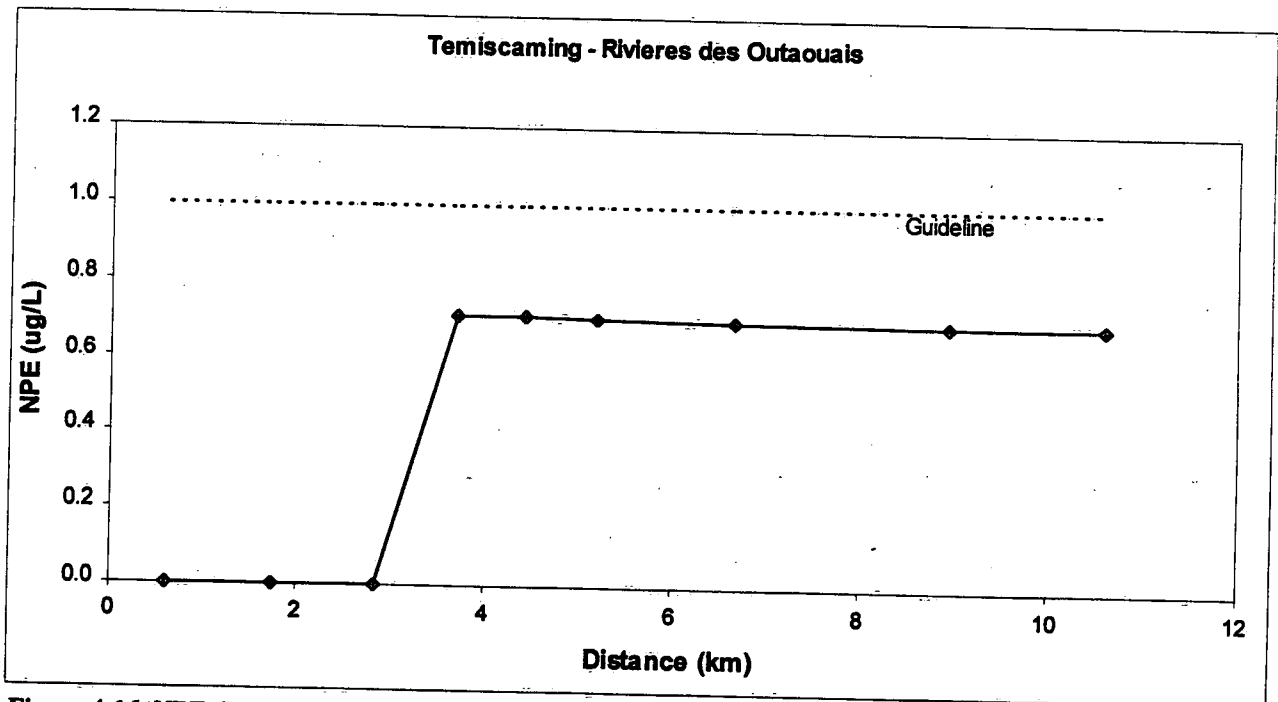


Figure 4-16 NPE Concentration – Ottawa River, Temiscaming, Quebec

4.10 Crown Packaging Ltd., Burnaby, British Columbia.

The Burnaby site is subject to tidal effects, which cannot be accounted for in the EXWAT model. Therefore, analysis of the Burnaby site was not conducted in this Study.

5 SENSITIVITY ANALYSIS

Certain parameters in the EXWAT model are estimates and subject to variation. Some of these parameters can affect the results of the model. The following sensitivity analysis can be used to determine the uncertainty of results and help prioritize future data gathering.

The Prince Albert site was used for sensitivity analysis since it is not a complex river system, there is only NPE loading from the mill, and the calculated NPE concentration was close to the guideline. Parameters were adjusted plus and minus 20%. The resulting concentrations were then compared to the original calculated values (base case). The sensitivity analysis results are presented in Table 5.1

Table 5.1 Sensitivity Analysis Results - Prince Albert Site

Parameter	Conc		ConcS		Notes
	Parameter - 20%	Parameter +20%	Parameter - 20%	Parameter +20%	
OrgC	0.0%	0.0%	0.2%	0.2%	
Rsed	0.0%	0.0%	0.1%	-0.1%	
Rwater	0.2%	-0.2%	16.4%	-12.4%	
BCF	0.0%	0.0%	0.0%	0.0%	ConcBM +/-20%
SS	0.0%	0.0%	0.2%	-0.2%	ConcSS+18%,-20%
pH	0.0%	0.0%	0.0%	0.0%	
NPE Load	-20%	20%	-20%	20%	
Koc	0.0%	0.0%	0.2%	-0.2%	ConcSM & ConcSS +/-20%

The results presented in Table 5.1 show that the total water concentration of NPE (Conc) is mainly sensitive to loading. Concentration in the sediment (ConcS) is sensitive mainly to the overall degradation rate in water (RWater) and loading. Other parameters including BCF, SS, and Koc had significant affects on other concentrations such as in biomass, suspended sediment, and sediment matrix but did not significantly affect the water and sediment concentrations.

6 CONCLUSIONS AND RECOMMENDATIONS

The EXWAT model was used to estimate NPE concentrations at all of the sites, except for Burnaby. NPE was modelled under river 7Q20 flow conditions and used the 1999 average mill loadings for NPE, flow etc.. The Burnaby site could not be modelled due to tidal affects. In addition, the Thunder Bay site was also modelled with the Kaministiquia River Water Quality Model. A summary of the maximum computed concentrations is presented in Table 6.1.

Table 6.1 Summary of Computed NPE Concentrations

Site	NPE water ¹ (ug/L)	NPE Sediment ² (ug/kg)	Mill NPE Load (kg/d)	River 7Q20 Flow (m ³ /s)
Thunder Bay (EXWAT)	1.77	0.41	3.07	20.
Thunder Bay (Kam.)	1.2 to 2.0	-	3.07	20.
Gatineau	0.13	0.78	0.67	60.
Grande Prairie	1.5	26	0.929	6.41
Dryden	9.8	2.3	1.797	0.789
Prince Albert	0.59	0.13	0.82	14.9
Masson-Angers	0.18	3.1	1.23	81.
Temiscaming	0.71	55	10.16	164.
Burnaby	-	-	-	-

¹ Guideline for NPE in water (freshwater) is 1.0 ug/L

² Guideline for NPE in sediment (freshwater) is 1,400 ug/kg

As shown in Table 6.1, of the seven (7) sites only Thunder Bay, Grande Prairie and Dryden had river NPE concentrations that exceed the guideline of 1 ug/L. The Dryden site NPE is approximately 1,000% above the guideline where as Thunder Bay and Grande Prairie are only 50% to 100% above the guideline. The Prince Albert and Temiscaming sites had NPE concentrations 30 to 40% below the guideline while Gatineau and Masson-Angers sites were approximately 80% below the guideline.

Included in Table 6.1 are the mill loadings for NPE used in the models (1999 averages) and the river 7Q20 flow rates at the site of the mills. Based on a dilution analysis, the Dryden site's high NPE concentration can be explained based on the relatively low river 7Q20 flow rate. None of the sites had sediment NPE concentrations above or close to the guideline of 1,400 ug/kg.

The sensitivity analysis of section 5 found that mill loading is the main parameter affecting computed NPE concentrations. The sediment concentration of NPE was also found to be sensitive to the degradation rate in water. However, the sediment concentrations were far below the guideline.

During this Study, possible data and model shortcomings were revealed. Future work could involve the following recommendations:

- NPE concentrations are very sensitive to loading. River upstream/background concentrations were not available and were set to zero in this Study. This data should be acquired for future modelling.
- Mill loadings used in the models were the averages for 1999. If these loadings fluctuate then using the average values in the models can be misleading and an analysis using varying loadings should be done.
- At several sites there were neighbouring sewage treatment plants (STP) discharging to the same river system. It was not know if there are NPE loadings from these STP's, which could significantly affect river

NPE concentrations. However, according to MaGuire (1999) in STP's the nonylphenol ethoxylates can be biologically degraded and degradation products, including nonylphenol, are more persistent than the parent compounds and can be found in the receiving waters. Also, the flow, TSS and pH from the STP's can affect the river NPE. Besides NPE loadings, the following data were missing for the STP's:

- Gatineau: no STP data
 - Grande Prairie: no STP pH data
 - Dryden: no STP data (flow rate used was very approximate)
 - Temiscaming: no STP data
- Computed NPE concentrations were not very sensitive to organic carbon content but these values were required in the EXWAT model. The Gatineau, Grande Prairie, and Masson-Angers sites did not have observed organic content values. Also, the available observations (Maddison per. comm.) should be reconfirmed since the Temiscaming value was found to be 10^6 times higher than other sites.
 - Previous studies found that plumes from the mills outlets can exist under certain conditions. The EXWAT model assumes complete mixing (no plume), which could produce lower concentrations than would actually occur in a plume. Additional data including detailed river geometry would be required to run more detailed 2D plume models.

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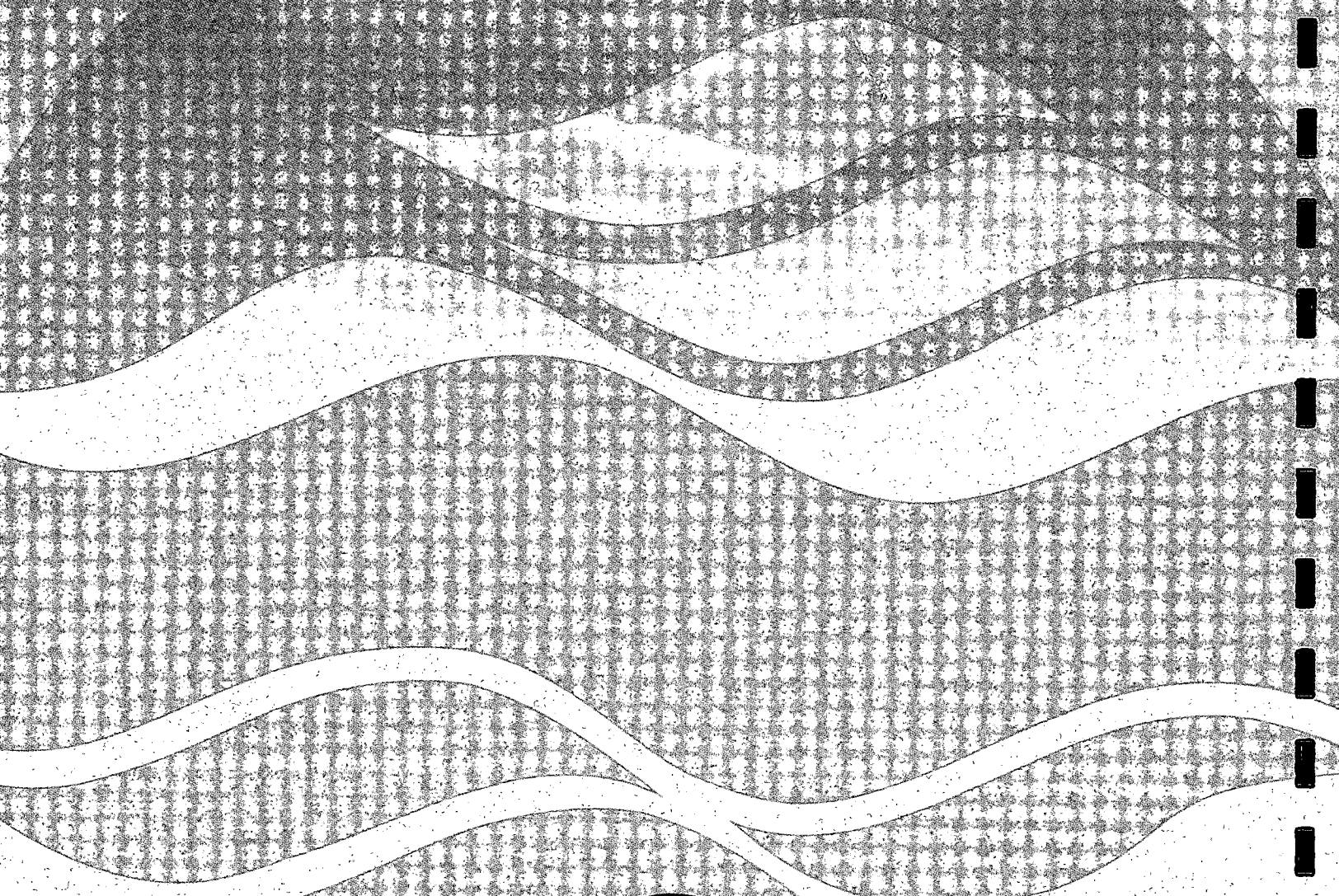


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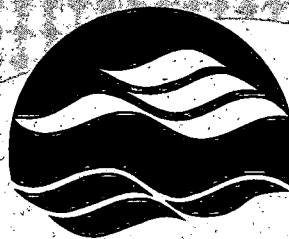


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