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DYNAMIC IN-STREAM FATE MODELING OF XENOBIOTIC ORGANIC COMPOUNDS: A CASE STUDY OF LINEAR ALKYLBENZENE SULFONATES IN THE LAMBRO RIVER, ITALY

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Abstract—Using a conceptual hydraulic model, a one-dimensional dynamic river water quality model has been developed to assess the short-term fate of linear alkylbenzene sulfonates (LAS) in the river compartments water and benthic sediment. The model assumes local equilibrium sorption and that both dissolved and sorbed chemical are available for biodegradation. To investigate the interaction of nutrient dynamics and organic contaminant fate, the model is coupled with a basic water quality model. On the basis of the Lambro River (Italy) as a case study, the result shows that the model predictions agree well with the measured data set. The model output sensitivity to model parameters has been tested, and the results depict that the model is highly sensitive to the biodegrading parameters. Also, a comparison of a steady state with a dynamic simulation and the effect of nutrient dynamics on the LAS fate in the Lambro River as a scenario analysis are presented. The results indicate the usefulness of the proposed model for the short-term simulation of organic contaminant fate in unsteady environmental conditions.

Keywords—Exposure modeling Integrated modeling Organic contaminant fate River water quality

INTRODUCTION

The current exposure assessment in the European Union is based on the generic multimedia ‘‘unit world’’ approach fate model, a steady-state level III fugacity model [1], which should be parameterized to simulate the real region. Such models have been indicated to have some limitations [2]. It does not describe the time course of recovery, which is related to the environmental persistence, after emission reduction. It cannot be readily validated because environmental conditions are not at steady state. The exposure concentrations of environmental pollutants can be variable because of varying rates of input and dilution, changes in chemical form and solubility, and degradation. Furthermore, different circumstances, such as runoff events or sewer overflows, can also result in a time-varying exposure concentration.

Such time-varying exposure concentration can result in a time-varying toxic response (effect), and toxicity depends not only on exposure concentration (exposure amplitude) but also on the exposure duration and frequency [3]. For example, a lower exposure concentration requires either a longer period or a more frequent exposure to result in adverse effect or toxicity than a higher concentration. A dynamic simulation provides a time-series output of exposure concentrations based on which exposure frequency and duration can be derived.

Consequently, a dynamic in-stream fate model is proposed for a time-dependent exposure analysis: to simulate the time profile of pollutant concentrations in different environmental compartments and to investigate short-term (high temporal resolution, e.g., daily and subdaily) and long-term variation of exposure concentration.

Despite the fact that dynamic in-stream fate models might already exist for basic water quality and organic contaminant fate, there are still some practical problems to apply such models in integrated water quality studies. Three major problems can be considered. First, the flow propagation in rivers is often described using the St. Venant equations, a complex hydrodynamic model [4,5]. The application of full St. Venant equations in integrated water quality studies, however, results in a long computation time, and detailed information about the system is needed, which is not often the case. As an alternative, a conceptual hydraulic model, Continuously Stirred Tanks Reactor in Series (CSTRS), was proposed [6].

The second problem is that the traditional organic contaminant fate models are treated separately as a single-issue model despite the fact that the effect of both conventional pollutants (nutrients enrichment or eutrophication) and contamination by xenophobic organic pollutants may interact in many direct or indirect ways [7]. Eutrophication may cause dilution of contaminants by increasing amounts of microbial biomass, enhancing biodegradation in the presence of oxygen, organic contaminant scavenging with suspended particulate organic matter (POC), sedimentation of contaminants, and contaminant uptake in the food chain. Besides, organic contaminants may have a direct or an indirect toxic effect on aquatic organisms, which in turn affects the organic contaminant fate and nutrient cycles [8]. As single-issue models do not address these interactions, coupling basic water quality to organic contaminant fate is very essential.

The third problem is selecting an appropriate single-issue basic water quality (eutrophication) and organic contaminant fate model. The most widespread eutrophication model for rivers is the QUAL2 [9] type of model, but it has many limitations presented elsewhere [10]. The sediment is not considered a state variable, and thus the mass balance is not complete. Furthermore, despite the fact that the activity of bacteria dominates the rates of biotransformation processes, this model does not consider bacteria a state variable and cannot therefore han-

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dle an increase or decrease of microbial biomass. A suitable basic water quality model must then be coupled to an appropriate organic contaminant fate model, with sufficient complexity, in order to make various scenario analyses.

Concerning the existing organic contaminant fate model, a dynamic multimedia fugacity model level IV was proposed for unsteady environmental conditions [1]. Though the fugacity model level IV was shown to describe the time course of pollutant fate and transport in the environment, it treats the environment as a single well-mixed box. This is rarely applicable for lakes, rivers, or estuaries in which the contaminant concentration can vary longitudinally, vertically, or laterally. To account for this spatial variation in addition to the temporal variation in lakes and rivers, another modeling approach, the so-called Quantitative Water Air Sediment Interaction (QWASI), was proposed [1]. In the QWASI modeling approach, a conceptual dynamic hydraulic model (completely mixed tank in series) is applied. However, the practical difficulties in applying QWASI model in fully dynamic conditions (fugacity model level IV) are indicated in Mackay [1]. In the fugacity level IV model, changes in flow volume, velocity, or river depth cannot be easily included. Therefore, these equations necessarily apply to idealized conditions or may apply for a long simulation time, such as a yearly basis [2].

Hence, for the short-term emission management in non–steady-state conditions, we still need an alternative dynamic exposure model that takes into account both spatial and temporal variability and that is suitable for integrated modeling of basic water quality and organic contaminant fate.

To tackle the previously mentioned three main problems, attempts have been made to develop a relatively simple dynamic in-stream fate model that takes into account the interaction of nutrient dynamics and organic contaminant fate and that can be applied for short-term simulation. A simple completely mixed tank-in-series model (CSTRS) was applied as a surrogate model for a complex hydrodynamic model (the St. Venant equations) [5]. The model can simulate the short-term (daily or subdaily) in-stream fate of chemicals in rivers and can readily be applied to a river system with variable flow or depth.

In addition to the hydraulic submodel (transport term), the biochemical conversion submodel (reaction term) that contains both basic water quality and organic contaminants was set so that the model can simultaneously simulate the basic water quality (nutrient dynamics) and organic contaminant fate in rivers. This allows one to investigate the effect of nutrient dynamics on organic contaminant fate in rivers. Subsequently, the IWA River Water Quality Model No. 1 (RWQM1 [10]) was extended to include the organic contaminant fate submodel. Furthermore, the proposed model considers both the bulk water and the benthic sediment compartments as state variables, in which, in addition to many physicochemical processes, detailed process descriptions for biodegradation process are presented. The usefulness of the proposed model is presented by using linear alkylbenzene sulfonates (LAS), which are widely used anionic surfactants in synthetic detergents for household and industrial use, as a case study in the Lambro River. A comparison of the proposed model predictions and monitoring data is presented. Furthermore, a sensitivity analysis, the comparison of dynamic and steady-state simulations, and a scenario analysis are given.

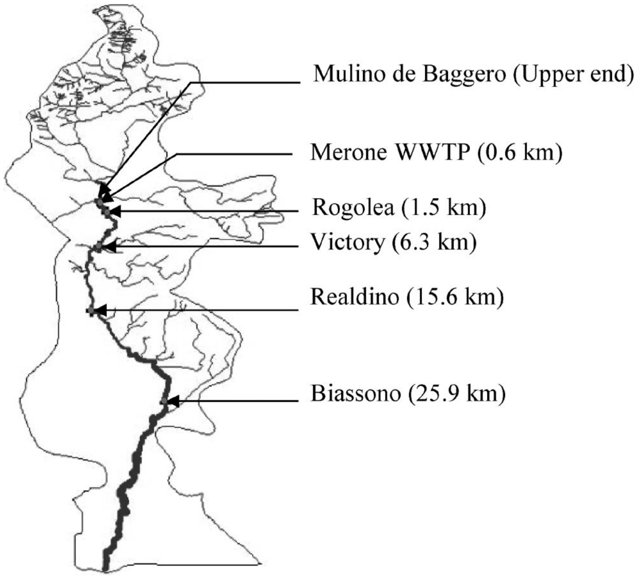

Fig. 1. The Lambro River, Italy, catchment with water quality measurement stations. WWTP = wastewater treatment plant.

STUDY SITE

The study was conducted at the Lambro River in Italy. The Lambro River catchment is located to the north of Milan with a total drainage area of about 1,950 km^2. The Lambro River flows southward from the Pre-Alps (1,450 m above sea level) to the confluence with the Po River (50 m above sea level) and has an approximate length of 130 km. Its average annual rainfall varies between 900 and 1,500 mm. The site under consideration is limited to the part of the Lambro River between Mulino de Baggero (as upstream end) and Biassono (as downstream end) (Fig. 1). The area drained by this river section at Biassono covers 400 km^2. Just downstream of Mulino de Baggero, the most relevant pollutant discharge in this section is from the wastewater treatment plant in Merone. The river receives a variable wastewater treatment plant effluent and combined sewer overflows from a pollution equivalent of 118,200 inhabitants, which produce in total 1,400 m^3/d. The holding capacity of the wastewater treatment plant is only 1,000 m^3. Therefore, 400 m^3/d of sewer overflows occur, and consequently the river is contaminated every day by sewer overflows. For this study site, twice-hourly measured data sets of 2 d in February and May 1998 and 10 d of daily flow and water quality data are available [11]. Using these data sets, water quality modeling and evaluation of the proposed model was carried out.

METHODS

Model development activities conducted in this study can be divided into the following component steps: hydraulics, biochemical conversion, general mass balances, generic organic contaminant mass balances, dissolved organic carbon (DOC) and POC mass balances, parameter calculation, model implementation, sensitivity analysis, model calibration and validation, and scenario analysis.

Hydraulics

For easy application of biochemical conversion mass balances and fast computation, a conceptual hydraulic modeling approach, a CSTRS in series [12], is applied as a surrogate

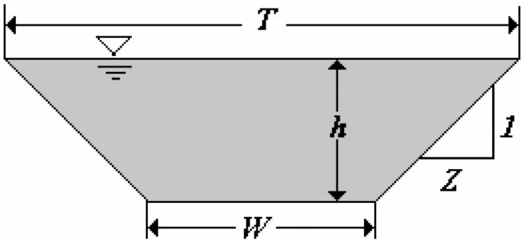

Fig. 2. Schematic representation of trapezoidal cross section for the Lambro River, Italy. Top width T, bottom width W, water depth h, and channel slope in the cross section $1/Z$.

model to the typically used complex hydrodynamic model (the St. Venant equations). Like the hydrodynamic model, the tank-in-series model can be applied to time-variable or non–steady-state conditions. The principle is that each tank (river stretch) has a time-variable volume with the outflow rate increasing with the water level in the tank. A time-variable-volume approach requires minimum hydraulic information, such as stage and discharge measurement in time, stage/discharge relations, or cross-sectional area/stage relationships. Based on such minimum hydraulic information, the main hydraulic equations that are required to formulate a water quality submodel are given here.

In a mixed tank-in-series model, the hydraulics of every river tank in series can be expressed as follows:

$$\frac{dV}{dt} = Q_{\mathrm{in}}(t) - Q_{\mathrm{out}}(t) \tag{1}$$

$$Q_{\mathrm{out}} = \alpha h^2(t) - \beta h(t) + \gamma \tag{2}$$

where V is the volume of the tank at time t (m^3); $Q_{\mathrm{in}}(t)$ and $Q_{\mathrm{out}}(t)$ are the inflow rate and the outflow at time t (m^3/d), respectively; h is the hydraulic depth (m); and α, β, and γ are river-specific hydraulic parameters that are typically estimated on the basis of stage-flow relationship. In Equations 1 and 2, V, Q_{in}, Q_{out}, and h are time variable. Equation 1 can be used to approximate both steady-state and dynamic hydraulics. Under dynamic conditions, the ordinary differential equation must be solved numerically.

Equation 2 can be easily formulated based on the analysis of field stage-flow relationships. Assuming that river reaches have a trapezoidal cross section (see Fig. 2), the cross-sectional area A_{cross} and the flow depth h can be calculated as follows [13]:

$$h(t) = \sqrt{\frac{A_{\mathrm{cross}}(t)}{Z} + \left(\frac{W}{2Z}\right)^2} - \frac{W}{2Z} \tag{3}$$

$$A_{\mathrm{cross}}(t) = \frac{V(t)}{L} \tag{4}$$

where $A_{\mathrm{cross}}(t)$ is the cross-sectional area at time t (m^2), L is the length of river tank (m), Z is the inverse of the river channel slope in the cross section (−), and W is the bottom width (m).

If the flow rate is constant, Equation 1 becomes steady state. One may use a constant or average flow with time-variable concentration as model input in order to simulate the temporal variation of concentrations. In this study, both the constant flow (average flow) and the time-variable flow conditions are considered, and a comparison of the results is presented.

Biochemical conversion

The biochemical conversion term involves all the governing equations that determine the fate of pollutants. It refers to the water quality submodel that includes all possible physicochemical and biochemical processes taking place in the system. In this paper, the biochemical conversion term is divided into two categories: the basic water quality (nutrient dynamics and microbial biomass growth) and organic contaminant fate.

Basic water quality. On the basis of advantages described in the introduction section of this paper, the RWQM1 [10] was applied for the basic water quality submodel. The RWQM1 is a set of equations that can be implemented in any suitable modeling and simulation software. It was developed to be a standard river water quality model for conventional pollutants such as nutrients, suspended solids, and algal blooms. The transformation processes are formulated on the basis of Monod kinetics, and the stochiometric coefficients are calculated by taking into account both elemental and charge balances. The model takes into account both suspended and benthic microbial biomass as state variables, and thus the mass balances are complete. This makes RWQM1 different from QUAL2E [9], which does not consider microbial biomass concentration as a state variable, and the variation of microbial biomass concentration cannot be simulated. As the RWQM1 was developed as a comprehensive river water quality model and is relatively complex eutrophication model with many model parameters and state variables [10], its simplification is highly recommended for practical/specific applications. The procedure for model simplification or submodel selection is documented in Vanrolleghem et al. [14]. In this paper, the model was simplified on the basis of selecting the most dominant biochemical processes that may occur in the river under consideration [15]: both aerobic and anoxic growth of microbial biomass, both aerobic and anoxic respiration of microbial biomass, hydrolysis of particulate organic materials, and adsorption and desorption of phosphate. The consequence of nutrient enrichment (algal bloom) is not considered in this version of the proposed model.

Organic contaminant fate. The simplified RWQM1 model was extended to include the in-stream fate model of xenobiotic organic pollutants so that the model can be used to study the effect of conventional pollutant dynamics (nutrients, carbonaceous organic matter as biological oxygen demand, and suspended solids) on the fate of toxic organic contaminants. For instance, consider the aerobic biodegradation of toxic organic chemicals. The concentration of dissolved oxygen and heterotrophic biomass will determine the biodegradation rate. However, both dissolved oxygen and heterotrophic biomass concentration are also affected by the concentration of biological oxygen demand in water. On the one hand, a high concentration of biological oxygen demand can result in low dissolved oxygen concentrations that will consequently decrease the aerobic degradation rate of the xenobiotic organic chemical under consideration. On the other hand, a low biological oxygen demand load can stimulate the growth of biomass, which can increase the degradation rate of organic contaminants. Thus, integrated modeling of basic water quality and fate of organic contaminants in rivers or streams can lead to a better understanding of the interaction of nutrient dynamics and toxic organic contaminants than can a single-issue model (either basic water quality or organic contaminant fate model).

The organic contaminant fate submodel was formulated on the basis of a simple mass balance (see Eqns. 5–7). The biochemical conversion processes that are included in this submodel are biodegradation, volatilization, sedimentation, resuspension, and mass transfer between bulk water and benthic

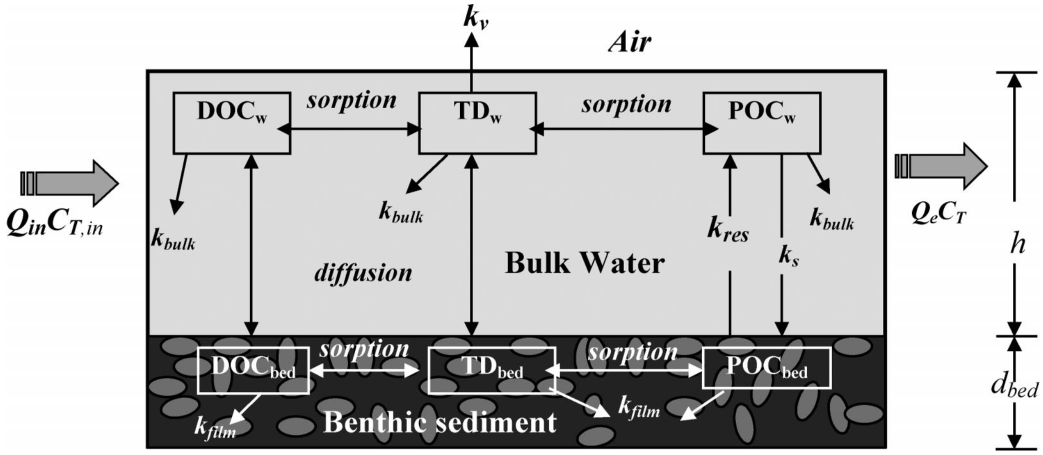

Fig. 3. Schematic representation of the in-stream fate mode in the Lambro River, Italy. POC = particulate organic carbon, DOC = dissolved organic carbon, and TD = truly dissolved phase; h and d_{bed} are the depth of bulk water and active sediment layer (benthic sediment), respectively; k_{bulk} and k_{film} are the pseudo-first-order biodegradation coefficients in the bulk water and benthic sediment, respectively; the subscripts *w* and *bed* indicate the bulk water and the benthic sediment compartments, respectively.

sediment. In the biodegradation processes, the distinction was made between bulk water and biofilm biodegradation, and their detail mathematical expressions are presented here.

Figure 3 indicates the scheme of the overall model structure for the fate of organic contaminants in the river system. Three environmental compartments—air, water, and benthic sediment (the active sediment layer)—are considered. If one ignores atmospheric deposition in the river under consideration, the air compartment can be considered a sink for volatile compounds. The water compartment is further subdivided into three subcompartments: truly dissolved phase in the bulk water (TD$_{\text{w}}$), sorbed phase to suspended particulate organic carbon in the bulk water compartment (POC$_{\text{w}}$), and sorbed phase to dissolved organic carbon in the bulk water compartment (DOC$_{\text{w}}$). The benthic sediment is also subdivided into three subcompartments: sorbed phase to POC in the bulk volume of the benthic sediment (POC$_{\text{bed}}$), truly dissolved phase in the pore water in the benthic sediment compartment (TD$_{\text{bed}}$), and sorbed phase to DOC in the pore water (DOC$_{\text{bed}}$). The air compartment and volatilization processes are included in the model for a generic compound but will not be considered for the LAS case study because LAS is not a volatile compound.

General mass balances

Combining hydraulics (Eqn. 1) and biochemical conversion submodels, the general mass balances of a substance in a CSTRS in series can be described as follows:

$$\frac{d(VC)}{dt} = Q_{\text{in}}(t)C_{\text{in}}(t) - Q_{\text{out}}(t)C(t) - rV(t) \tag{5}$$

where $d(VC)/dt$ is the change of mass of the substance over time (accumulation), C_{in} and C are inflow and outflow concentrations, r is the net conversion rates of the substance reactions (mg/L/d), and r is given as the sum of the products of processes rates and the stochiometric coefficients of the substance as documented in [10] for the basic water quality submodels.

The basic water quality submodel refers to the biochemical reaction equations for nutrients (both inorganic substrates and organic substrates), total suspended solids, and microbial biomass. In the process equations, Monod limitation kinetics is used. In this paper, the basic water quality model was extended to link the organic contaminant fate model, in which r can be replaced by $kC(t)$, where k is the over all pseudo-first-order rate constant even though the actual biotransformation follows Monod or Michaelis–Menten enzyme kinetics [16]. Selection of the first-order kinetics is based on the fact that the concentrations of organic contaminants in the environment are very low, in the order of microgram per liter, which is considerably lower than the half-saturation constants [16]. Assuming negligible atmospheric deposition, the air compartment is considered a source/sink, and the mass balances of the generic compound, POC, and DOC are presented here for the other two compartments (water and benthic sediment).

Generic organic contaminant mass balances

On the basis of the hydraulic model (Eqns. 1–4), instantaneous local equilibrium assumption, and pseudo-first-order kinetics, the general mass balances for the total organic contaminant concentration in the bulk water and benthic sediment, respectively, can be expressed as follows:

Bulk water

$$\begin{aligned}\frac{d(VC_{\text{T}})}{dt} = {} & Q_{\text{in}}C_{\text{Tin}} - Q_{\text{out}}C_{\text{T}} - k_{\text{film}}(f_{\text{d}} + f_{\text{DOC}})C_{\text{T}}V \\ & -k_{\text{bulk}}C_{\text{T}}V - k_{\text{V}}C_{\text{T}}V - k_{\text{sed}}f_{\text{POC}}C_{\text{T}}V \\ & + k_{\text{res}}f_{\text{POC,bed}}C_{\text{T,bed}}V_{\text{bed}} \\ & + K_{\text{LC}}\left[\frac{(1 - f_{\text{POC,bed}})^{C_{\text{T,bed}}}}{\Phi - (1 - f_{\text{POC}})^{C_{\text{T}}}}\right]A\end{aligned} \tag{6}$$

Benthic sediment

$$\begin{aligned}\frac{d(V_{\text{bed}}C_{\text{T,bed}})}{dt} = {} & k_{\text{sed}}f_{\text{POC}}C_{\text{T}}V - k_{\text{film}}C_{\text{T,bed}}V_{\text{bed}} \\ & - k_{\text{res}}f_{\text{POC,bed}}C_{\text{T,bed}}V_{\text{bed}} \\ & - K_{\text{LC}}\left[\frac{(1 - f_{\text{POC,bed}})^{C_{\text{T,bed}}}}{\Phi - (1 - f_{\text{POC}})^{C_{\text{T}}}}\right]A\end{aligned} \tag{7}$$

where C_{T} is the unfiltered/total whole water chemical concentration (g/m^3); $C_{\text{T,bed}}$ is the volumetric total chemical concentration in the benthic sediment (g/m^3); k_{sed}, k_{v}, k_{res}, k_{bulk}, and k_{film} are pseudo-first-order rate constants for sedimentation, volatilization, resuspension, biodegradation only in the bulk water, and biodegradation in the benthic sediment or biofilm (per day), respectively; f_d and $f_{d,bed}$ are the truly dissolved fraction in the bulk water and in the pore water, respectively; f_{POC} and $f_{POC,bed}$ are the fraction sorbed to suspended and benthic sediment POC, respectively; f_{DOC} and $f_{DOC,bed}$ are the fractions sorbed to DOC in the bulk water and pore water, respectively; K_{LC} is the mass transfer coefficient for the organic contaminant; $S_{DOC,bed}$ is the concentration of DOC in the benthic sediment; $S_{POC,bed}$ is the concentration of POC in the benthic sediment; V_{bed} and A are the volume of benthic sediment (m^3) and surface area of the river tank (m^2), respectively; and Φ is the porosity of benthic sediment.

The formulation of Equations 6 and 7 is based on the following assumptions. The truly dissolved fraction of organic contaminant (f_d) and sorbed fraction to dissolved organic carbon (f_{DOC}) in the bulk water can be degraded both by suspended microbial biomass (k_{bulk}) and by benthic biofilm (k_{film}), removed by volatilization (k_v) for volatile organic compounds, and removed or gained by mass transfer (diffusion) between benthic sediment and bulk water (K_{LC}). The sorbed fraction in the bulk water can be degraded by suspended microbial biomass (k_{bulk}), removed by sedimentation of POC (k_{sed}), or gained by resuspension of POC (k_{res}). Furthermore, the generic compound concentration in the benthic sediment is described in terms of mass of the substance per bulk volume of benthic sediment. In order to get the concentrations of the contaminant in the pore water, the concentrations of substances in the benthic sediment must be divided by the porosity Φ as indicated in Equations 6 and 7.

DOC and POC mass balances

In Equations 5 and 6, DOC and POC are state variables, and their mass balances in both river compartments can be formulated using a similar approach. The general mass balance including transport for both forms of organic carbon in the bulk water can be formulated as follows:

$$\frac{d(S_{DOC}V)}{dt} = Q_{in}S_{DOC,in} - Q_{out}S_{DOC} + K_{L,doc}\left(\frac{S_{doc,bed}}{\Phi - S_{DOC}}\right)A - rV \quad (8)$$

$$\frac{d(S_{POC}V)}{dt} = Q_{in}S_{POC,in} - Q_{out}S_{POC} - k_{sed}S_{POC} + k_{res}S_{POC} - rV \quad (9)$$

The general mass balances for the POC and DOC in the benthic sediment can be expressed as follows:

$$\frac{d(S_{DOC,bed}V_{bed})}{dt} = K_{L,DOC}\left(\frac{S_{DOC,bed}}{\Phi - S_{DOC}}\right)A \quad (10)$$

$$\frac{d(S_{POC,bed}V_{bed})}{dt} = k_{sed}S_{POC}V - k_{res}S_{POC,bed}V_{bed} \quad (11)$$

where S_{DOC} and S_{POC} are the concentrations of DOC and POC, respectively, in the bulk water (g/m^3); $S_{POC,bed}$ and $S_{POC,bed}$ are the concentration of POC and DOC in the bulk volume of benthic sediment (g/m^3; and $K_{L,doc}$ is the mass transfer coefficient for the DOC between bulk water and benthic sediment (m/d).

The formulation of the previously mentioned general mass balances (Eqns. 6–11) is based on five general simplifying assumptions. First, only biodegradation, sorption, sedimentation, and resuspension are considered dominant processes in the decay and transport pathways of the specific chemical. Second, as the apparent desorption equilibrium occurs rapidly [17], instantaneous local sorption equilibrium can be assumed, and an equilibrium partition coefficient can be used. The literature also suggests that when the sorption and desorption processes are faster than the other transformation processes, this assumption holds [18]. Third, a constant depth of the active sediment layer is considered, but the sediment solids concentration/density within this depth varies with time. Fourth, the specific compound and sediment-solids loss due to sediment burial is assumed negligible. This can be supported considering the suggested value given in the literature [16] of 0.889 mm/year. This is very low compared to the sedimentation and resuspension velocity. Fifth, the transport processes for the benthic sediment is assumed to be only sedimentation, resuspension, and diffusion. The advection from downstream to upstream and between benthic sediment and the overlaying water is neglected.

Note that the previously mentioned mass balances (Eqns. 5–11) can be applied for steady-state conditions by assuming that accumulation term ($d(VC)/dt$) equals zero. In the dynamic simulation, the ordinary differential equations must be solved numerically.

Parameter calculation

The total chemical concentration (C_T) given in Equation 6 (in the bulk water) and Equation 7 (in the benthic sediment) is the sum of the truly dissolved phase, C (g/m^3); the phase sorbed to the POC, C_{POC} (g/g); and the phase sorbed to the DOC, C_{DOC} (g/g). This can be expressed in a general form as follows:

$$C_{T,i} = C_i + C_{POC,i}S_{POC,i} + C_{DOC,i}S_{DOC,i} \quad (12)$$

Assuming instantaneous sorption equilibrium and the toxicant associates similarly with both POC and DOC, Equation 12 can be rewritten as follows:

$$C_{T,i} = C_i[1 + K_{OC}(S_{POC,i} + S_{DOC,i})] \quad (13)$$

where K_{OC} is the equilibrium partition coefficient (m^3/g) and i is the compartment: bulk water or benthic sediment.

Partition coefficients. One of important parameters in the contaminant mass balances is the partitioning coefficient K_{OC}, which can be estimated on the basis of either the sorption experiment or the literature study. The K_{OC} is often estimated on the basis of the octanol–water partition coefficient (K_{OW}) and the organic carbon content of the environmental compartments [19]. This approach assumes that K_{OC} is a function of organic carbon content. It is also called the hydrophobic mechanism, which is indicated as an unreliable approach to calculate K_{OC} for the chemical under study, LAS [18]. The main reason is that the LAS sorption does not correlate well with the organic carbon content, as would be expected for a simple hydrophobic mechanism. As the fraction of organic carbon increases, the cation exchange capacity increases, and the surface becomes more negative, which consequently diminishes hydrophobic bonding by increasing repulsion. Consequently, the experimental determined literature value was applied.

When the partition coefficients K_{OC} and the concentration of POC and DOC are known in compartment i, the model parameters f_d, f_{DOC}, and f_{POC} in each compartment can be calculated as follows:

$$f_{\mathrm{DOC,i}} = \frac{k_{\mathrm{OC}} S_{\mathrm{DOC,i}}}{1 + K_{\mathrm{OC}}(S_{\mathrm{POC,i}} + S_{\mathrm{DOC,i}})}$$

$$f_{\mathrm{POC,i}} = \frac{K_{\mathrm{OC}} S_{\mathrm{POC,i}}}{1 + K_{\mathrm{OC}}(S_{\mathrm{POC,i}} + S_{\mathrm{DOC,i}})} \tag{14}$$

$$F_{\mathrm{d,i}} = 1 - f_{\mathrm{DOC,i}} - f_{\mathrm{POC,i}}$$

Note that in the dynamic simulation, both $S_{\mathrm{DOC,i}}$ and $S_{\mathrm{POC,i}}$ are varying in time (see Eqns. 8–11), and hence $f_{\mathrm{DOC,i}}$, $f_{\mathrm{POC,i}}$, and $f_{\mathrm{d,i}}$ are as well.

Equation 14 is very important for the mass balance of generic organic contaminants and their partitioning in the environmental compartments and also has a very crucial role in exposure assessment. The sorption of xenobiotic organic compounds to DOC was indicated to be the driving force in determining the bioavailability [20]. The dissolved but sorbed LAS to the DOC (mainly humic substance) is not available for gill uptake. As the sorbed LAS to the DOC is not available for gill uptake, considering the overall dissolved phase in the exposure concentration can overestimate the exposure concentration on the one hand and underestimate the risk on the other. Thus, incorporating the third-phase partitioning can enable one to take into account the effect of DOC so that a better characterization of the exposure concentration can be obtained.

Pseudo-first-order reaction rate constants. As indicated previously, only five key processes are considered in the generic organic contaminant fate model: biodegradation, volatilization, sedimentation, and resuspention. For every process, the pseudo-first-order reaction coefficient must be calculated. The pseudo-first-order reaction rate constants included in the general mass balances (see Eqns. 6–11) are k_{bulk}, k_{film}, k_{v}, k_{sed}, and k_{res}. Except k_{bulk} and part of k_{film}, these pseudo-first-order reaction rate constants were estimated on the basis of the existing relations given in literature as described in the following.

Biodegradation. The degradation kinetics of organic contaminant is typically described as a first-order kinetics without coupling with the limiting substrate [16]. Chemicals like LAS do not degrade in the absence of oxygen. Hence, coupling dissolved oxygen to the degradation of organic contaminant for such type of chemicals is essential. Therefore, assuming that the same rate constant holds for the sorbed and the dissolved phases, because of rapid sorption/desorption [17], the pseudo-first-order biodegradation rate constant for total LAS in the bulk water, k_{bulk} (per day) can be calculated with the following relation:

$$k_{\mathrm{bulk}}(t) = k_{\mathrm{b,bulk}}\left[\frac{S_{\mathrm{O_2}}(t)}{K_{\mathrm{O_2}} + S_{\mathrm{O_2}}(t)}\right]X_{\mathrm{H}}(t) \tag{15}$$

For slow sorption and desorption, as it is possibly the case for other organic contaminants, assuming the same degradation rate constant (Eqn. 15) cannot be applied. In that case, k_{bulk} can be calculated by introducing biodegradable fraction for the sorbed phases as follows:

$$k_{\mathrm{bulk}}(t) = k_{\mathrm{b,bulk}}(f_{\mathrm{d}} + f_{\mathrm{POC}}\varepsilon + f_{\mathrm{DOC}}\theta) \times \left[\frac{S_{\mathrm{O_2}}(t)}{K_{\mathrm{O_2}} + S_{\mathrm{O_2}}(t)}\right]X_{\mathrm{H}}(t) \tag{16}$$

where $k_{\mathrm{b,bulk}}$ is the second-order biodegradation rate constant (m^3/g/d), $S_{\mathrm{O_2}}$ is the dissolved oxygen concentration (g/m^3), X_{H} is the heterotrophic biomass concentration (g/m^3), and ε and θ are the biodegradable fractions for LAS sorbed to suspended particulates and DOC, respectively. Note that both $S_{\mathrm{O_2}}$ and X_{H} are time variable.

The heterotrophic biomass, X_{H}, is assumed to be the concentration of all rounder heterotrophic organisms that can grow aerobically and many of them also anoxically (denitrification). Such assumption is typical in activated sludge models and is also used in RWQM1. It was followed here for the sake of model simplicity. These organisms are therefore responsible for metabolizing or degrading all degradable organic substances. Since LAS does not degrade in anoxic conditions, only aerobic growth of X_{H} is considered.

In addition to bulk water biodegradation, biofilm biodegradation is included in the model because the activities of a biofilm attached to the riverbed of shallow streams may be predominant in the biodegradation process [21,22]. With the assumption that the rate of diffusion is balanced by the rate of substrate biodegradation in the biofilm (steady state), the biofilm pseudo-first-order biodegradation rate constant can be approximated by the method presented elsewhere [23]:

$$k_{\mathrm{film}}(t) = a_{\mathrm{f}}(t)K_{\mathrm{L}}\frac{D_{\mathrm{f}}\, r \tanh(rL_{\mathrm{f}})}{D_{\mathrm{f}}\, r \tanh(rL_{\mathrm{f}}) + K_{\mathrm{L}}}$$

$$r = \sqrt{\frac{X_{\mathrm{f}}\, k_{\mathrm{b}}}{D_{\mathrm{f}}}}$$

$$K_{\mathrm{L}} = \frac{D}{L} \qquad D_{\mathrm{f}} = 0.8D \tag{17}$$

where a_{f} is the specific interfacial area at a time t (m^2/m^3), K_{L} is the external mass transfer coefficient (m/d), D is the molecular diffusion rate constant in the bulk water (m^2/d), D_{f} is the molecular diffusion rate constant in biofilm (m^2/d), L_{f} is the biofilm thickness (m), and X_{f} is the biofilm density (g/m^3), where k_{b} is the second-order biodegradation rate coefficient (m^3/g/d). For simplification, a single biofilm species with constant biofilm density X_{H} is assumed; otherwise, it leads to a more complicated biofilm model like the one presented elsewhere [24] for mixed culture biofilms.

The a_{f} can be roughly estimated from river geometry when assuming a trapezoidal cross section modified from [23]:

$$\begin{aligned} a_{\mathrm{f}}(t) &= \xi \cdot \frac{2[h(t) - d_{\mathrm{bed}}]\sqrt{1 + Z} + (W + Zd_{\mathrm{bed}})d_{\mathrm{bed}}a_{\mathrm{bed}}}{[W + Zh(t)]h(t)} && \textit{if } d_{\mathrm{bed}} > 0 \\ &= \xi \cdot \frac{W + 2h(t)\sqrt{1 + Z^2}}{[W + Z \cdot h(t)]h(t)} && \textit{if } d_{\mathrm{bed}} = 0 \end{aligned} \tag{18}$$

where ξ is a correction factor for not a plane biofilm surface area (2 m^2/m^2) [22], d_{bed} is the active sediment depth (m), and a_{bed} is the bed material–specific surface area (100 m^2/m^3) [22].

As one notices from Equation 18, k_{film} depends on the river cross section, which allows k_{film} to vary with the flow depth. As the depth of water increases a_{f} decreases, which in turn reduces the k_{film}. This indicates that rivers with a high ratio of surface area to volume (shallow rivers) are expected to have higher biofilm activity than deep rivers.

Besides, the pseudo-first-order biodegradation rate constants (k_{bulk} and k_{film}) are temperature dependent. The estimated values at water temperature T_{w} can be calculated on the basis of the temperature correction factor Θ as

$$k_{\mathrm{i,T_w}} = k_{\mathrm{i,T_{ref}}} \cdot \theta^{(\mathrm{T_w} - \mathrm{T_{ref}})} \tag{19}$$

where $k_{\mathrm{i,T_w}}$ is pseudo-first-order biodegradation rate constant

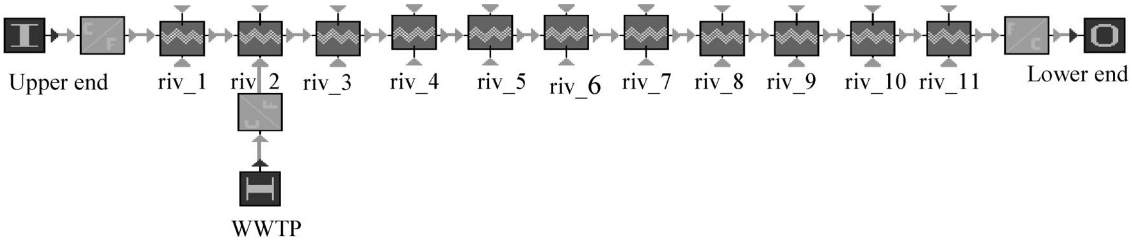

Fig. 4. Tank-in-series model for the Lambro River, Italy. Upper end is the upstream input, wastewater treatment plant (WWTP) is the side stream of wastewater discharge, and riv_1 to riv_11 are river reaches that are internally subdivided into a total of 47 tanks in series.

k_{bulk} or k_{film} at water temperature T_w, T_{ref} is the reference temperature, k_i is the rate constant at the reference temperature, and Θ is a constant temperature coefficient greater than 1.0 and usually within the range of 1.0 to 1.10 [16]. Despite the fact that Θ must normally be determined experimentally, which is beyond the scope of this study, we have chosen the literature value. Subsequently, the suggested value for aerobic degradation 1.047 [25] was applied.

Volatilization. Despite the fact that LAS is a nonvolatile compound, volatilization is included in the model because the proposed model is intended also for other xenobiotic organic compounds. For such molecules, a good estimation of the pseudo-first-order volatilization rate constant is required. A chemical may be ionized, un-ionized, or sorbed, in which only the unionized and unsorbed fraction ζ can volatilize. The pseudo-first-order rate constant k_v can then be estimated as follows:

$$k_V(t) = -K_V \cdot \frac{A}{V(t)} \cdot \zeta \tag{20}$$

$$\zeta = \begin{cases} \dfrac{1}{1 + 10^{(\text{pH} - \text{p}Ka)}} & \text{if it is acid} \\ \dfrac{1}{1 + 10^{(\text{p}Ka - \text{pH})}} & \text{if it is base} \end{cases} \tag{21}$$

where K_v is the overall air–water transfer velocity at time t, which can be estimated on the basis of the well-known two-film model of a gas–liquid transfer velocity given elsewhere [26].

Sedimentation and resuspension. In sediment–water interactions, sedimentation and resuspension must be considered. The pseudo-first-order sedimentation (k_{sed}) and resuspension (k_{res}) rate constants can be approximated on the basis of the particle settling velocity U_{sed} and resuspension/scouring velocity U_{res} as follows [16]:

$$k_{\text{sed}} = \frac{U_{\text{sed}}}{h_m} \tag{22}$$

$$k_{\text{res}} = \frac{U_{\text{res}}}{h_m} \tag{23}$$

where U_{sed} is the settling velocity (m/d), U_{res} is the resuspension velocity (m/d), and h_m is the mean water depth (m).

Note that according to the state of the art, the settling velocity is estimated using Stoke's law [16], in which the settling velocity is linearly dependent on the particle density and quadratically dependent on the particle diameter. It also depends on the shape of the particles (e.g., spherical particles settle faster than nonspherical particles of the same equivalent diameter). As particles in natural waters have a range of diameters and have complex shapes, it is practically difficult to calculate the U_{sed} with Stoke's law. Similarly, the resuspension velocity U_{res} depends on a number of factors: the magnitude of shear stress exerted at the bottom, the horizontal flow velocity, and the type of bottom sediment. This implies that both U_{sed} and U_{res} depend on many factors that require more unknown parameters to be estimated. Subsequently, we decided to use literature values as an initial guess and obtain the real value by calibration. Chapra [18] indicated that the sedimentation velocity ranges between 0.1 and 1 m/d for natural organic matter. The resuspension velocity is also indicated to be in the range between 0 and 0.005 m/d [16,27].

Model implementation

The proposed model was implemented in the WEST® modeling and simulation software [28], which has been applied mainly to wastewater treatment plant systems. However, the WEST simulator can also be applied readily to river water quality systems by extending the open model base. This simulation software is materially not different from other simulation software packages but has some important advantages: It does not require prior knowledge of any programming language, the tank-in-series model and the integrated water quality study that considers the interaction between a wastewater treatment and the receiving water can be easily implemented, and a large model base, sensitivity, and optimization tools are already available.

Figure 4 shows the configuration of the complete tank-in-series model in WEST simulator for the Lambro River case study.

Sensitivity analysis

Prior to the model calibration for the biochemical conversion submodel, a sensitivity analysis was performed in order to examine the effect of the model parameters and their relative importance to the model predictions. Sensitivity analysis allows one to select those parameters that are most important to be estimated (others may remain on default values). This was done using the WEST simulation and modeling software [28,29]. Two types of sensitivity function can be distinguished: the relative sensitivity function S_R and the absolute sensitivity function S_A, which can be calculated numerically on the basis of the change in predicted concentration C on a very small change of each parameter P. To obtain the sensitivity, first a reference simulation is run without changing the parameter value. Then the parameter value is changed with a very small perturbation factor, and, by evaluating the difference in simulation results, both S_A and S_R can be calculated in every time step as follows:

$$S_A(t) = \frac{\Delta C}{\Delta P} \tag{24}$$

$$S_R(t) = \frac{\Delta C / C(t)}{\Delta P / P} = \frac{\Delta C}{\Delta P} \cdot \frac{P}{C(t)} \tag{25}$$

Table 1. Description of river tanks in Lambro River (Italy)

River reach	No. of tanks in series	Tank length (m)	Monitoring sites
riv_1	1	600	Mulino-Merone
riv_2	1	477	Merone-Sect_Rogo
riv_3	1	477	Merone_Rogolea
riv_4	4	602.75	Rogolea-Section_1
riv_5	4	602.75	Section_1-Victory
riv_6	6	514.17	Victory-Section_2
riv_7	6	514.17	Section_2-Section_3
riv_8	6	514.17	Section_3-Realdino
riv_9	6	570.33	Realdino-Section_4
riv_10	6	570.33	Section_4-Section_5
riv_11	6	570.33	Section_5-Biassono
Sum	47	26,000	

Either of these two equations can be used, but using relative sensitivities is more meaningful than absolute sensitivities, particularly if one is interested in comparing the sensitivity of the model to different parameters. In contrast to S_A, the relative sensitivity S_R is indeed unitless, or it does not depend on the unit of C and P.

As the values of sensitivity function for a dynamic simulation are expressed as a time series, the average of the absolute values of S_R is used to rank the relative importance of the parameters as follows:

$$\overline{S_R} = \frac{\sum_{i=1}^{n} |S_{R,i}|}{n} \tag{26}$$

where $\overline{S_R}$ is the average relative sensitivity, $S_{R,i}$ is the relative sensitivity at a time i, and n is number of data points.

Model calibration and validation

The calibration procedure includes two steps. First, the optimum number of tanks in series for the pollution transport is determined, and, second, the model is calibrated for its reaction rate parameters. In the tank-in-series model, the number of tanks determines the dispersion of the substance in the system. The higher the number of tanks one uses, the less the dispersion of the substance will be. Thus, the optimum number of tanks must be determined first. The optimum number of tanks in series can be determined on the basis of a tracer study in which a pulse of an inert substance is followed as it proceeds downstream. For this case study, the optimum number of tanks in series has already been determined in a previous study using boron as a tracer [6]. In this study, 47 tanks were considered to represent an acceptable compromise between calculation time and accurate representation of the river system under consideration. As indicated in Figure 4, the river was divided into 11 different river stretches, and each of these is internally further subdivided into a number of equal-size tanks in series (see Table 1).

Subsequently, the reaction rates were calibrated on the basis of data collected in February 1998 by varying some key parameters. Such key parameters were selected on the basis of sensitive analysis results as indicated in the following sections. The key parameter values were tuned until the best fit between model prediction and measured data sets was obtained. The minimum sum of squared errors is applied to evaluate the fit.

Once the model is calibrated with data collected in February 1998 [11], all we really know is that the model is able to fit a single data set. However, before the model can be used with confidence to make management decisions, it has to be validated. To do this, the calibrated model should be run for a new data set (or, ideally, several data sets), with the physical parameters (e.g., water temperature) and the forcing functions changed to reflect the new conditions. Subsequently, the model was validated with data collected in May 1998 [11]. Different statistical methods can be used for model validation (e.g., Mayer and Butler [30] and Bird et al. [31]). In this study, however, Equation 27 is selected because of the limited available data, as suggested in Garratt [32] and Zhang et al. [33]:

$$U = \frac{\sqrt{\frac{1}{n}\sum_{i=1}^{n}(y_{i,simul} - y_{i,measrd})^2}}{\left(\sqrt{\frac{1}{n}\sum_{i=1}^{n} y_{i,simul}^2} + \sqrt{\frac{1}{n}\sum_{i=1}^{n} y_{i,measrd}^2}\right)} \tag{27}$$

where U is the coefficient that can be used as a quantitative criterion to express the model validity, $y_{i,simul}$ is the simulated value at time i, $y_{i,measrd}$ is the measured value at time i, and n is the number of data points. The value of U ranges from 0 (when the simulated data overlap perfectly with the measured data, complete fit) to 1 (when the fit is the worst). When the value is below 0.5, it is assumed that the model gives an acceptable fit.

In addition to hydraulic and physical variables (e.g., temperature), the model variables that were measured and used as model inputs in the model calibration and validation data sets include ammonia nitrogen, nitrate nitrogen, inorganic phosphate phosphorus, chemical oxygen demand (COD), LAS, and microbial biomass.

Scenario analysis

In this study two main scenario analysis were made. First, a comparison of steady-state and variable-flow simulation was conducted. Note that the flow rate of the Lambro River in the upstream of the Merone wastewater treatment plant was almost constant during the measuring campaign. However, the downstream river flow varies with time because of intermittent sewer overflows. Based on the simulation results obtained in the last river section (Biassono), the consequence of four different approaches was examined: time-variable inflow, average flow with time-variable inflow concentration, daily averaged flow with daily averaged inflow concentration, and average flow with overall averaged inflow concentration.

Second, the effect of nutrient dynamics on the fate of organic contaminant was evaluated: To investigate the effect of nutrient dynamics on the fate of LAS, two substrates, such as ammonia nitrogen and soluble readily biodegradable organic substrates as COD, were considered. By increasing the concentration of ammonia nitrogen and COD (one variable at a time) in the model input, the effect of nutrient dynamics on the fate of LAS was examined by comparing the reference simulated concentration of LAS (without changing the variables) with the result obtained after increasing the two variables.

RESULTS AND DISCUSSION

Sensitivity analysis

The model sensitivity to different categories of model parameters, such as biodegradation, porosity, sedimentation and resuspension velocity, and partition coefficients, was examined. On the basis of relative sensitivity functions (Eqn. 25),

Table 2. Sensitivity analysis: Parameters ranked on the basis of average absolute values of relative sensitivity ($|S_R|$)

Rank	Parameters: Symbol	Parameters: Description	Average $|S_R|$ (%)	Maximum $|S_R|$ (%)	Minimum $|S_R|$ (%)
1	d_{bed}	Active sediment depth (m)	2.316	4.772	0.918
2	a_{bed}	Bed material specific surface area (m^2/m^3)	2.304	4.748	0.914
3	X_f	Biofilm density (g/m^3)	2.293	4.726	0.909
4	$k_{b,bulk}$	Second-order biodegradation rate coefficient in the bulk water ($m^3/g/d$)	2.273	4.448	1.007
5	L_f	Biofilm thickness (m)	0.377	14.103	0.052
6	k_b	Second-order biodegradation rate coefficient (biofilm) ($m^3/g/d$)	0.081	0.260	0.061
7	K_{CL}	Mass transfer coefficient for the compound (m/d)	0.012	0.023	0.005
8	U_{sed}	Settling velocity (m/d)	0.0027	0.1079	0.00005
9	K_{OC}	Equilibrium partition coefficient (m^3/g)	0.0019	0.0054	0.0008
10	ϕ	Porosity of benthic sediment	0.0004	0.0008	0.00019
11	ϵ	Biodegradable fractions of sorbed phase to POC[a]	0.00021	0.0007	0.0002
12	θ	Biodegradable fractions for sorbed phase to DOC[b]	0.00017	0.0010	0.00011
13	U_{res}	Resuspension/scouring velocity (m/d)	2.1E-05	0.00094	1.2E-06

[a] POC = particulate organic carbon.

[b] DOC = dissolved organic carbon.

the parameters were ranked (see Table 2) on the basis of the average of the absolute values of S_R (Eqn. 26). The maximum and minimum absolute values of S_R are also given (Table 2). The results show that the model is most sensitive to the biofilm biodegradation parameters d_{bed}, a_{bed}, X_f, and L_{film} and to the bulk water biodegradation parameters $k_{b,bulk}$. The model is moderately sensitive to k_b and K_{CL}. The model is more sensitive to the biofilm biodegradation parameters than bulk water biodegradation parameters. This is due to the difference in the microbial biomass density, which is higher in the benthic sediment than in the bulk water. The model is also considerably sensitive to the sedimentation velocity U_{sed} and the partition coefficient K_{OC}. The model is also reasonably sensitive to small changes of porosity Φ and the biodegradable fraction of sorbed organic contaminants to the POC and DOC (ε and θ). This indicates that the parameter values of ε and θ need a proper estimation for a chemical with slow sorption/desorption. However, in the LAS case study, previous experimental studies [18] indicted fast sorption and desorption of LAS, and for this situation the equal degradation rate holds, and introduction of ε and θ are not important. The model sensitivity to porosity and resuspension velocity is very low. Thus, exact estimation of their values is not necessary.

Model calibration and validation

Based on the previously mentioned sensitivity analysis result, key model parameters were selected for calibration. On the basis of the monitoring data collected in February 1998 [11], the calibration result is indicated in Figure 5. Table 3 depicts the values of key model parameters given in the literature and the parameters values obtained after calibration. The sum of squared errors at four river stations, starting from Rogolea, is 0.002, 0.013, 0.01, and 0.024, respectively. The results show that the predicted data sets generally agree well with the measured data sets, within 20% error.

To validate the model, the calibrated model was run for a new data set collected in May 1998 [11]. As indicated in Figure 6, the general trend of the model predictions in most of the cases agrees well with the measured data set, again within 20% error. The U values at the four monitoring locations are 0.14, 0.19, 0.29, and 0.09 at Rogolea, Victory, Realdino, and Biassono, respectively. The results show that the U values at all four monitoring locations are less than 0.3; that is, it is by far less than 0.5, and hence the model fit with the measurements can be assumed acceptable.

The concentration of LAS in the benthic sediment is simulated and found to be generally very low (see Fig. 7). The concentrations of sorbed LAS in the benthic sediment at 1.5 and 26 km are less than 15 μg/g and less than 1 μg/g, respectively. Unfortunately, no monitoring data are available to validate these values in the benthic sediment. However, the sorbed LAS concentration in the benthic sediment downstream of a normally operating wastewater treatment plant effluent discharge was reported to be very low (<1 μg/g) [34,35]. The concentration decreases indeed significantly with increasing distance below the outfall (Fig. 7). This indicates that LAS will not accumulate in the aerobic river sediment because it degrades rapidly in the benthic sediment. Takada et al. [21] also indicated that LAS does not accumulate in the benthic sediment because of its fast desorption and biofilm degradation.

Scenario analysis

Comparison of steady-state and variable-flow simulation. In this subsection the consequences of four different approach-

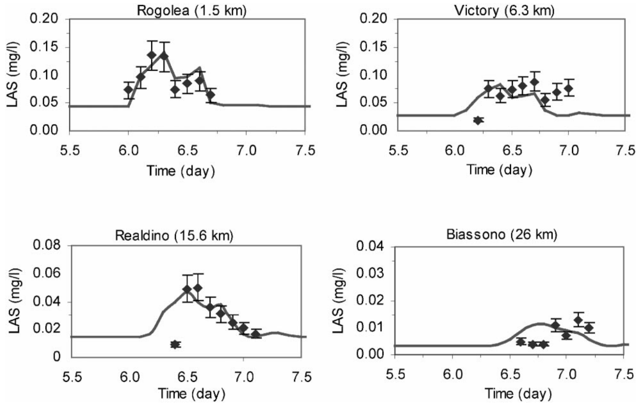

Fig. 5. Model calibration results in the Lambro River, Italy. Data are simulated (lines) and measured (symbols) total linear alkylbenzene sulfonates (LAS) concentration in the bulk water.

Table 3. Key model parameters and their calibrated values

Rank	Parameter		Literature values	References	Calibrated values
	Symbol	Description			
1	L_f	Biofilm thickness (m)	0.0001	[22,23,37,38]	0.0001
2	X_f	Biofilm density (10^3 g/m^3)	30.5–60	[22,23,37,38]	40
3	d_{bed}	Active sediment depth (m)	0.001–0.1	[27]	0.085
4	a_{bed}	Bed material specific surface area (m^2/m^3)	100	[22]	100
5	k_b	Second-order biodegradation rate coefficient (10^{-3} m^3/g/d)	4.8–35	[23]	28
6	U_{sed}	Settling velocity (m/d)	0.1–1	[18]	0.25
7	K_{OC}	Equilibrium partition coefficient (10^{-3} m^3/g)	4.8–85	[17]	5.7
8	U_{res}	Resuspension/scouring velocity (m/d)	0.0–0.005	[18,39]	0.0008

es were examined. The comparison of simulated results is indicated in Figure 8. The results show that all information about the peak can be simulated by the first approach (using variable flow). In the second approach (using averaged flow with time-variable concentration of LAS), the time profile of LAS concentration can be simulated with slight underestimation of the peak values. If one follows the third approach (constant flow with daily averaged concentration), most information related to the peak is lost. In the fourth approach (using overall averaged flow and concentration), all information related to the peak is lost.

The result suggests that though the steady-state simulation may describe the long-term averaged exposure concentration adequately, dynamic simulation is still needed to obtain details or a higher temporal resolution of exposure assessment (e.g., for pulse exposure). In pulse exposures, toxicity depends not only on the concentration but also on the frequency and the time interval between consecutive pulses [3]. A higher frequency of the pulsed exposure with a shorter time interval between the pulses can result in more toxicity than a less frequent exposure with longer pulse interval. This is due to the fact that in a longer pulse interval, the exposed organism can get enough time to recover.

The effect of nutrient dynamics on the organic contaminant fate. Using a 10-mg/L heterotrophs concentration (X_H) in the inflow, the simulation results are presented in Figure 9. The trend shows that in the low ammonia–loaded waters, increasing the ammonia nitrogen concentration up to 5 mg/L in the upstream end of the river section can enhance the removal of LAS by biodegradation. However, a further increase of ammonia concentration does not considerably improve the LAS removal rate because biodegradable soluble COD becomes limiting. By a slight increase of COD input in the upstream end, the LAS removal can further increase because of heterotrophic biomass growth. However, further increases of biodegradable soluble COD (e.g., up to 92 mg/L) decreases the removal rate because of oxygen depletion. This suggests that the interaction of nutrient dynamics and organic contaminant fate can be either positive or negative depending on which substrate is limiting. At higher concentrations of ammonia nitrogen and biodegradable soluble COD, the dissolved oxygen (S_{O_2}) is depleted, and hence the removal rate of LAS decreases. If S_{O_2} is not limiting, a small increase of nutrients (ammonia or biodegradable soluble COD) can enhance the removal rate of LAS in rivers by regulating microbial growth.

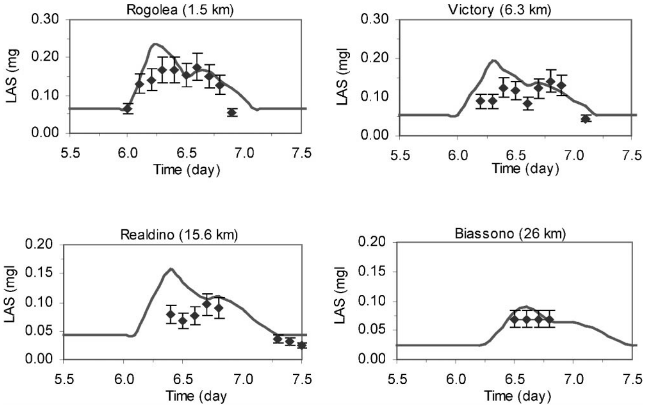

Fig. 6. Model validation results in the Lambro River, Italy. Data are simulated (lines) and measured (symbols) total linear alkylbenzene sulfonates (LAS) concentration in the bulk water.

It is also important to note that Figure 9 seems to indicate that an increase in nutrients has minimal consequences to the predicted exposure levels. This may not always be the case. Recent experimental studies (a microcosm study), in the continuation of this study, showed that the exposure level of LAS is very sensitive to ammonia but relatively less sensitive to the readily biodegradable COD [36]. This is due to the fact that ammonia enhances the activities of ammonia oxidizers, which are responsible for the LAS degradation. In the simulation study, a sensitivity analysis was also made (submitted to the IWA World Congress and Exhibition, Marrakech, Morocco, September 19–24, 2004), and the results show that the model output (LAS concentration) is very sensitive to ammonia nitrogen, heterotrophic microbial biomass, and dissolved oxygen but is less sensitive to the concentration of COD. The reason is that ammonia nitrogen, microbial biomass, and dissolved oxygen are explicitly considered in the organic contaminant fate submodel, while increasing the COD level only indirectly influences LAS degradation by regulating the growth of heterotrophic biomass and increasing oxygen consumption.

Furthermore, consider the previously mentioned scenario analysis in oligotrophic and eutrophic systems. It is obvious that nutrient is limiting in an oligotrophic system, and therefore a little increase of nutrient can enhance LAS removal, whereas in a eutrophic system, S_{O2} is limiting, and more nutrient load to the system can result in further depletion of S_{O_2}, which in turn can lead to a decrease of LAS degradation. Note that sorption to the high concentration of suspended solids in the eutrophic system can also cause dilution of the contaminants.

CONCLUSION

A dynamic fate model of xenobiotic organic chemicals in a river system was presented using a conceptual hydrological simplification and local sorption equilibrium. The model was

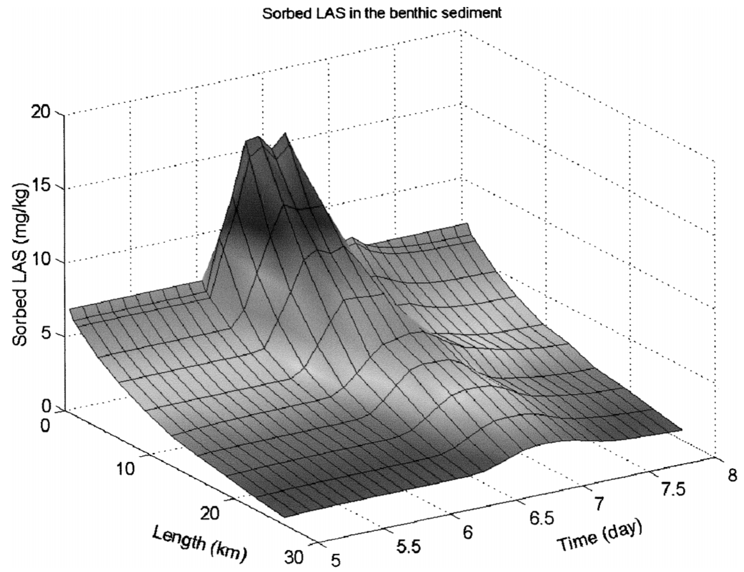

Fig. 7. Simulated sorbed linear alkylbenzene sulfonates (LAS) concentration in the benthic sediment of the Lambro River, Italy.

evaluated on the basis of a LAS case study in the Lambro River. Model predictions and measured data were compared, and a parameter sensitivity analysis of the model was presented.

The model sensitivity analysis results show that the model output is very sensitive to the biodegradation parameters (e.g., d_{bed}, a_{bed}, X_{f}, and L_{film}) as compared to the other parameters (e.g., sedimentation, resuspension, and partition coefficient). The important biodegradation parameters are mainly biofilm biodegradation parameters, which indicates that these parameters need to be measured or estimated accurately.

Coupling of dissolved oxygen and organic contaminant to biodegradation and allowing variation of biodegradation with the sorbed fraction are important considerations in the short-term analysis of organic contaminant fate in rivers. This is due to the fact that LAS degrades only in aerobic conditions. Furthermore, LAS has a high affinity to be sorbed to organic carbons.

Assuming that the model validation result is accepted, the usefulness of the proposed model was evaluated on the basis of scenario analysis. In the first scenario analysis, dynamic and steady-state simulations were compared. This comparison illustrated that for short-term simulation, more information is required to simulate the short-term dynamics of the environment. In such a case, a dynamic simulation needs to be considered. When one is interested only in long-term simulation, the steady-state simulation can be considered. Based on this analysis, it can be concluded that the choice of either dynamic or steady-state simulation depends on the required information. The availability of data also needs to be considered. Dynamic simulation is, however, a realistic approach, as the environment is indeed not at steady state because of runoff events and sewer overflows. Consequently, in the real environment organisms may be exposed to single or multiple pulses [3].

In the second scenario analysis, the effect of ammonia and readily biodegradable COD on the fate of LAS was examined. The results confirm the importance of integrating modeling of the fate of conventional pollutants and xenobiotic organic compounds in rivers, as it allows one to study the interaction of the two [7].

The limitation of the proposed model is that the conceptual hydraulic model (CSTRS) does not simulate backwater effects due to dams, weirs, or tidal effects. For the backwater effect problem, complex hydrodynamic models (St. Venant equations) can be applied. The model comprises an extensive complex biodegradation submodel, and as such it is suitable to assess the fate of aerobically biodegradable xenobiotic organic compounds in rivers or streams. If anaerobic degradation needs to be included in the model as well, only minor modifications are needed. Besides, for persistent or nonbiodegradable organic contaminants, the proposed extensive biodegradation

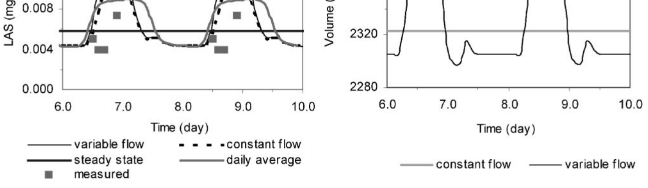

Fig. 8. Comparison of the steady-state and dynamic simulations for linear alkylbenzene sulfonates (LAS) concentration (**a**) and river stretch flow volume (**b**) in the Lambro River, Italy. In steady state, both flow and LAS concentration are assumed constant over time.

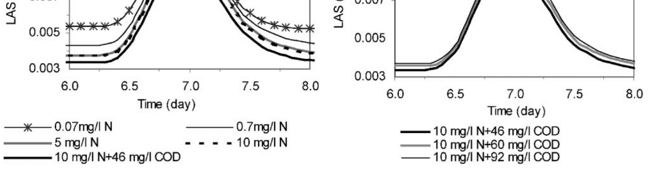

Fig. 9. The effect of nutrient dynamics on the fate of linear alkylbenzene sulfonates (LAS) in the last river section (26 km) in the Lambro River, Italy. Data are ammonia nitrogen (N) and chemical oxygen demand (COD) (as a measure of carbonaceous organic matters).

submodel is not required and can be omitted. In this way the computation time can be decreased.

In the future, the applicability of the proposed model needs to be further evaluated/validated using more data sets. The model prediction of the exposure level in the benthic sediment also needs to be evaluated. As eutrophication (mainly algal blooms) can have considerable effects on the fate and effect of organic contaminants [7], the proposed model needs to be extended to include algal blooms so that the interactions of eutrophication and contamination by xenophobic organic compounds in rivers or streams can be studied.

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