Predicting the Fate of Emerging Contaminants in Wastewater Treatment Plants

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ABSTRACT

The aim of this work was to model and assess the efficacy of different wastewater treatment trains on the removal of selected emerging contaminants under dynamic conditions. To this end, state-of-the-art wastewater treatment models were extended with emerging contaminants fate sub-models to predict the performance of treatment trains such as conventional (CAS), nitrifying (NAS) and nutrient removal (BNR) activated sludge plants, CAS with sand filtration and enhanced primary clarification with ozonation. Engineers and plant managers can use these models to design and optimize wastewater treatment plants in order to reduce the release of emerging contaminants in the environment. The results show that rain events can significantly alter the performance of the plant with regards to the removal of emerging contaminants and that tertiary treatment (ozone) and long sludge age systems are more efficient to remove recalcitrant pollutants.

KEYWORDS: Activated sludge systems, biodegradation, chemicals of emerging concern, micropollutants, modeling, ozonation, primary clarification, sand filtration, sorption, volatilization.

INTRODUCTION

The influent of wastewater treatment plants (WWTPs) typically contains a wide range of emerging contaminants originating from pharmaceuticals and personal care products, other chemicals used in households, fertilizers, run-off from roads, etc. Several studies have shown that these compounds can negatively affect living organisms even at low concentrations (Bolong et al., 2009). Moreover, wastewater discharges are sometimes solely responsible for the presence of emerging contaminants in drinking water sources (Benotti et al., 2009). Unfortunately, most WWTPs were built to remove traditional pollutants (organic matter and ammonia) and therefore were not designed to treat other contaminants. Nevertheless, some WWTPs are able to achieve high removal efficiencies for the non-recalcitrant emerging contaminants. Their removal from wastewaters depends on the treatment trains of the WWTP, the operating conditions, and the physicochemical properties of the pollutants. The main removal processes for these compounds are volatilization, biodegradation, sorption, and even photolysis (in lagoons).

Several models are nowadays available to simulate the fate of various compounds in wastewater treatment plants. Traditional pollutants such as organic matter, nitrogen and phosphorus are well represented by the Activated Sludge Model (ASM) suite developed by an International Water

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Association (IWA) Task Group (Henze et al., 2000). Models that can predict the behavior of emerging contaminants in WWTPs have been around for the last 20 years such as SimpleTreat (Struijs et al., 1991), WW-TREAT (Cowan et al., 1993) and TOXCHEM (Melcer et al., 1994). More recently, modelers came up with ASM-based sub-models that can be combined with standard ASM models to simulate the behavior of both the traditional pollutants and the emerging contaminants (Plósz et al., 2012). Under dynamic conditions, their behavior are closely related given that the fate of the latter is often driven by the concentration of active biomass (biodegradation) and suspended solids (sorption) that can be predicted using the ASM suite.

This study aims at assessing the performance of different treatment trains with regards to the removal of selected emerging contaminants. Indeed, the fate of emerging contaminants in WWTPs differs from one treatment train to another because they behave differently according to their physicochemical properties. The influence of weather conditions, sludge retention time and tertiary treatment are also taken into consideration.

METHODOLOGY

Modeling and simulation were carried out in the software tool WEST® version 3.7.6 (www.mikebydhi.com) to represent the dynamics and fate of pollution in different wastewater unit processes (Vanhooren et al., 2003). The fate models that are used to simulate the fate of priority pollutants in various units of an integrated urban wastewater system (IUWS) were developed as part of the ScorePP project (Source Control Options for Reducing Emissions of Priority Pollutants, www.scorepp.eu) and a Canadian Water Network project on the removal of emerging contaminants in different treatment trains. These models were implemented by extending the state-of-the-art water quality ASM models with fate sub-models for micropollutants (Benedetti et al., 2009). An ozonation model based on Zimmermann et al. (2011) was also implemented as it is being used as a tertiary treatment process in various cities around the world.

The removal efficiencies of three emerging contaminants with quite different properties, 17α-ethinylestradiol (EE2), trichloroethylene (TCE), and bis(2-ethylhexyl) phthalate (DEHP) were studied in five different wastewater treatment trains: conventional activated sludge (CAS), nitrifying activated sludge (NAS), biological nutrient removal (BNR), CAS with sand filtration (CAS+SF), and enhanced primary clarification directly followed by an ozonation process (EPC+O_3). For all these experiments, a modified version for micropollutants of the well-known Takács et al. (1991) model from the IUWS model base was selected to describe the dynamics inside the primary clarifier and the secondary settler. The initial concentrations of the state variables for each treatment train were determined by running a steady-state simulation.

Conventional activated sludge (CAS) and nitrifying activated sludge (NAS)

The CAS and NAS processes are represented by a primary clarifier, three aerobic reactors in series and a secondary settler. The only difference between the two processes is the longer sludge retention time of the NAS system which allows for the growth of nitrifying bacteria. The plant configuration and the operating conditions are shown in Table 1.

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Table 1. Plant configuration and operating conditions of the CAS and NAS processes.

Components	Parameters	Units	CAS values	NAS values
Primary clarifier	Area	m^2	700	700
	Height	m	3	3
	Underflow	m^3/d	500	500
Aerobic reactors (x3)	k_La	d^{-1}	68, 37, 28	177, 98, 53
	Volume	m^3	2500, 2500, 2500	2500, 2500, 2500
Secondary settler	Area	m^2	1500	1500
	Height	m	4	4
	Underflow	m^3/d	9415	9415
Waste activated sludge	Flow rate	m^3/d	560	295

Biological nutrient removal (BNR)

The BNR process consists of a primary clarifier, six reactors in series (1 anaerobic, 2 anoxic and 3 aerobic) and a secondary settler. An internal recycle after the aerobic reactors brings the nitrified mixed liquor back to the anoxic reactors for denitrification. The plant configuration and the operating conditions are presented in Table 2.

Table 2. Plant configuration and operating conditions of the BNR process.

Components	Parameters	Units	Values
Primary clarifier	Area	m^2	700
	Height	m	3
	Underflow	m^3/d	500
Anaerobic reactor	k_La	d^{-1}	0
	Volume	m^3	2500
Anoxic reactors (x2)	k_La	d^{-1}	0, 0
	Volume	m^3	2500, 2500
Aerobic reactors (x3)	k_La	d^{-1}	163, 101, 60
	Volume	m^3	2500, 2500, 2500
Secondary settler	Area	m^2	1500
	Height	m	4
	Underflow	m^3/d	9415
Internal recycle	Flow rate	m^3/d	46016
Waste activated sludge	Flow rate	m^3/d	276

Conventional activated sludge with sand filtration (CAS+SF)

The CAS+SF process has the same configuration as the CAS treatment train described above, but a sand filtration unit was added after the secondary settler. It uses an extension of the SimpleDownFlow model for sandfilters with an emerging contaminants fate sub-model available in the IUWS model base. The configuration of the sand filter is presented in Table 3.

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Table 3. Configuration of the sand filter unit.

Components	Parameters	Units	Values
Sand filter	Area	m²	150
	Height	m	0.75
Buffer tank	Volume	m³	5000

Enhanced primary clarification with ozonation (EPC+O_3)

The last treatment train studied is a highly efficient primary clarifier followed by an ozonation unit. To increase the efficiency of the primary clarifier, the values of the hindered settling (r_H), low concentration settling (r_P), maximum theoretical settling velocity (v_0) and maximum practical settling velocity (v_{00}) were chosen in order to have an effluent suspended solids concentration of less than 20 mg/l in dry weather conditions, an effluent concentration that can be achieved by enhanced primary clarifiers. The plant configuration and the operating conditions are presented in Table 4.

Table 4. Configuration of the enhanced primary clarifier with ozonation.

Components	Parameters	Units	Values
Primary clarifier	Area	m²	700
	Height	m	3
	Underflow	m³/d	500
	r_H	m³/g	5.76E-4
	r_P	m³/g	2.86E-3
	v_0	m/d	474
	v_{00}	m/d	250
Ozonator	k_La	d^{-1}	5
	Ozone/oxygen ratio	%	1.5
	Volume	m³	2500

Plant influent

The input to the model was derived from the first 40 days of the dynamic influent file for the Benchmark Simulation Model 2 (Nopens et al., 2010) that includes two significant rain events between days 10 and 15. The influent flow rate and total chemical oxygen demand (COD) are presented in Figure 1. The components in the influent file were converted from an ASM1 composition to ASM2d as explained in Gernaey et al. (2002).

A constant concentration of around 8.5 ng/l of each contaminant was added to allow for the comparison between the different treatment trains. Physicochemical and biological properties of the compounds (aerobic and anoxic half-lives, partition coefficient, rate constants, molecular weight and Henry's constant) were found in the literature and are shown in Table 5.

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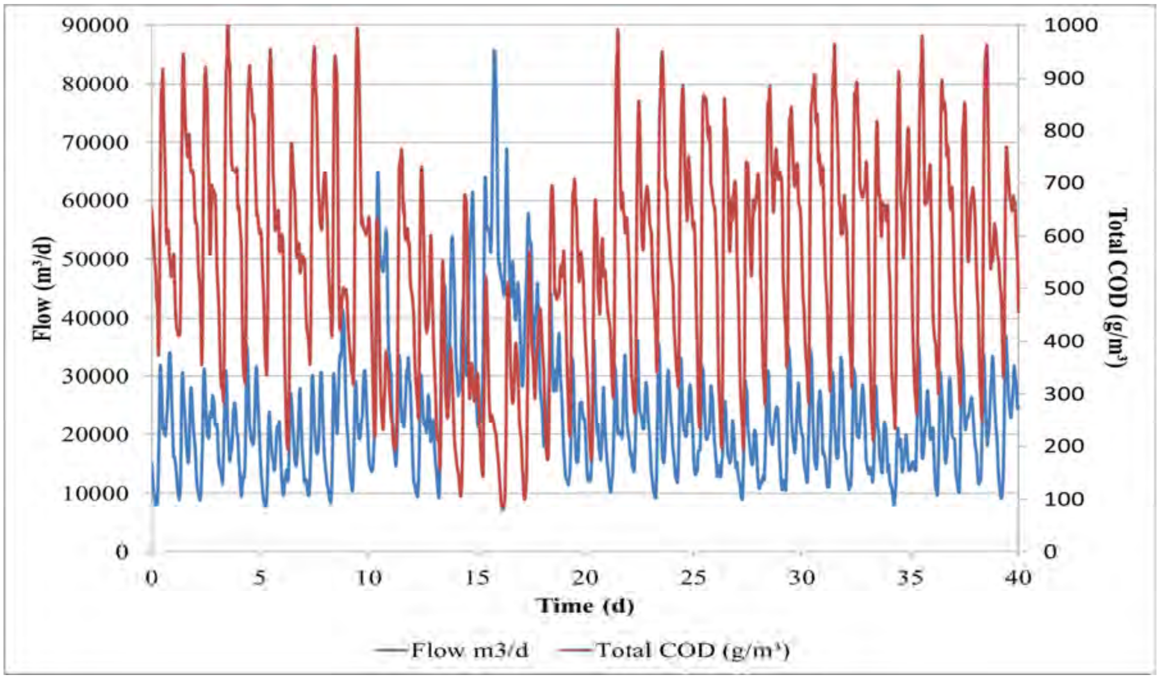

Figure 1. Influent flow rate and total COD with rain events on day 11 and days 14-18.

Table 5. Physicochemical and biological properties of the selected emerging contaminants.

Parameters	**Units**	**EE2**	**DEHP**	**TCE**
Aerobic half-life	d	3	0.029	0
Anoxic half-life	d	0	0.087	0
Henry's constant	Pa.m³/mol	8.045E-7	4.43	1030
Sorption coefficient	m³/d.g	0.04	0.1	0.01
Organic carbon partition coefficient	l/kg	4840	165000	90.2
Rate constant for reaction with ozone	$mol.g^{-1}s^{-1}$	$7.0*10^9$	0.2	17
Rate constant for reaction with OH radicals	$mol.g^{-1}s^{-1}$	$9.8*10^9$	$5.3*10^9$	$4.0*10^9$
Molecular weight	g/mol	296.4	390.54	131.5
Reference		de Mes et al. (2005), Shi et al. (2004), Huber et al. (2003)	European Chemicals Bureau (2008)	European Chemicals Bureau (2004), Kong et al. (2003)

RESULTS

Removal efficiencies were calculated in dry weather conditions and are presented in Table 6 for all treatment trains studied. The percent removal by sorption, volatilization and biodegradation for the three emerging contaminants as well as that of ammonia (NH_4), COD and total suspended

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solids (TSS) were calculated. It can be seen that no NH_4 was removed during the CAS experiment: a proof that no growth of nitrifying bacteria occurred. COD and TSS are well removed by all the treatment trains with a higher efficiency observed for the CAS+SF system thanks to the removal of extra TSS and particulate COD by the sand filter. TSS plays an important role in the sorption mechanism, which is described by a pseudo-first order reaction proportional to the concentrations of soluble emerging contaminant and TSS.

Table 6. Removal efficiencies (total and fraction per process) of the treatment trains studied under dry weather conditions.

Pollutants ↓	**Treatment trains →**	**CAS**	**NAS**	**BNR**	**CAS+SF**	**EPC+O_3**
EE2	Sorption (%)	46.5	43.7	45.0	49.4	69.0
	Volatilization (%)	0.0	0.0	0.0	0.0	0.0
	Degradation (%)	0.0	8.0	8.7	0.0	30.3
	Total (%)	**46.5**	**51.7**	**53.7**	**49.4**	**99.3**
TCE	Sorption (%)	3.9	3.8	3.8	3.9	6.9
	Volatilization (%)	95.5	96.2	95.4	95.4	10.2
	Degradation (%)	0.0	0.0	0.0	0.0	64.5
	Total (%)	**99.4**	**100**	**99.2**	**99.3**	**81.6**
DEHP	Sorption (%)	63.7	59.3	60.0	63.8	80.4
	Volatilization (%)	2.4	5.7	5.0	2.4	0.1
	Degradation (%)	32.3	33.0	33.2	33.3	14.6
	Total (%)	**98.4**	**98.0**	**98.2**	**99.5**	**95.1**
NH_4	**Total (%)**	**0.0**	**95.1**	**97.7**	**5.6**	**0.8**
COD	**Total (%)**	**93.7**	**92.9**	**93.7**	**95.5**	**82.2**
TSS	**Total (%)**	**97.5**	**96.7**	**96.8**	**99.5**	**96.0**

Results show that EE2, which is neither volatile nor easily biodegradable, is mostly removed by sorption to sludge (Figure 2). However, it can be degraded by nitrifying bacteria if the sludge retention time is long enough to allow their growth (Clouzot et al., 2010). This explains the higher removal obtained by the NAS and the BNR systems and the absence of biodegradation in the CAS system. EE2 was almost totally removed by the EPC+O_3 where more sorption occurred. In fact, the EPC alone led to better results than the long retention time systems.

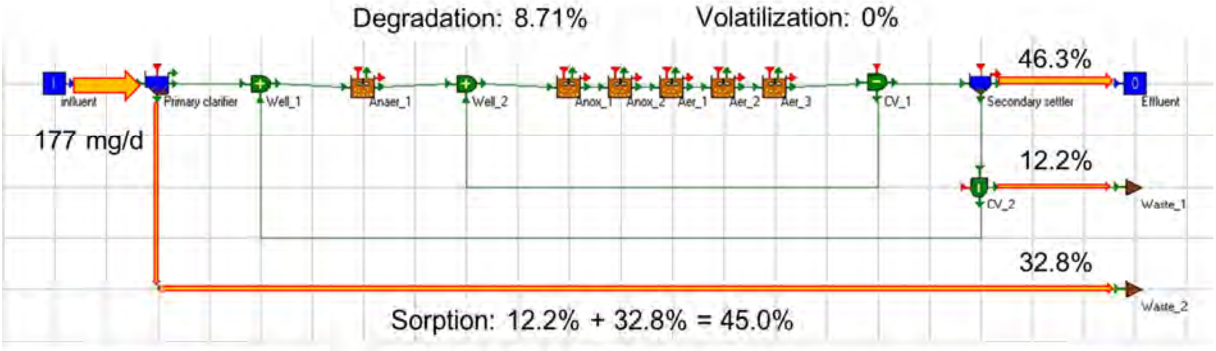

Figure 2. Fate of EE2 in the BNR system under dry weather conditions.

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Conversely, TCE (volatilization) and DEHP (sorption and biodegradation) are easily removed (>95%) in all treatment trains studied, with this time a worse removal efficiency for the enhanced primary clarification with ozonation (80%). However, this is mainly due to the fact that TCE is hardly sorbing, which means that a larger amount of TCE entered the ozonation unit in comparison to the other contaminants. Moreover, almost no volatilization occurred in the ozonation unit due to the very low hydraulic retention time. As shown by the model, the addition of a tertiary treatment such as ozonation can significantly increase the removal of several emerging contaminants (Huber et al., 2005). The use of a sand filter after the secondary settler helps removing additional suspended solids on which sorption may have occurred. In this case, the effluent was freed of an extra 2.9% of EE2 and 1.1% of DEHP, but no effect was observed on TCE.

The results reported in Table 7 show that disturbances caused by storms can decrease the removal efficiencies of the pollutants by altering the sedimentation in the clarifiers and by decreasing the hydraulic retention time of the system. Under wet weather conditions the removal of EE2 was reduced by around 50% in the CAS, NAS, BNR and CAS+SF systems. The removal of TCE by volatilization remains nearly unaffected by the surge of water while the NAS and BNR systems show lower removal efficiency than the CAS system for DEHP. This can be explained by the fact that the hydraulic overload mostly affected the settlers in these two systems as can be seen by the removal efficiency of the suspended solids; i.e, DEHP that sorbed to particles was washed out with the effluent.

Table 7. Removal efficiencies (total and fraction per process) of the treatment trains studied under wet weather conditions.

Pollutants ↓	**Treatment trains →**	**CAS**	**NAS**	**BNR**	**CAS+SF**	**EPC+O_3**
EE2	Sorption (%)	24.0	16.4	17.8	25.2	62.6
	Volatilization (%)	0.0	0.0	0.0	0.0	0.0
	Degradation (%)	0.0	6.5	5.4	0.0	32.2
	Total (%)	**24.0**	**22.9**	**23.2**	**25.2**	**94.8**
TCE	Sorption (%)	1.6	1.6	1.6	1.7	5.0
	Volatilization (%)	94.2	97.9	97.6	94.1	9.3
	Degradation (%)	0.0	0.0	0.0	0.0	47.5
	Total (%)	**95.8**	**99.5**	**99.2**	**95.8**	**61.8**
DEHP	Sorption (%)	48.8	23.8	25.2	49.8	70.9
	Volatilization (%)	2.8	4.6	3.7	2.8	0.1
	Degradation (%)	37.7	48.3	45.2	39.4	9.5
	Total (%)	**89.3**	**76.7**	**74.1**	**92.0**	**80.5**
NH_4	**Total (%)**	**7.3**	**64.3**	**69.3**	**8.0**	**2.0**
COD	**Total (%)**	**85.1**	**56.2**	**56.6**	**88.3**	**71.3**
TSS	**Total (%)**	**89.0**	**50.3**	**34.9**	**93.0**	**84.0**

Data evaluated for wet weather conditions were selected on the basis of a period of three consecutive days where the average flow rate is twice the annual average flow rate.

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CONCLUSIONS

In this work, the performance of different treatment trains with respect to the removal of selected emerging contaminants was studied. Results from simulations have shown that the fate of the pollutants is influenced by the sludge retention time of the system, i.e., a higher removal is observed in long retention time systems. The physicochemical properties of the pollutants affect the way they are behaving in the different units of the plant. Wet weather conditions can significantly influence the efficiency of the plant by altering the sedimentation in the settlers.

In the end, the use of state-of-the-art wastewater treatment models with micropollutant sub-models allows predicting the fate of traditional pollutants and emerging contaminants in various types of treatment trains. Engineers and plant managers can use these models to design and optimize WWTPs in order to reduce the amount of emerging contaminants released in the environment.

Further work will include modeling of the formation of by-products after ozonation, the study of other popular treatment trains such as lagoons and the removal of emerging contaminants by photolysis.

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REFERENCES

Benedetti, L.; De Keyser, W.; Vezzaro, L.; Atanasova, N.; Gevaert, N.; Verdonck, F.; Vanrolleghem, P.A.; Mikkelsen, P. S. (2009) *Integrated dynamic urban scale sources-and-flux models for PPs*. ScorePP project deliverable D7.4. p. 40. Available at http://www.scorepp.eu

Benotti, M.J.; Trenholm, R.A.; Vanderford, B.J.; Holady, J.C.; Stanford, B.D.; Snyder, S.A. (2009) Pharmaceuticals and endocrine disrupting compounds in U.S. drinking water. *Environ. Sci. Technol.*, **43**, 597-603.

Bolong, N.; Ismail, A. F.; Salim, M. R.; Matsuura, T. (2009) A review of the effects of emerging contaminants in wastewater and options for their removal. *Desalination*, **239**, 229–246.

Clouzot, L.; Doumenq, P.; Roche, N.; Marrot, B. (2010) Kinetics parameters for 17α-ethinylestradiol removal by nitrifying activated sludge developed in a membrane bioreactor. *Biores. Tech.*, **101**, 6425-6431.

Cowan, C.E.; Larson, R.J.; Feijtel, T.C.J.; Rapaport, R.A. (1993) An improved model for predicting the fate of consumer product chemicals in wastewater treatment plants. *Water Res.,* **27**, 561-573.

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de Mes, T.; Zeeman, G.; Lettinga, G. (2005) Occurence and fate of estrone, E2 and EE2 in STPs for domestic wastewater. *Rev. Environ. Sci. Biotechnol.*, **4**, 275–311.

European Chemicals Bureau (2004) *Trichloroethylene*. European Union Risk Assessment Report. Institute for Health and Consumer Protection, European Commission, 348 pp.

European Chemicals Bureau (2008) *Bis(2-ethylhexyl)phthalate (DEHP)*. European Union Risk Assessment Report. Institute for Health and Consumer Protection, European Commission, 588 pp.

Gernaey, K.; Mussati, M.; Yuan, Z.; Nielsen, M.K.; Jørgensen, S.B. (2002) Control strategy evaluation for combined N and P removal using a benchmark wastewater treatment plant. In: *Proceedings of the 15th IFAC World Congress on Automatic Control*, Barcelona, Spain, July 21-26 2002.

Henze, M.; Gujer, W.; Mino, T.; van Loosdrecht, M. (2000) *Activated Sludge Models ASM1, ASM2, ASM2d and ASM3*. IWA Publishing; London, UK.

Huber, M.M.; Göbel, A.; Joss, A.; Hermann, N.; Löffler, D.; McArdell, C.S.; Ried, A.; Siegrist, H.; Ternes, T.A.; von Gunten, U. (2005) Oxidation of pharmaceuticals during ozonation of municipal wastewater effluents: A pilot study. *Environ. Sci. Technol.*, **39**, 4290–4299.

Huber, M. M.; Canonica, S.; Park, G. Y.; Von Gunten, U. (2003) Oxidation of pharmaceuticals during ozonation and advanced oxidation processes. *Environ. Sci. Technol.*, **37**, 1016–1024.

Kong, S.H.; Kwon, C.I; Kim, M.H. (2003) Ozone kinetics and diesel decomposition by ozonation in groundwater. *Korean J. Chem. Eng.*, **20**, 293-299.

Melcer, H.; Bell, J.; Thompson, D.J.; Yendt, C.M.; Kemp, J.; Steel, P. (1994) Modeling volatile organic contaminants' fate in wastewater treatment plants. *J. Environ. Eng.*, **120**, 588-609.

Nopens, I.; Benedetti, L.; Jeppsson, U.; Pons, M.-N.; Alex, J.; Copp, J.B.; Gernaey, K.V.; Rosen, C.; Steyer, J.-P.; Vanrolleghem, P.A. (2010) Benchmark Simulation Model No 2: Finalisation of plant layout and default control strategy. *Wat. Sci. Tech.*, **62**, 1967-1974.

Plósz, B.G.; Langford, K.H.; Thomas, K.V. (2012) An activated sludge model for xenobiotic trace chemicals (ASM-X): Assessment of diclofenac and carbamazepine. *Biotechnol. Bioeng.*, (accepted).

Shi J.; Fujisawa S.; Nakai S.; Hosomi M. (2004) Biodegradation of natural and synthetic estrogens by nitrifying activated sludge and ammonia-oxidizing bacterium *Nitrosomonas europaea*. *Water Res.*, **38**, 2323-2330.

Struijs, J.; Stoltenkamp, J.; Van de Meent, D. (1991) A spreadsheet-based box-model to predict the fate of xenobiotics in a municipal wastewater treatment plant. *Water Res.*, **25**, 891-900.

Takács, I.; Patry, G.G.; Nolasco, D. (1991) A dynamic model of the clarification-thickening process. *Water Res.*, **25**, 1263-1271.

Vanhooren, H.; Meirlaen, J.; Amerlinck, Y.; Claeys, F.; Vangheluwe, H.; Vanrolleghem, P.A. (2003) WEST: Modelling biological wastewater treatment. *J. Hydroinformatics*, **5**, 27-50.

Zimmermann, S.G.; Wittenwiler, M.; Hollender, J.; Krauss, M.; Ort, C.; Siegrist, H.; von Gunter, U. (2011) Kinetic assessment and modeling of an ozonation step for full-scale municipal wastewater treatment: Micropollutant oxidation, by-product formation and disinfection. *Water Res.*, **45**, 605-617.