

# Comparison between Water Quality Models for Toxics

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**Abstract:** Water quality models have been applied increasingly to represent the interaction between pollutants and aquatic environment due to transport and transformation phenomena: These models can be used to better understand pollution phenomena and to choose between different, alternative management strategies. The paper compares the results of two different water quality models, which have been applied to a water column-sediments system of a lake with an inflow contaminant loading. In the former, the system is idealized as well-mixed surface-water underlain by a well-mixed active sediment layer, where the resulting concentrations are attained by direct analytical solutions at the steady-state and in time-variable conditions. The latter is TOXI5 model, which is part of WASP5 modeling framework developed by USEPA. The models were applied to an idealized case in order to predict steady-state and time-variable concentrations in the water-column and in the active sediment layer for 4 pesticides. Comparison between the results obtained through the two models shows a good agreement both for the steady-state concentrations and for the time-variable ones. The transients from no-concentrations to the steady-state and from steady-state to negligible concentrations were performed; the simulations have pointed out the very long time for attaining both steady-state conditions and the system recovery in the lake and in the active sediments layer especially.

**Keywords:** Environmental hydraulics, water quality modeling, lakes, toxics

## 1. INTRODUCTION

Toxics pollution of surface waters is a complex and relevant problem requiring a comprehensive control strategy; in fact, potentially toxic substances have been largely produced since about 50 years and may be transferred to humans with subsequent short-term or long-term impact on public health [Thomann and Mueller, 1987]. Toxics effects are also related to their concentrations, by means of threshold values for acute or chronic toxicity. Thus, control process should take into account the needs for ecosystem and human health protection, the desirable water use or uses (e.g. recreation, water supply, agriculture, etc.) and the related water quality standards, the toxic potential of the compound being present in the discharged effluent and, finally, the resulting toxics concentration in the water body. These factors should lead to permit limits development, which should be considered as the final step of the whole process. Thus, control process, which can be termed water quality-based, is forwarded from water quality standard to permit limits. In USA, water quality standards are achieved and maintained through a integrated strategy, which uses for the protection of aquatic

life three control approaches. They are the chemical-specific approach, the whole effluent toxicity approach and the biological criteria/bioassessment and biosurvey approach; furthermore, for the protection of human health, chemical-specific assessment and control techniques are used [USEPA, 1991]. The first approach uses a specific chemical effluent limits, which are developed from laboratory-derived, biologically-based numeric water quality criteria.

The whole-effluent approach involves the use of toxicity tests and water quality criteria to assess and control the aggregate toxicity of effluents, while, finally, the biological criteria are numerical values or narrative statements that describe the reference biological integrity of aquatic community inhabiting waters of a given designated aquatic life use. Each approach has its advantage and shortcomings, so they should be integrated.

A water quality standard defines water quality goals of a water body, of portion thereof, by designating the use or uses to be made of the water, by setting criteria necessary to protect the uses and by establishing antidegradation policies and implementation procedures that serve to maintain and protect water quality; these criteria are specifications of water quality designed to

ensure protection of the assigned uses. Notably, each criteria has three components, magnitudo, i.e. numeric value of toxic concentration which is allowable, duration, that is the period of time (averaging period) over which the in-stream concentration is averaged for comparison with criteria concentrations, and frequency, i.e. how often the criteria can be exceeded. Then, once the applicable designated uses and water quality criteria for a water body are determined, the effluent must be characterized and the permitting authority must determine the need for permit limits to control the discharge. If the discharge causes or has the reasonable potential to cause or contributes to the excursion of water quality criteria, these authority must develop permit limits to control the discharge. Whereas a water quality problem has been identified, a waste load allocation study (WLA) based on total maximum daily load (TMDL) must be performed. A TMDL is the sum of the individual WLAs for point sources and load allocations (LAs) for diffuse sources of pollution and natural background sources, tributaries or adjacent segments. WLAs represent that portion of a TMDL that is established to limit the amount of pollutants from existing and future point sources so that the surface water quality is protected at all flow conditions. The TMDL process uses water quality models, to predict water quality conditions and pollutant concentrations. Finally, limits on wastewater pollutant loads are set and non-point source allocations will be established so that predicted receiving water concentrations do not exceed water quality criteria. Thus, in toxic control process to obtain a reliable prediction of concentration resulting from toxics discharge in surface waters is a remarkable goal.

The paper compares the results of two different water quality models, which have been applied to a water column-sediments system of a lake with an inflow contaminant loading; the models were applied to an idealized case to predict steady-state and time-variable concentrations in the water-column and in the active sediment layer for 4 pesticides.

## 2. MODELS DESCRIPTION

### 2.1 Introduction

The selected models are quite different; in the former, the system is idealized as well-mixed surface-water underlain by a well-mixed active sediment layer, where the resulting concentrations are attained by direct analytical solutions both at

the steady-state and in time-variable conditions, while the latter is TOX15 model, which is part of WASP5 modeling framework developed by USEPA [USEPA, 1992].

For both models, in the system there are an inflow rate  $Q_{in}$  ( $L^3 T^{-1}$ ) with a contaminant concentration  $c_{in}$  ( $M L^{-3}$ ) and an outflow rate  $Q_{out}$  ( $L^3 T^{-1}$ ); the contaminant is partitioned into particulate and dissolved fraction. The former fraction is subjected only to settling, resuspension and burial with velocities, respectively, of  $v_s$ ,  $v_r$  and  $v_b$  ( $L T^{-1}$ ), while the latter one could volatilize across the air-water interface, with net transfer velocity  $v_{vol}$  ( $L T^{-1}$ ), and diffuse between water column and sediments layer, with diffusive mixing velocity  $v_{diff}$  ( $L T^{-1}$ ) (Fig.1).

### 2.2 Analytical model

In the analytical model, if  $V_{lake}$  and  $V_{sed}$  are, respectively, water column and sediments volumes ( $L^3$ ) and  $A$  is the water column and active sediments area ( $L^2$ ), mass balances for contaminant in the water column and in the active sediment layer can be written as [Chapra, 1997; Gualtieri, 1997; Gualtieri, 1998]:

$$V_{lake} \frac{dc_{lake}}{dt} = Q_{in} c_{in} - Q_{out} c_{lake} - v_s A F_{p-lake} c_{lake} - v_{vol} A F_{d-lake} c_{lake} + v_r A F_{p-sed} c_{sed} + v_{diff} A (F_{d-sed} c_{sed} - F_{d-lake} c_{lake}) \quad (1a)$$

$$V_{sed} \frac{dc_{sed}}{dt} = v_s A F_{p-lake} c_{lake} - v_r A F_{p-sed} c_{sed} - v_b A F_{p-sed} c_{sed} + v_{diff} A (F_{d-lake} c_{lake} - F_{d-sed} c_{sed}) \quad (1b)$$

where  $F_{d-lake}$ ,  $F_{p-lake}$ ,  $F_{d-sed}$  and  $F_{p-sed}$  are, respectively, dissolved and particulate fractions in the lake and in the sediments and  $c_{lake}$  and  $c_{sed}$  are, respectively, water column and sediments contaminant concentrations ( $M L^{-3}$ ).

Notably, the active sediments layer represents the bed volume which is involved in transport exchange phenomena with water column, i.e. settling and resuspension; thus, this layer could be considered having a constant volume. Furthermore, the water column volume is assumed to be constant too. If diffusion mechanism could be considered quantitatively negligible and, thus, could be skipped, (1a) and (1b) yield:

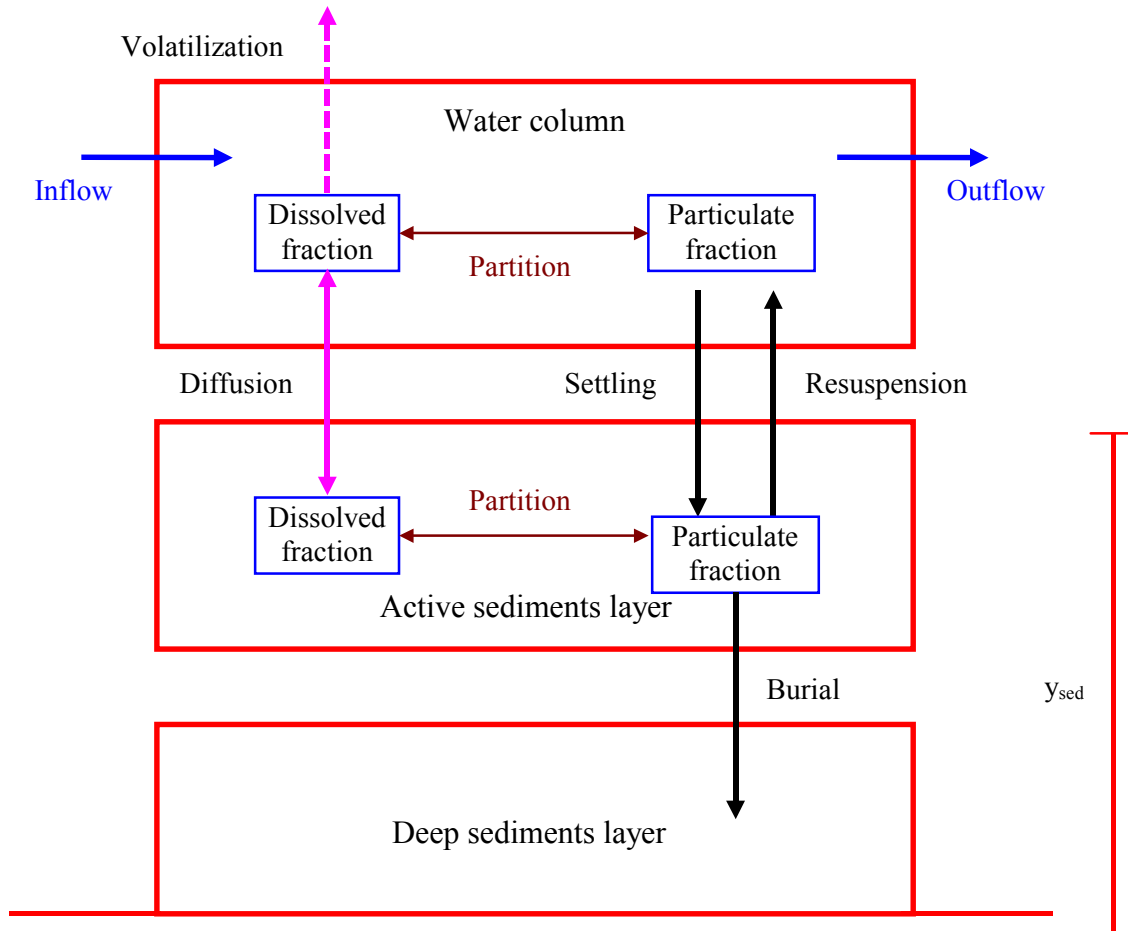


Fig.1 - Water column-sediments system in a lake

$$V_{\text{lake}} \frac{dc_{\text{lake}}}{dt} = Q_{\text{in}} c_{\text{in}} - Q_{\text{out}} c_{\text{lake}} - v_s A F_{\text{p-lake}} c_{\text{lake}} - v_{\text{vol}} A F_{\text{d-lake}} c_{\text{lake}} + v_r A F_{\text{p-sed}} c_{\text{sed}} \quad (2a)$$

$$V_{\text{sed}} \frac{dc_{\text{sed}}}{dt} = v_s A F_{\text{p-lake}} c_{\text{lake}} - v_r A F_{\text{p-sed}} c_{\text{sed}} - v_b A F_{\text{p-sed}} c_{\text{sed}} \quad (2b)$$

At steady-state, dividing for A, (2a) and (2b) yield:

$$v_f c_{\text{in}} - v_f c_{\text{lake}} - v_{\text{vol}} F_{\text{d-lake}} c_{\text{lake}} - v_s F_{\text{p-lake}} c_{\text{lake}} + v_r F_{\text{p-sed}} c_{\text{sed}} = 0 \quad (3a)$$

$$v_s F_{\text{p-lake}} c_{\text{lake}} - v_r F_{\text{p-sed}} c_{\text{sed}} - v_b F_{\text{p-sed}} c_{\text{sed}} = 0 \quad (3b)$$

where, for steady-state condition,  $Q_{\text{in}}=Q_{\text{out}}=Q$  and  $v_f=Q/A$ , that is called filling rate [Gualtieri and Pulci Doria, 1998a, 1998b]. Both steady-state and dynamics conditions can be analytically solved [Gualtieri, 1997, 1998]. Also, mass balance equations for dynamic conditions is often

numerically solved.

### 2.3 WASP 5 model

TOX15 is the part of WASP5 modeling framework devoted to simulate transport and fate of toxic contaminants [USEPA, 1992]. TOX15 has been recently applied to pesticides pollution real scenario [Gualtieri, 1999b; Gualtieri and Pulci Doria, 2000, Gualtieri, 2001b].

WASP5 traces each water quality constituent, such as a toxic, from the point of spatial and temporal input to its final point of export, conserving mass in space and time. Thus, WASP5 solves a finite difference approximation of mass balance equation for each constituent in a model network that represents the main characteristics of the real water body. This is divided into a set of control volumes, where mass balance is performed. These volumes or *segments* can be both water column or bed sediment ones. Sediment compaction is considered and diffusion is modeled following Fick's law. Also, wind-driven volatilization can be

modeled using different approaches. WASP5 uses a forward-time/backward-space difference (FTBS) approximations with a second order Runge-Kutta solving algorithm; an advection factor could be specified to modify the finite approximation of  $\partial c/\partial x$  used in the advection term [USEPA, 1992]. The system hydrodynamics is simulated by a separate program DYNHYD5 that is based on both momentum and volume conservation equations.

### 3. COMPARISON OF MODELS RESULTS

The two models has been applied to the same hypothetical scenario, which main characteristics are outlined in Table 1. Resuspension and burial velocities were obtained through a mass balance of solids incoming the system, whereas settling rate corresponds to a literature value [O'Connor, 1988a, 1988b; Gualtieri, 1998]. Notably, burial rate  $v_b$  can be estimated using radioactive tracers [Gualtieri, 1999a]. Also, wind-driven resuspension can be predicted using turbulence-based models.

**Table 1.** Characteristics of water column-active sediments layer.

Parameter	Units	Water column	Active sediments
Volume	m <sup>3</sup>	864×10 <sup>5</sup>	576×10 <sup>3</sup>
Area	m <sup>2</sup>	1.44×10 <sup>6</sup>	1.44×10 <sup>6</sup>
Q <sub>in</sub>	m <sup>3</sup> /year	20×10 <sup>6</sup>	----
Q <sub>out</sub>	m <sup>3</sup> /year	20×10 <sup>6</sup>	----
C <sub>in</sub>	g/m <sup>3</sup>	0.10	----
M	g/m <sup>3</sup>	5.00	----
V <sub>s</sub>	m/year	365.0	----
V <sub>r</sub>	m/year	----	0.0011
V <sub>b</sub>	m/year	----	0.0038

Moreover, models application required some additional environmental parameters. They have been assigned using literature values, that are listed in Table 2. Particularly, wind speed  $W_{10}$ , that is measured 10 m above the water surface, affects volatilization rate since in standing waters mass-transfer depends also on wind stress at air-water interface, as shown by Gualtieri et al. [in press]. Notably, a proper approach to mass-transfer at air-water interface can be obtained using dimensional analysis, as shown by Gualtieri et al. [2002].

**Table 2.** Environmental parameters for the system.

Parameters	Units	Water column
Temperature	°C	10
$W_{10}$	m/s	4.47
Porosity $\phi_{sed}$		0.85

Density $\rho_{sed}$	g/m <sup>3</sup>	2.5×10 <sup>6</sup>
Organic fraction $f_{oc}$		0.05

Also, sediment porosity and density are relevant properties for the evaluation of dissolved and particulate fractions within the bed sediments.

For the simulation, 4 pesticides were considered: TCDD, DDD, Endrin and Toxaphene. They are contaminants of environmental concern and they are inserted in lists of hazardous substances. They exhibits different properties that affect their final fate in the aquatic environment as it is shown in Table 3.

TCDD and DDD are strong sorbers because of their high value of  $K_{ow}$ ; thus, their tend to be associated with solid matter both in the water column and , especially, in the sediments (Table 4). On the contrary, Endrin and Toxaphene sorb weakly reflecting their low  $K_{ow}$  values. Thus, they are completely in dissolved form within the water column. Moreover, TCDD is not greatly affected by volatilization because it exhibits a relevant particulate fraction; however, its volatilization rate is high, whereas DDD is soluble. Also, Toxaphene is highly volatile reflecting is high  $H_e$  value, whereas Endrin has low  $v_{vol}$ .

Finally, diffusion rates are similar and very low.

**Table 3.** Contaminants characteristics.

Parameter	Units	TCDD	DDD
Molecular weight M	G/mole	322	320
Henry constant $H_e$	Atm m <sup>3</sup> /mole	0.002089	2.187×10 <sup>-8</sup>
Partition coefficient $K_{ow}$	(mg/m <sup>3</sup> ) <sub>ottanolo</sub> / (mg/m <sup>3</sup> ) <sub>acqua</sub>	6.918×10 <sup>6</sup>	1.318×10 <sup>6</sup>
Partition coefficient $K_d$	g/m <sup>3</sup>	0.213430	0.040668
Transfer coefficient $K_l$	m/year	177.36	177.64
Transfer coefficient $K_g$	m/year	133280	133487
Diffusion rate $v_{diff}$	m/year	1.255	1.260
Volatilization rate $v_{vol}$	m/year	174.779	0.126
Parameter	Units	Endrin	Toxaphene
Molecular weight M	g/mole	381	430
Henry constant $H_e$	atm m <sup>3</sup> /mole	1.995×10 <sup>-9</sup>	0.20893
Partition coefficient $K_{ow}$	(mg/m <sup>3</sup> ) <sub>ottanolo</sub> / (mg/m <sup>3</sup> ) <sub>acqua</sub>	1412.54	1995.262
Partition coefficient $K_d$	g/m <sup>3</sup>	0.000044	0.000062
Transfer coefficient $K_l$	m/year	170.06	164.99
Transfer coefficient $K_g$	m/year	127790	123983
Diffusion rate $v_{diff}$	m/year	1.122	1.035
Volatilization rate $v_{vol}$	m/year	0.011	164.967

As a result, their removal mechanism from water column are very different. TCDD level in the water depends both on water-sediment interactions, i.e. settling/resuspension fluxes, and volatilization, whereas Endrin concentration is the higher low because both those processes are very

low. Thus, Endrin is removed only by advection with the outcoming flowrate.

Furthermore, Toxaphene is removed mainly by volatilization, whereas DDD level depends only on exchange process with the bed sediments. Finally, TCDD and DDD tend to accumulate within the bed sediments due their high particulate fractions, whereas Endrin and Toxaphene exhibit lower levels. Particularly, TCDD and DDD levels differ from Endrin and Toxaphene concentration for  $1 \times 10^3$  ratio.

**Table 4.** Dissolved and particulate fractions.

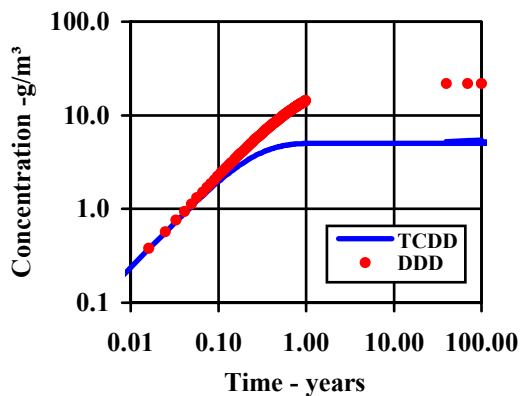
Fractions	TCDD	DDD	Endrin	Toxaphene
$F_{d-lake}$	0.48376	0.83102	0.99978	0.99969
$F_{p-lake}$	0.51624	0.16898	0.00022	0.00031
$F_{d-sed}$	0.00001	0.00007	0.05817	0.04178
$F_{p-sed}$	0.99999	0.99993	0.94183	0.95822

Model results are shown in Table 5, where steady-state concentration computed both by the analytical model and TOXI5 are presented. They indicate that their results are very similar, in spite of the simplifications of the analytical model, such as system geometry and diffusion/volatilization characterization.

**Table 5.** Comparison of models results.

Toxic	$c_{lake} - g/m^3$		$c_{sed} - g/m^3$	
	WASP5	Analytical	WASP5	Analytical
TCDD	5.68	5.67	218900	218438
DDD	22.3	22.41	284100	282960
Endrin	99.5	99.37	1720	1985.7
Toxaphene	7.76	7.76	186	214.3

Finally, attention has been focused on transients from zero-concentrations to steady-state or vice versa. These transients are used to assess the impact of changing conditions on system response.



**Figure 2a.** Transient for TCDD and DDD in the water column.

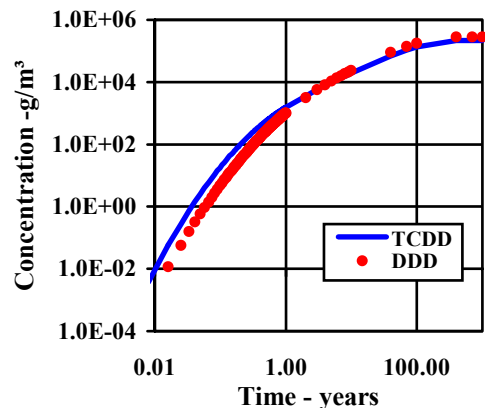
In fact, this condition could be applied in order to predict the time it takes for the lake to complete a fixed percentage  $\phi$  of its recovery.

The transient to negligible contaminants levels after the toxics loading in the lake is terminated due, for example, to the implementation of a waste removal project, has relevant consequences in decision-making contexts.

This time is called *response time*  $t_{r-\phi}$  [Chapra, 1997; Gualtieri, 2001a], because it is useful to characterize system response to loading termination. Notably, response time is both lake and contaminant parameter [Gualtieri, 2001a].

Model results for all the contaminants both in the water column and in the active sediments layer are in Fig.2a/2b/2c/2d, where steady-state conditions are at the end of the transient.

Simulations have pointed out the very long time for attaining both steady-state conditions and the system recovery in the lake and in the active sediments layer especially. This result confirms that, for strong sorbers, sediments represent the main source of pollutants over the time whereas, for dissolved toxics, volatilization and/or advection are the purging mechanisms.



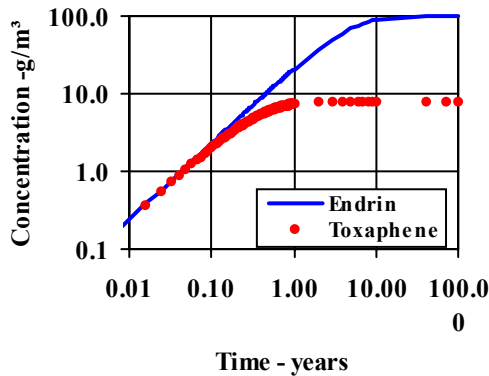
**Figure 2b.** Transient for TCDD and DDD in the sediments.

#### 4. CONCLUSIONS

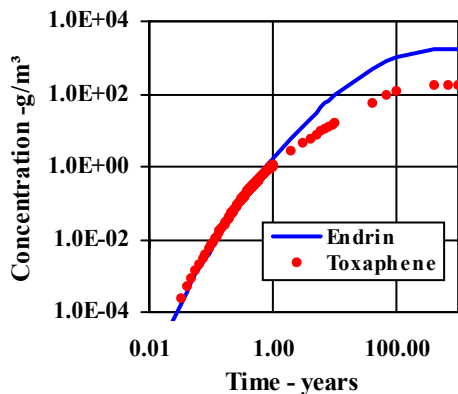
Application of water quality models is an established tool in water resources management.

The paper has shown that predictive tools based on numerical methods offer results reliable if compared with those deriving from analytical solutions, that can be applied only for idealized system geometry and exhibits a simplified volatilization/diffusion characterization. Moreover, the impact of different removal mechanisms on final contaminant levels has been assessed for 4 pesticides.

Finally, important lessons can be learnt observing transient occurring after the toxic loading is terminated in order to predict system recovery. In fact, for strong sorbers, bed sediments represent the main source of pollutants over the time, whereas, for dissolved toxics, volatilization and/or advection are the purging mechanisms.



**Figure 2c.** Transient for Endrin and Toxaphene in the water column.



**Figure 2d.** Transient for Endrin and Toxaphene in the sediments.

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