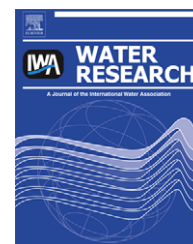


Available at [www.sciencedirect.com](http://www.sciencedirect.com)journal homepage: [www.elsevier.com/locate/watres](http://www.elsevier.com/locate/watres)

# Dynamic experiments with high bisphenol-A concentrations modelled with an ASM model extended to include a separate XOC degrading microorganism

Erik Lindblom<sup>a,\*</sup>, Kåre Press-Kristensen<sup>a</sup>, Peter A. Vanrolleghem<sup>b</sup>, Peter S. Mikkelsen<sup>a</sup>, Mogens Henze<sup>a</sup>

<sup>a</sup>Department of Environmental Engineering, Technical University of Denmark, Bygningstorvet, Building 115, DK-2800 Kongens Lyngby, Denmark

<sup>b</sup>modelEAU, Département de génie civil, Université Laval, Laval, QC G1K 7P4, Canada

## ARTICLE INFO

### Article history:

Received 5 January 2009

Received in revised form

14 April 2009

Accepted 16 April 2009

Published online 3 May 2009

### Keywords:

Activated sludge

Bisphenol-A

Model

Parameter estimation

Wastewater

Xenobiotic organic compound

## ABSTRACT

The perspective of this work is to develop a model, which can be used to better understand and optimize wastewater treatment plants that are able to remove xenobiotic organic compounds (XOCs) in combination with removal of traditional pollutants. Results from dynamic experiments conducted with the endocrine disrupting XOC bisphenol-A (BPA) in an activated sludge process with real wastewater were used to hypothesize an ASM-based process model including aerobic growth of a specific BPA-degrading microorganism and sorption of BPA to sludge. A parameter estimation method was developed, which simultaneously utilizes steady-state background concentrations and dynamic step response data, as well as conceptual simplifications of the plant configuration. Validation results show that biodegradation of BPA is sensitive to operational conditions before and during the experiment and that the proposed model structure is capable of capturing important characteristics of the observed BPA removal, thus increasing the potential for generalizing knowledge obtained from plant specific experiments.

© 2009 Elsevier Ltd. All rights reserved.

## 1. Introduction

The influent to a typical municipal wastewater treatment plant (WWTP) may contain several thousand different xenobiotic organic compounds (XOCs) originating from e.g. pharmaceuticals, chemicals, personal care products and hormones, which are discharged into wastewater from e.g. households, hospitals and the industry. In WWTPs, XOCs are removed by on the one hand physical-chemical processes such as sorption and volatilization and on the other hand by biological degradation. Still, hazardous XOCs are being

detected in WWTP effluents in potentially toxic concentrations due to insufficient removal (Press-Kristensen et al., 2007).

Biological degradation is an important removal process in WWTPs for several XOCs as well as for the estrogenic effect of wastewater (Jacobsen and Guildal, 2000; Bachman Christiansen et al., 2002; Fauser et al., 2003; Tanaka et al., 2003). The extent of biodegradation of a specific XOC will be a function of operational conditions (e.g. the plant configuration, the hydraulic retention time (HRT), the sludge retention time (SRT)), environmental parameters (e.g. temperature) as well as of compound-specific parameters (e.g. sorption potential,

\* Corresponding author. Tel.: +46 (0)709 996941; fax: +46 (0)8 402 1281.

E-mail address: [erik.lindblom@dhi.se](mailto:erik.lindblom@dhi.se) (E. Lindblom).

0043-1354/\$ – see front matter © 2009 Elsevier Ltd. All rights reserved.

doi:10.1016/j.watres.2009.04.030

Nomenclature			
$b_{\text{XOC}}$	decay rate ( $\text{d}^{-1}$ )	$X_{\text{B,A}}$	concentration of active autotrophic biomass ( $\text{mg COD l}^{-1}$ )
BPA	bisphenol-A	$X_{\text{B,H}}$	concentration of active heterotrophic biomass ( $\text{mg COD l}^{-1}$ )
HRT	hydraulic retention time (d)	$X_{\text{B,XOC}}$	concentration of specific XOC degrading bacteria ( $\mu\text{g COD l}^{-1}$ )
$k_{\text{sor}}$	sorption rate ( $\text{l mg VSS}^{-1} \text{d}^{-1}$ )	$X_{\text{S}}$	concentration of slowly biodegradable substrate ( $\mu\text{g COD l}^{-1}$ )
$k_{\text{des}}$	desorption rate ( $\text{d}^{-1}$ )	$X_{\text{XOC}}$	particulate concentration of XOC ( $\mu\text{g COD l}^{-1}$ )
$K_{\text{d}}$	solid/liquid partition coefficient ( $\text{l g SS}^{-1}$ )	$X_{\text{P}}$	concentration of particulate products arising from biomass decay ( $\mu\text{g COD l}^{-1}$ )
$K_{\text{O,XOC}}$	half saturation coefficient for oxygen ( $\text{mg -COD l}^{-1}$ )	XOC	xenobiotic organic compound (in this paper bisphenol-A)
$K_{\text{XOC}}$	half saturation coefficient for XOC ( $\mu\text{g COD l}^{-1}$ )	$Y_{\text{XOC}}$	yield coefficient (g COD biomass formed per g COD XOC oxidized)
$Q_{\text{in}}$	influent flow rate ( $\text{m}^3 \text{d}^{-1}$ )	$\theta$	Temperature correction factor (-)
$Q_{\text{w}}$	wastage sludge flow rate ( $\text{m}^3 \text{d}^{-1}$ )	$\gamma_{\text{aer}}$	Fraction of aerobic reactor volume (%)
$S_{\text{O}}$	dissolved oxygen concentration ( $\mu\text{g -COD l}^{-1}$ )	$\hat{\mu}_{\text{XOC}}$	Maximum specific growth rate ( $\text{d}^{-1}$ )
$S_{\text{XOC}}$	soluble concentration of XOC ( $\mu\text{g COD l}^{-1}$ )	in	index denoting influent
SRT	sludge retention time (d)	0	index denoting initial condition
SS	suspended solids ( $\text{mg l}^{-1}$ )	*	Index denoting steady state conditions
T	temperature of activated sludge ( $^{\circ}\text{C}$ )		
ThOD	theoretical oxygen demand		
V	total reactor volume ( $\text{m}^3$ )		
VSS	volatile suspended solids ( $\text{mg l}^{-1}$ )		

degradability). Our ability to optimize and control XOC removal in activated sludge systems depends on our understanding of these parameters and how they interact with the removal processes. Mathematical models describing WWTP processes are excellent tools for analyzing such interconnections and can today be regarded as state-of-the-art at both universities and among practitioners, especially when aiming to generalize knowledge attained from plant specific experiments.

For dynamic biological and chemical activated sludge processes, the models prepared by the International Water Association (IWA) Task Group on Mathematical Modelling for Design and Operation of Biological Wastewater Treatment are the most widespread (Henze et al., 2000). These models were developed to describe removal of chemical oxygen demand (COD), nitrogen and phosphorus and are not concerned with specific chemical compounds. Therefore, they cannot be applied directly to establish the fate and transport of XOCs and consequently models for this have been developed and published. An example of a frequently cited static fate model is the SimpleTreat model (Struijs, 1996). Among the dynamic models, they range from simple first order kinetic models (e.g. Melcer et al., 1994) to more complex models considering inhibition kinetics (Siegrist et al., 1989) and metabolic models (e.g. Carvalho et al., 2004).

The aim of this work was to formulate, calibrate and validate a process model for the removal of bisphenol-A (BPA) in activated sludge systems using data from an experiment designed to investigate the possible presence of specific BPA-degrading biomass. BPA is a widely used endocrine disrupting chemical mainly originating from polycarbonate. During the model formulation phase, we strived to apply the most simple model capable of describing the observations as well as a model that can easily be combined with the traditional growth-based activated sludge models in Henze et al. (2000). The perspective is to develop an integrated model structure, which after calibration can be used for designing and operating WWTPs removing XOCs in addition to other organic matter and nutrients.

## 2. Material and methods

### 2.1. The pilot plant

Experiments were performed in a pilot plant placed next to the Lynetten WWTP receiving a mixture of urban and industrial wastewater from Copenhagen, Denmark. The pilot plant is operated as the activated sludge system of the full scale plant and includes one anaerobic reactor, two aerobic/anoxic reactors operated according to the BIODENIPHO™ principle (see Henze et al., 2002) and one secondary clarifier. The influent to the pilot plant consists of a fixed constant flow with preclarified wastewater from the full-scale plant. The wastage sludge is taken directly from the aeration basins, i.e. thickening in the settler does not need to be considered for the calculation of the SRT. Table 1 summarizes the operational conditions of the plant during the experiments.

**Table 1 – Operational conditions of the pilot plant during the three experiments. SRT =  $V/Q_{\text{w}}$ .**

Parameter		Experiment		
		Background	Dosage 1	Dosage 2
Influent flow rate	$Q_{\text{in}}$ ( $\text{m}^3 \text{d}^{-1}$ )	10	12	10
Wastage sludge flow rate	$Q_{\text{w}}$ ( $\text{m}^3 \text{d}^{-1}$ )	0.43	0.23	0.43
Total reactor volume	V ( $\text{m}^3$ )	11.6	11.6	11.6
Sludge retention time	SRT (d)	27	50	27
Fraction of aerobic reactor volume	$\gamma_{\text{aer}}$ (%)	43	39	43
Temperature of activated sludge	T ( $^{\circ}\text{C}$ )	13–16	15–16	19–22

2.2. Bisphenol-A

Solid/liquid partition coefficients ( $K_d$ ) for BPA in literature range from 0.07 l g SS<sup>-1</sup> (ECB, 2003) up to 1 l g SS<sup>-1</sup> (Clara et al., 2004). Henry's law constant for BPA is  $1.7 \times 10^{-9}$  (ECB, 2003) and BPA can thereby be considered as non-volatile in WWTPs. In Kjølholt et al. (2003) it is concluded that BPA is readily biodegradable under aerobic conditions and that biodegradation under anoxic and anaerobic conditions is unlikely. The theoretical oxygen demand (ThOD) for BPA (C<sub>15</sub>H<sub>16</sub>O<sub>2</sub>) is 2.5 g O<sub>2</sub> per gram BPA.

2.3. Sampling and analyses

Grab samples were collected from the (pre-settled) influent and effluent with a 2-litre jug made of polypropylene. One-litre blue-cap bottles were used as containers. Sodium azide (2.5 g) was added as preserving agent. The samples were stored at 15 °C less than 3 weeks before extraction. BPA was extracted and quantified by liquid-liquid extraction with di-isopropyl ether. BPA-d6 was used as internal standard. Analyses were done using GC-MS. All analyses were conducted with non-filtered samples, e.g. the presented results represent the total (soluble + particulate) BPA concentration. The sampling and analysis procedure is further described in Press-Kristensen (2007).

2.4. Experimental protocol

The experimental results have been grouped into three data sets: one set (*Background*) that is assumed to represent steady-state conditions (constant average daily means) of the plant and two data sets with constant flow but with dynamic step changes of the influent BPA concentration (*Dosage 1* and *Dosage 2*). The operational conditions of the pilot plant during the three experiments are given in Table 1.

*Background:* Thirty-nine influent and 19 effluent samples were collected and analysed for total BPA concentration. The results from these are summarized in Table 2.

*Dosage 1:* The influent wastewater was continuously spiked with 10 g BPA per day, which together with the background levels corresponds to a total influent BPA concentration of 842 µg l<sup>-1</sup>. Ninety-one grab samples were collected from the effluent during 46 days and analysed for total BPA concentration. The experimental results are shown as dots in Fig. 1.

*Dosage 2:* The influent wastewater was continuously spiked with 10 g BPA per day, corresponding to a total influent BPA concentration of 1009 µg l<sup>-1</sup>. Forty-six grab- and flow-proportional samples were collected from the effluent during 34 days and analysed for total BPA concentration. The experiment had

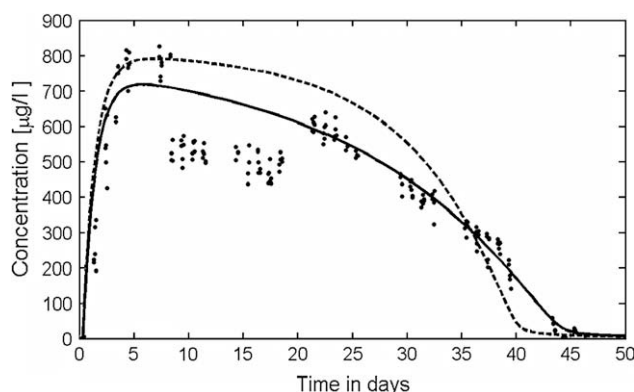


Fig. 1 – Calibration of BPA model based on the *Background* and *Dosage 1* experiments. Dots: Measured effluent BPA concentrations. Dashed line: Estimation i. Solid line: Estimation ii.

been preceded by continuous addition of 1 g BPA d<sup>-1</sup> over 60 days. This corresponds to a total influent BPA concentration of 109 µg l<sup>-1</sup>. The experimental results are shown as dots in Fig. 2.

3. The model

3.1. Rationale

The step response to *Dosage 1* (Fig. 1) shows that the measured effluent BPA concentration converged towards the influent concentration after approximately 5 days. The delay in the response is to a large degree explained by the dilution process and thus the experimental results suggest that removal processes in the fast dynamic region, such as sorption and volatilization, are not dominant for the fate of BPA. This is in accordance with the chemical properties of BPA given above.

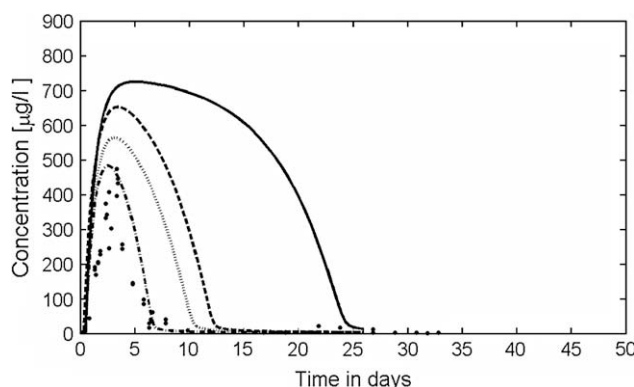


Fig. 2 – Evaluation of BPA model by simulating the *Dosage 2* experiment. Dots: Measured effluent BPA concentrations. Solid line: No preceding BPA dosage. Temperature corrections according to the heterotrophs ( $X_{B,H}$ ) of ASM1. Dashed line: Temperature corrections according to  $X_{B,H}$ . Dotted line: Temperature corrections according to the autotrophs ( $X_{B,A}$ ) of ASM1. Dashed-dotted line: Fitted temperature corrections.

Table 2 – Results from the *Background* experiment. SD: standard deviation. Measured influent and effluent total BPA concentrations in µg BPA l<sup>-1</sup>.

	Mean	Minimum	Maximum	SD	Median
Influent	8.7	5.5	19	3.2	7.9
Effluent	4.1	1.0	11.1	2.8	3.4

The subsequent BPA removal increases during 40 days until the measured effluent concentrations were at the same level as during the *Background* experiment. Despite the high SRT of the period (50 days), it was judged that new steady state effluent concentrations had been obtained after 46 days and the experiments were ended. Regarding the removal, which increases over time, it is logical to assume that the biomass capable of degrading BPA in the system also increases. The most simple explanation is growth of specific heterotrophic organisms of the activated sludge. The observed biodegradation during the *Background* experiment (Table 2) is consistent with the assumption that such degraders are naturally present in the activated sludge. The results from a number of batch experiments (Press-Kristensen, 2007) showed that if this explanation is true, the growth is carried out under aerobic conditions; no biological degradation was observed during anoxic or anaerobic conditions. Based on the above considerations the WWTP process model used in Lindblom et al. (2006), which includes aerobic biodegradation and sorption/desorption, has been considered as hypothesized below.

It should be noted that the upcoming model formulation is one of several possible hypotheses and that other biological models are possible as well. At low concentrations such as during the *Background* experiment, a mixed substrate growth model (co-metabolism) might be closer to reality. The formation of non-biodegradable or slowly-biodegradable metabolic intermediates, instead of complete mineralization as proposed here, or metabolization of BPA by nitrifying biomass (Kim et al., 2007), are also possible mechanisms not considered by the proposed model.

The experimental data shown in this paper establish the presence and growth of BPA-degrading biomass. The used data do not contain information about the behaviour of this biomass on other substrates, nor about relevant metabolites. What is clear from the experimental and modelling results though, is that the mechanism, by which the removal capacity for BPA is introduced in the biomass, is due to growth and not due to the activation of enzymes that are non-constitutively present in the biomass. The time constant of the latter process is much faster than what is observed here (Roels, 1983).

In Lindblom et al. (2006) it was assumed that the BPA-degrading biomass could also use readily biodegradable COD as an energy and carbon source. The experience from this

simulation study was however that the relation between the influent concentration of specific XOC degrading bacteria and traditional heterotrophic microorganisms was a very uncertain and sensitive model parameter. This approach cannot be motivated here; only under special situations (e.g. absence of other COD sources in the influent) such a more complex model would lead to a better system description. A simple single substrate growth-based model is instead formulated, serving as a first step towards understanding the optimal way of describing the removal of BPA in engineered activated sludge systems.

### 3.2. Model formulation

The proposed XOC model is here shown as an add-in to the activated sludge model ASM1 (Henze et al., 1987). The structure is however general and possible to integrate with other ASMs as well. It includes three additional model components (formulated in COD units) and four additional processes, as summarized in the matrix notation of Table 3. The three components are the soluble concentration of (non-dissociated) XOC,  $S_{XOC}$  ( $\mu\text{g COD l}^{-1}$ ), the particulate concentration of XOC,  $X_{XOC}$  ( $\mu\text{g COD l}^{-1}$ ) and a third component describing the concentration of specific XOC degrading bacteria,  $X_{B,XOC}$  ( $\mu\text{g COD l}^{-1}$ ). The COD of an XOC is assumed to equal its ThOD.

#### 3.2.1. Removal to solids

Although a majority of previously published models for XOCs in WWTPs assume instant equilibrium between the concentration of sorbed and soluble XOC, chemical equilibrium is not attained instantaneously. To allow for possible slow established equilibria, the distribution of an XOC between the water phase and the activated sludge is therefore described with two reverse processes. The structure mimics the one of Jacobsen and Arvin (1996), as well as the way chemical phosphorus precipitation is described in ASM2d (Henze et al., 1999). Sorption is modelled as a mixed second order expression including a sorption rate  $k_{sor}$  ( $\text{l mg VSS}^{-1} \text{d}^{-1}$ ), the concentration of soluble XOC and the concentration of volatile suspended solids VSS ( $\text{mg l}^{-1}$ ). VSS is calculated from the particulate COD components of ASM1 assuming an average COD/VSS ratio of 0.75. Sorption to inorganic particulate material is not considered. Desorption is assumed to be

**Table 3 – The proposed model in matrix notation. VSS is calculated from the particulate COD components of ASM1 assuming an average COD/VSS ratio of 0.75.**

i Component → j Process ↓	1 $S_O$	2 $S_{XOC}$	3 $X_{XOC}$	4 $X_{B,XOC}$	Process rate ↓
1 Aerobic growth of specific organisms on XOC	$\frac{1 - Y_{XOC}}{Y_{XOC}}$	$\frac{1}{Y_{XOC}}$		1	$\hat{\mu}_{XOC} \cdot \left( \frac{S_O}{K_{O,XOC} + S_O} \right) \cdot \left( \frac{S_{XOC}}{K_{XOC} + S_{XOC}} \right) \cdot X_{B,XOC}$
2 Decay of specific organisms				$-1^a$	$b_{XOC} \cdot X_{B,XOC}$
3 Sorption of XOC		$-1$	1		$k_{sor} \cdot S_{XOC} \cdot VSS$
4 Desorption of XOC		1	$-1$		$k_{des} \cdot X_{XOC}$
	Oxygen [g –COD m <sup>-3</sup> ]	Soluble XOC [g COD m <sup>-3</sup> ]	Sorbed XOC [g COD m <sup>-3</sup> ]	Specific XOC degraders [g COD m <sup>-3</sup> ]	Kinetic parameters: $\hat{\mu}_{XOC}, b_{XOC}, K_{O,XOC}, K_{XOC}, k_{sor}, k_{des}$
					Stoichiometric parameter: $Y_{XOC}$

a Decay of specific XOC degraders produces  $X_S$  and  $X_P$  (in ASM1).

proportional to the concentration of particulate XOC in a first order manner with a desorption rate  $k_{des}$  ( $d^{-1}$ ). For a vessel without inflow, outflow or other reactions the ratio  $k_{sor}/k_{des}$  will equal  $X_{XOC} (S_{XOC} \cdot VSS)^{-1}$  at equilibrium, i.e. be proportional to the  $K_d$  value, which can be used for calibration. The dynamics can be assumed to be fast if no other information is available.

### 3.2.2. Removal by biological degradation

Degradation of BPA is assumed to be performed by a specific population of the microbial community,  $X_{B,XOC}$  ( $\mu g \text{ COD l}^{-1}$ ), which possesses the genetic capability to metabolize the XOC under aerobic conditions and utilize it for growth. In the proposed model the BPA specialists grow with  $S_{XOC}$  as the single substrate with growth rate determined by the maximum specific growth rate  $\hat{\mu}_{XOC}$  ( $d^{-1}$ ) and half saturation coefficients  $K_{XOC}$  ( $\mu g \text{ COD l}^{-1}$ ) and  $K_{O,XOC}$  ( $mg -COD l^{-1}$ ). The decay follows the same 1<sup>st</sup> order kinetics as in ASM1, with decay rate  $b_{XOC}$  ( $d^{-1}$ ). The degradation process will finally depend on the yield coefficient  $Y_{XOC}$  ( $g \text{ COD biomass formed/g COD oxidized}$ ).

## 4. Model parameter tuning

The data from the *Background* and *Dosage 1* experiments were used for calibration of the model parameters. The *Dosage 2* data were subsequently used for model validation.

### 4.1. Simplifying the plant configuration

Although average daily means can be assumed to be constant in the Biotenpho™ system, it is never at steady state from a mathematical viewpoint. This, together with the sometimes long SRT (50 days during the *Dosage 2* experiment) of the plant involves that for every model parameter set to be evaluated, a long (time-consuming) dynamic simulation needs to be done. Therefore, to estimate the parameters in this paper the plant configuration was mathematically simplified to a chemostat with a constant inflow and outflow  $Q_{in}$  ( $m^3 d^{-1}$ ), a total volume  $V$  ( $m^3$ ) and wastage sludge flow rate  $Q_w$  ( $m^3 d^{-1}$ ). By including the processes shown in the matrix (Table 3) the following three model equations are obtained:

$$\frac{dS_{XOC}}{dt} = \frac{Q_{in}}{V} \cdot (S_{XOC,in} - S_{XOC}) - \frac{\mu_{XOC} \cdot \gamma_{aer}}{Y_{XOC}} \cdot X_{B,XOC} - k_{sor} \cdot S_{XOC} \cdot VSS + k_{des} \cdot X_{XOC} \quad (1)$$

$$\frac{dX_{XOC}}{dt} = k_{sor} \cdot S_{XOC} \cdot VSS - \left( k_{des} + \frac{Q_w}{V} \right) \cdot X_{XOC} \quad (2)$$

$$\frac{dX_{B,XOC}}{dt} = \left( \mu_{XOC} \cdot \gamma_{aer} - b_{XOC} - \frac{Q_w}{V} \right) \cdot X_{B,XOC} \quad (3)$$

with

$$\mu_{XOC} = \mu_{XOC}(S_{XOC}) = \hat{\mu}_{XOC} \cdot \left( \frac{S_{XOC}}{K_{XOC} + S_{XOC}} \right) \quad (4)$$

The Monod function for oxygen ( $S_O/(K_{O,XOC} + S_O)$ ) was replaced by a parameter for the fraction of aerobic volume,

$\gamma_{aer}$  (-). It was thus assumed that the Monod-term was one under aerobic conditions and zero else. The relatively low concentrations of suspended solids in the influent ( $\approx 100 \text{ mg l}^{-1}$ ) and effluent ( $\approx 5\text{--}10 \text{ mg l}^{-1}$ ) of the pilot plant and the  $K_d$  value for BPA states that the soluble form of BPA in the sampled streams is dominating and therefore particulates in the influent and effluent have been neglected in the model. Compared to the full system model, the equations consider neither the transient concentrations of the Biotenpho process nor any dynamics governed by the settling process. It is assumed that these simplifications do not have a significant impact upon the results and conclusions. In the following, the measured operational parameters  $Q_{in}$ ,  $Q_w$  and  $V$  were adopted as given in Table 1.  $\gamma_{aer}$  was calculated based upon information of the phase operation of the Biotenpho process during the periods.

### 4.2. Sorption parameters

We applied  $k_{des} = 1000 \text{ d}^{-1}$  and  $k_{sor} = 0.5 \text{ l mg VSS}^{-1} \text{ d}^{-1}$ , which gives results that are in accordance with both the experimental results in Fig. 1 and with other sludge analyses (Press-Kristensen, 2007). The chosen sorption parameter values correspond to a  $K_d$  of  $0.5 \text{ l g}^{-1} \text{ VSS}$ , i.e. approximately to the mid-point of the wide range of the literature partition coefficients. It is however noted that choosing even the highest reported literature value for  $K_d$  ( $1 \text{ l g}^{-1} \text{ SS}$ ) would result in less than 7% of the influent BPA load being removed by sorption in the *Dosage 1* experiment, i.e. the choice of sorption parameters are not very sensitive to the following results.

### 4.3. Biological process parameter estimation

For the determination of the biological process parameters, the rate of the sorption–desorption process was assumed to have a small effect and thus immediate sorption equilibrium was assumed. With  $dX_{XOC}/dt = 0$ , Eq. (2) was then used to express  $X_{XOC}$  as a function of  $S_{XOC}$  and  $Q_w$ :

$$X_{XOC} = \frac{k_{sor} \cdot VSS}{k_{des} + Q_w/V} \cdot S_{XOC} \quad (5)$$

which, if inserted to Eq. (1) gives:

$$\frac{dS_{XOC}}{dt} = \frac{Q_{in}}{V} \cdot S_{XOC,in} - A \cdot S_{XOC} - \frac{\mu_{XOC} \cdot \gamma_{aer}}{Y_{XOC}} \cdot X_{B,XOC} \quad (6)$$

with

$$A = \frac{Q_{in}}{V} + \frac{k_{sor} \cdot VSS \cdot Q_w/V}{k_{des} + Q_w/V} \quad (7)$$

where the first term in  $A$  accounts for disposal with the effluent and the second term for removal with the wastage sludge.

With the above assumptions the model consists of Eq. (3) and Eq. (6), where the parameters  $\hat{\mu}_{XOC}$ ,  $K_{XOC}$ ,  $b_{XOC}$  and  $Y_{XOC}$  need to be given numerical values. If as here, step response data are used for calibration, the initial conditions  $S_{XOC}^0$  and  $X_{B,XOC}^0$  must be evaluated as well. Although we strived to apply the simplest model capable of describing our observations, the remaining parameters of the Monod model are correlated and

the current experiments not extensive enough to allow a separate identification of all new parameters. Therefore, as will be explained below, some were assumed to be known while others were estimated from the data of the *Dosage 1* and *Background* experiments simultaneously.

$Y_{XOC}$  was assumed to be 0.67 g cell COD formed g COD<sup>-1</sup> oxidized, which corresponds to a typical yield for aerobic oxidation of organic matter; yields for aerobic degrading organisms do not vary strongly and are in the range of 0.55–0.7 (Henze et al., 2000, 2002). It was assumed that data did not contain information enough to differentiate  $\hat{\mu}_{XOC}$  from  $b_{XOC}$ , and therefore the decay rate at 15 °C was assumed to be 0.05 d<sup>-1</sup>. With these assumptions, four parameters still needed to be fitted:  $\hat{\mu}_{XOC}$ ,  $K_{XOC}$  and the initial conditions  $S_{XOC}^0$  and  $X_{B,XOC}^0$ .

If steady-state conditions (indexed with \* below) are known, this information can be included in the estimation procedure as follows: From Eqs. (3) and (4), it is seen that the modelled steady state effluent concentration ( $S_{XOC}^*$ ) is solely a function of the biological process parameters and sludge age (e.g. not dependent on the influent concentration). For a fixed value of  $S_{XOC}^*$ , Eqs. (3) and (4) can be used to express  $K_{XOC}$  as a function of  $\hat{\mu}_{XOC}$ :

$$K_{XOC} = K_{XOC}(\hat{\mu}_{XOC}) = \left( \frac{\hat{\mu}_{XOC} \cdot \gamma_{aer}}{b_{XOC} + Q_w/V} - 1 \right) \cdot S_{XOC}^* \quad (8)$$

$$\hat{\mu}_{XOC} > \frac{b_{XOC} + Q_w/V}{\gamma_{aer}}$$

where the constraint is included to not allow negative  $K_{XOC}$  values. The steady state specific biomass concentration will depend on the influent ( $S_{XOC,in}^*$ ) and effluent steady-state concentrations, i.e. the steady state XOC removal. From Eqs. (6) and (4) we have:

$$X_{B,XOC}^* = X_{B,XOC}^*(\hat{\mu}_{XOC}) = \frac{Y_{XOC}}{\mu_{XOC}(S_{XOC}^*) \cdot \gamma_{aer}} \cdot \left( \frac{Q}{V} \cdot S_{XOC,in}^* - A \cdot S_{XOC}^* \right) \quad (9)$$

Thus, if it is assumed that the effluent XOC concentration prior to a step dosage equals the effluent steady state concentration,  $\hat{\mu}_{XOC}$  can be estimated by minimizing the sum of squared errors between simulated (Eqs. (3) and (6)) and measured effluent concentrations, with  $K_{XOC}$  replaced with Eq. (8) and  $X_{B,XOC}^0$  with Eq. (9). By following these steps, the maximum growth rate is estimated from the high concentration XOC data during dosage while the half-saturation constant is found from the low concentration data during normal conditions.

Following the parameter estimation methodology derived above we assumed that, in a first estimation attempt (estimation i), the measured mean XOC concentrations of the *Background* experiment reflected steady state influent and effluent concentrations, and that the influent concentration were representative also for the period prior to *Dosage 1*.  $K_{XOC}$  was expressed with Eq. (8) with  $S_{XOC}^*$  being the mean *Background* effluent concentration (4.1 µg l<sup>-1</sup>) and operational parameters according to the *Background* experiment. The initial specific biomass concentration was calculated from Eq. (9) with  $S_{XOC,in}^*$  being the mean *Background* influent concentration (8.7 µg l<sup>-1</sup>) and operational parameters according to *Dosage 1*.

## 5. Results and discussion

### 5.1. Calibration results

The results of the first estimation (i) of the parameter  $\hat{\mu}_{XOC}$  on the step response data can be seen as the dashed line in Fig. 1. The values of the estimates are given in Table 4 (column i). The estimated maximum specific growth rate (0.47 d<sup>-1</sup>) and the assumed decay rate (0.05 d<sup>-1</sup>) reveal similar kinetic characteristics of the specific BPA degraders as those of the slow growing nitrifying bacteria in ASM1. An aerobic sludge retention time above 13 d is required to support growth of BPA degrading bacteria, which means that growth on BPA will always be with simultaneous nitrification. Since  $X_{B,XOC}$  constitute a very small fraction of the biomass, it has little relevance whether the BPA degraders are autotrophic or heterotrophic. The simulated effluent BPA concentration shows a reasonable fit to the experimental data considering the time required to reach a new steady-state effluent concentration.

The two data clouds between  $t = 7.5$  d and  $t = 20$  d cannot be explained with the model proposed here and therefore these data have been excluded from the objective function in the optimization algorithm. We studied time series data of flow rates and temperature as well as both plant laboratory and on-line suspended solids and water quality concentration data to come up with an explanation for the trend of low BPA concentrations in this period. This attempt failed and we can only conclude that there are a number of uncertainties, for example uncertainty in the observations, e.g. in the sampling and analytical procedures, uncertainty in the input data, e.g. in data on plant operation settings or in the dosage equipment, and/or uncertainty in the hypothesized model structure.

One interpretation of the results of estimation i is a too high estimate of  $\hat{\mu}_{XOC}$ , which can be seen as a steeper slope of the simulated degradation compared to the measured data during  $t = 20$  d to  $t = 45$  d. The reason for this is that the initial biomass concentration proposed by the results of the *Background* experiment (83 µg COD l<sup>-1</sup>, Eq. (9)), require a maximum growth rate of this estimated magnitude to accurately predict the time to reach the new steady state. Therefore, in a second attempt (estimation ii) we evaluated whether improvement of the fit could be obtained by allowing a different initial biomass concentration than the one following from Eq. (9).  $K_{XOC}$  was still calculated as in i, which ensured an estimate in accordance with the *Background* effluent concentration results, but

**Table 4 – Results from biological process model parameter estimation on step response data of *Dosage 1* for T = 15 °C.**

Parameter	Estimation	
	i	ii
$\hat{\mu}_{XOC}$ (d <sup>-1</sup> )	0.47	0.34
$K_{XOC}$ (µg COD l <sup>-1</sup> )	13	6.8
$X_{B,XOC}^0$ (µg COD l <sup>-1</sup> )	83	666
$S_{XOC}^0$ (µg COD l <sup>-1</sup> )	10	10

in this case both  $\hat{\mu}_{XOC}$  and  $X_{B,XOC}^0$  were estimated from the data.

The results of the estimation (ii) of the parameter  $\hat{\mu}_{XOC}$  and  $X_{B,XOC}^0$  on the step response data can be seen as the solid line in Fig. 1. The values of the estimates are given in Table 4 (column ii). The results show a different and perhaps better fit than (i) considering the slope of the step response. The estimate gave a lower  $\hat{\mu}_{XOC}$  ( $0.34 \text{ d}^{-1}$ ), a lower  $K_{XOC}$  ( $6.8 \mu\text{g COD l}^{-1}$ ) and a significantly higher value of  $X_{B,XOC}^0$  ( $666 \mu\text{g COD l}^{-1}$ ). From Eq. (9), it can be calculated that an influent BPA concentration of around  $100 \mu\text{g l}^{-1}$  would be required to generate such a high specific biomass concentration, alternatively the yield would have to be 5.4. None of these explanations are feasible and the estimation results in (ii) cannot be obtained by simulating the model with measured BPA concentrations as input. A multiple-substrate model, where the specific biomass grows on both the XOC and on other substrates (e.g. readily degradable substrate,  $S_S$  in ASM1), would be required to simulate this phenomenon.

## 5.2. Validation results

The dashed line in Fig. 2 shows a simulation of the *Dosage 2* experiment with the parameter estimates from i above and current operational parameters, i.e. it can be viewed as a model validation scenario. In the validation scenario, the model was initiated by first adding 1 g BPA per day to the influent during 60 days followed by no addition during 14 days. The final values were then used as initial values to the subsequent simulation, which is shown in Fig. 2, with addition of 10 g BPA per day. This initialization/simulation procedure mimicked the experimental procedure.

It should be recalled that Figs. 1 and 2 show step responses of identical inputs; it is (a) the history of the activated sludge before the step changes and (b) the operational conditions that cause the varying outputs of *Dosage 1* and *Dosage 2*. To separate the influence of these two factors, the solid line in Fig. 2 shows a simulation where the initialization procedure was not applied. Thus, by comparing this simulation with the dashed line in Fig. 1, it can be seen that the higher temperature and the higher aerobic retention time of *Dosage 2* (compared to *Dosage 1*) both are factors that had a significant, but not sufficient, impact on explaining the variations of the two measured step responses.

In the model validation simulation (Fig. 2, dashed line), temperature effects were taken into account by multiplying the growth and decay rates from i with a temperature correction factor  $\theta^{\Delta T}$  where  $\Delta T$  was set to  $5 \text{ }^\circ\text{C}$  and the temperature correction factor  $\theta$  first was set to be 1.072 for both parameters (this is the factor used for heterotrophs in ASM1).

One more simulation with  $\theta$  set to 1.111 for growth and 1.116 for decay (this is the factor used for autotrophs in ASM1) was made and is shown as the dotted line in Fig. 2. As expected, the temperature correction factors are influential model parameters. To describe the experimental data even better temperature corrections of 1.18 (both parameters) were needed, a scenario which is shown as the dash-dotted line.

The validation does not give a perfect fit. Several months elapsed between the calibration and validation experiment and thus the microbial populations present in the sludge may have changed, leading to a different response. Overall,

however, the model seems to provide an acceptable description of the data, with a similar dynamic behavior as during the calibration period.

The sources of uncertainty mentioned in the calibration section are equally relevant for this validation phase. It is indeed also possible that the formulated model is too simple and neglects mechanisms, which from our data are not possible to establish, that possibly would give better validation results. Monitoring of the sludge or isolation of specific BPA-degrading organisms in new experiments is necessary to in more detail elucidate the mechanism of growth of the BPA-degrading population.

## 6. Conclusions

In this paper, the assumption that biological growth plays an important role in BPA removal has been shown to hold when comparing experimental data with a growth-based process model. The presented single-substrate model is the simplest one among the ones tested that allows describing the time evolution of the increase in the observed BPA-degradation capacity, which is consistent with a slow in-growth of an organism that is initially present in only small numbers. In the paper it has moreover been shown that processes with faster dynamics, such as sorption and volatilization, are not dominant for the fate of BPA. The hypothesized model was shown to be capable of describing observed effects of operational (e.g. sludge and hydraulic retention time) and environmental parameters (e.g. temperature) on the removal processes. Thereby, the possibilities for improved design and operation of WWTPs, removing XOCs in addition to traditional WWTP pollutants like organic matter and nutrients, are enhanced.

For application of the proposed model and parameter estimates to natural wastewater environments with low BPA concentrations, the results must be extrapolated. It should then be considered that the BPA concentrations during the dosage experiment were significantly higher than during normal WWTP operation and that some parameter values have been assumed as fixed in the calibration.

Further experiments in combination with possibly more complex model formulations and parameter sensitivity analyses may throw light on the behaviour of the established specific BPA degraders at low concentrations.

## Acknowledgements

We acknowledge Lynettefællesskabet I/S, and Spildevandscenter Avedoere I/S for supporting this study, and Mark Van Loosdrecht, Yves Comeau and Hansruedi Siegrist for discussions. Peter Vanrolleghem holds the Canada Research Chair in Water Quality Modelling.

## REFERENCES

- Bachman Christiansen, L., Winther-Nielsen, M., Helweg, C., 2002. Feminisation of fish. The effect of estrogenic compounds and

- their fate in sewage treatment plants and nature. Environmental project No. 729, Danish Environmental Protection Agency, Denmark, 184 pp. Available at <http://glwww.mst.dk/homepage/>.
- Carvalho, G., Novais, J.M., Pinheiro, H.M., Vanrolleghem, P.A., 2004. Model development and application for surfactant biodegradation in an acclimatising activated sludge system. *Chemosphere* 54 (10), 1495–1502.
- Clara, M., Strenn, B., Saracevic, E., Kreuzinger, N., 2004. Adsorption of bisphenol-A, 17 $\beta$ -estradiol and 17 $\alpha$ -ethinylestradiol to sewage sludge. *Chemosphere* 56 (9), 843–851.
- ECB (European Chemical Bureau), 2003. 4,4'-Isopropylidenediphenol (Bisphenol A). European Union Risk Assessment Report, Institute for Health and Consumer Protection, European Commission. 302 pp. Available at <http://ecb.jrc.it/>.
- Fausser, P., Vikelsøe, J., Sørensen, P.B., Carlsen, L., 2003. Phthalates, nonylphenols and LAS in an alternately operated wastewater treatment plant—fate modelling based on measured concentrations in wastewater and sludge. *Water Research* 37 (6), 1288–1295.
- Henze, M., Grady, C.P.L., Gujer, W., Marais, G.V.R., Matsuo, T., 1987. A general model for single-sludge wastewater treatment systems. *Water Research* 21 (5), 505–515.
- Henze, M., Gujer, W., Mino, T., Matsuo, T., Wentzel, M.C., Marais, G.V.R., Van Loosdrecht, M.C.M., 1999. Activated Sludge Model No.2d, ASM2d. *Water Science and Technology* 39 (1), 165–182.
- Henze, M., Gujer, W., Mino, T., van Loosdrecht, M., 2000. Activated Sludge Models ASM1, ASM2, ASM2d and ASM3. Scientific and Technical Report No 9. IWA Publishing, London, UK.
- Henze, M., Harremoës, P., Jansen, J.laC., Arvin, E., 2002. Wastewater Treatment, Biological and Chemical Processes, third ed. Springer, Berlin, Germany.
- Jacobsen, B.N., Arvin, E., 1996. Biodegradation kinetics and fate modelling of pentachlorophenol in bioaugmented activated sludge reactors. *Water Research* 30 (5), 1184–1194.
- Jacobsen, B.N., Guildal, T., 2000. Novel aspects for management of xenobiotic compounds in wastewater treatment plants—linking theory, field studies, regulation engineering, and experience. *Water Science and Technology* 42 (7-8), 315–322.
- Kim, J.Y., Ryu, K., Kim, E.J., Choe, W.S., Cha, G.C., Yoo, I.K., 2007. Degradation of bisphenol A and nonylphenol by nitrifying activated sludge. *Process Biochemistry* 42 (10), 1470–1474.
- Kjølholt, J., Nielsen, P., Stuer-Lauridsen, F., 2003. Endocrine disrupting compounds and pharmaceuticals in wastewater (in Danish: Hormonforstyrrende stoffer og lægemidler i spildevand). Environmental project No. 799, Danish Environmental Protection Agency, Denmark. 46 pp. Available at <http://glwww.mst.dk/homepage/>.
- Lindblom, E., Germaey, K., Henze, M., Mikkelsen, P.S., 2006. Integrated modelling of two xenobiotic organic compounds. *Water Science and Technology* 54 (6–7), 213–221.
- Melcer, H., Bell, J., Thompson, D.J., Yendt, C.M., Kemp, J., Steel, P., 1994. Modeling volatile organic contaminants' fate in wastewater treatment plants. *Journal of Environmental Engineering* 120 (3), 588–609.
- Press-Kristensen, K., 2007. Biodegradation of Xenobiotic Organic Compounds in Wastewater Treatment Plants. Ph.D. thesis. Institute of Environment & Resources, The Technical University of Denmark, Lyngby, Denmark. 51 pp. Available at <http://www2.er.dtu.dk/phdthesis/>.
- Press-Kristensen, K., Ledin, A., Schmidt, J.E., Henze, M., 2007. Identifying model pollutants to investigate biodegradation of hazardous XOCs in WWTPs. *Science of the Total Environment* 373 (1), 122–130.
- Roels, J.A., 1983. Energetics and Kinetics in Biotechnology. Elsevier Biomedical Press, Amsterdam.
- Siegrist, H., Alder, A., Gujer, W., Giger, W., 1989. Behaviour and modelling of NTA degradation in activated sludge systems. *Water Science and Technology* 21 (4–5), 315–324.
- Struijs, J., 1996. Simple Treat 3.0: A model to predict the distribution and elimination of chemicals by sewage treatment plants. RIVM Report No. 719101025, RIVM, Bilthoven, The Netherlands. Available at <http://www.rivm.nl/bibliotheek/rapporten/719101025.pdf>.
- Tanaka, H., Sato, C., Komori, K., Yakou, Y., Tamamoto, H., Miyamoto, N., Higashitani, T., 2003. Occurrence of endocrine disruptors in sewage and their behavior in sewage treatment plants in Japan. *Environmental Science* 10 (1), 1–24.