Modelling micro-pollutant fate in wastewater collection and treatment systems: status and challenges

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ABSTRACT

This paper provides a comprehensive summary on modelling of micro-pollutants' (MPs) fate and transport in wastewater. It indicates the motivations of MP modelling and summarises and illustrates the current status. Finally, some recommendations are provided to improve and diffuse the use of such models. In brief, we conclude that, in order to predict the contaminant removal in centralised treatment works, considering the dramatic improvement in monitoring and detecting MPs in wastewater, more mechanistic approaches should be used to complement conventional, heuristic and other fate models. This is crucial, as regional risk assessments and model-based evaluations of pollution discharge from urban areas can potentially be used by decision makers to evaluate effluent quality regulation, and assess upgrading requirements, in the future.

Key words | biotransformation and cometabolism, parent chemical retransformation, risk assessment and regulations, sorption–desorption, trace chemicals

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INTRODUCTION

A review of the current status, challenges and perspectives, lying ahead of micro-pollutant (MP) fate modelling, can help engineers and scientists to frame relevant and constructive future studies. Here, the term micro-pollutant denotes organic chemicals (e.g. pharmaceuticals, personal care products, combustion products, chlorinated solvents, biocides, flame retardants) occurring in nanoand low microgram per litre concentration in the aqueous and solids phase compartments of wastewater. Based on scientific literature and expert knowledge, NORMAN (2011) compiled a list of MPs. The database includes more than 700 chemicals with 19 main groups – i.e. fragrances, gasoline additives, industrial solvents, engineered nanoparticles, perfluoroalkylated substances, personal care products, pesticides, pharmaceuticals, wood preservatives, algal toxins, anticorrosives, antifoaming agents, antifouling compounds, antioxidants, biocides, complexing agents, detergents, disinfection by-products, flame retardants.

A comprehensive list of subjects relevant to the field of MP modelling in wastewater are summarised as follows.

Modelling methodology

- Current modelling approaches in simulation of MP fate in wastewater treatment plants (WWTPs).
- The question of grouping MPs (e.g. as organic pollution is lumped into chemical oxygen demand (COD)) so that their fate can be modelled without the need to each time find the specific compound's properties.
- Different scales in time and concentration between compounds/processes. Numerical problems related to this aspect.
- Cometabolism of MPs and the impact of growth substrate (e.g. competitive inhibition) on MP biotransformation.
- Modelling the sorption of charged MPs (e.g. negative ions, zwitterion) in WWTPs.
- Research developments required for MP fate modelling.

Technology and processes

- Modelling of new post-treatment processes, e.g. ozonation or powdered activated carbon (PAC) addition (effect of background dissolved organic carbon (DOC), reactor flow scheme, etc.) to improve design of post-treatment processes and calculate overall efficiency of the WWTP with respect to MP removal.

Data

- Data and parameters needed for MP fate models and their lack of availability or quality. Uncertainties and costs related to this aspect.
- The use of easily measurable 'surrogate' MPs as indicators (in a similar way to, e.g. *Escherichia coli* in bacterial contamination).
- Characterisation of municipal wastewater's MP content (e.g. human conjugates) for modelling purposes.
- Model calibration: parameter assessment from batch experimental data using pre-clarified municipal wastewater instead of spiking with reference substances.
- Validation of models: collecting representative samples to determine meaningful environmental concentrations and loads.

Model use

- Steady-state versus dynamic modelling of MPs: important for ecotoxicological risk assessment?
- Dynamic modelling of MP fate in secondary wastewater treatment as a means to assess the removal efficiency under cyclic flow and loading conditions and to optimise reactor design and chemical dosing in enhanced tertiary treatment.
- Adaptation phenomena at long sludge age and implications for operational procedures.
- Assessing MP degradation pathways and the ecotoxicological effects of degradation products, thereby defining the minimum biological removal requirements.
- The regulatory drivers for MP modelling – How and why can and will practitioners/users/engineers use MP fate models? At which temporal and spatial scale, for which MP, dynamically or in steady state?

The detailed discussion, evolving from the above list, is synthesised in this paper. Not all the topics are, however, covered, e.g. ecotoxicological risk assessment. The general objectives of this paper are to answer the questions 'How does the problem evolve?' followed by 'What are we supposed to do about it?' and then 'How shall we do it?'. Therefore, the main purposes of this work are to provide a comprehensive literature review on: (i) environmental risk assessment; (ii) international regulations; (iii) biochemical and physicochemical processes included in state-of-the-art process models – also discussing some recent examples in detail; and (iv) to propose future directions of MP modelling for urban wastewater management.

PERCEPTION OF ENVIRONMENTAL RISK

Experience with a number of environmental issues suggests that they are often dealt with in a consistent pattern.

Level 1 – Ignorance

It is ignorance that the constituent(s) of concern exists and/or that it is causing adverse impacts that are of sufficient magnitude to necessitate the level of effort and cost associated with their control.

Level 2 – Denial

At this level, it is recognised that the constituent(s) of concern cause adverse impacts but it is judged that the cost of control does not outweigh the adverse impacts being created. Denial often leads to conflict between those concerned about the adverse impacts associated with the constituent(s) and those who oppose the implementation of controls, resulting in building pressure to implement controls.

Level 3 – Acceptance

The typical result of the denial period is that some 'hazardous event' demonstrates an obvious example, triggering the acceptance of the risk posed and thus the need to implement controls. In such circumstances, controls must be implemented quickly and have to achieve reliable performance. For mitigation purposes, research has been conducted in the laboratory and at limited pilot-scale, which has produced some technology solutions, often physical–chemical. These technologies, which are installed in selected cases, experience the typical learning curve when early-phase technologies are implemented full-scale and quantification of the performance and cost of these technologies occurs. The ongoing chemical costs of these technologies then provide an incentive to develop biological technologies, with their inherently lower operating costs. Nutrient and odour control provide two examples of this general evolution.

The case of micro-pollutants

How might one expect the aforementioned three levels of risk perception to apply to MPs? We are currently in the denial phase where the benefits of control are uncertain and the costs are judged to be high (largely because of the lack of full-scale experience with control technologies). As some of the control technologies (e.g. ozonation) are already used in other areas (drinking water treatment), it is likely that distinct 'physical–chemical' and 'biological' phases may not occur in future mitigation of MP risk. However, when incidents occur that result in rapid implementation of increased MP control at wastewater treatment plants, it is likely that physical–chemical options will be selectively applied due to their greater perceived reliability, followed later by a transition to biological technologies. Physical–chemical technologies such as reverse osmosis, and advanced oxidation perhaps followed by biological activated carbon, are being applied, for example, in advanced water treatment and wastewater reclamation and reuse systems. Thus, full-scale learning is occurring, at least, on a select basis.

Risk assessment

To assess the environmental risk, given the large number of chemicals, MPs should first be prioritised for monitoring in the context of the European Union's (EU) Water Framework Directives (WFDs). A study by von der Ohe *et al.* (2011) assessed 500 organic substances based on observations in four European river basins. The authors present a classification approach, developed by NORMAN (2011), whereby the initial selection criteria are set by the assessment of chemical exposure indicators (typical environmental concentrations) and hazard (acute, chronic). Data scarcity for emerging MPs is specifically addressed by NORMAN (2011). This is because, in conventional prioritisation methodologies, emerging MPs are usually not considered, and therefore are monitored less often, thereby leading to little evidence of risk. NORMAN (2011) defines a number of MP categories, depending on the available exposure and hazard data as well as on analytical methods. Additionally, NORMAN proposes MP prioritisation within each category as a function of exposure, hazard and risk indicators.

REGULATIONS

The first important issue to clarify is what has actually to be accomplished with regard to MP removal, and therefore its modelling, in view of available regulatory requirements. The regulatory drivers for modelling MPs are likely to vary from one country or continent to another. Joss *et al.* (2008) shows that, as technically and economically feasible MP removal technologies are already available and because of the unknown environmental risk posed by the numerous MPs,

the preventive action ought to be taken based on the precautionary principle.

European Union

The Environmental Liability Directive (2004/35/EU) and the WFD (CEC 2000; 2000/60/EU) frame proactive approaches, rather than legal restrictions, to preserve the good ecological status of all types of water bodies. It regulates MPs in the aquatic environment (e.g. surface water, sediments) and the 'chemical status' of surface water bodies is assessed (Article 16, WFD). A list of MPs is regulated by the WFD by setting concentration limits in the receiving water. The WFD is periodically updated (most recent version: 2008/105/EU), and it requires the EU-wide monitoring of MPs. In the 2008 WFD, environmental quality standards (EQS) are defined for a list of 33 pollutants. Presently, not a single pharmaceutical or personal care product is among the WFD priority pollutants list. This is to change via a new proposal submitted to the EC in 2012, thereby adding new MPs (pesticides, industrial chemicals and byproducts, pharmaceuticals) to the list, notably, 17α-ethinylestradiol, 17β-estradiol and diclofenac. Further, von der Ohe *et al.* (2011) present a brief overview on how the WFD adopts emerging MPs in Europe. Importantly, should any additional MP be discharged in significant quantities in a specific region, they must be considered under the Ecological Status assessment. The WFD shows an 'Indicative list of the main pollutants' (Annex VIII) that EU countries should implement to identify chemicals of potential concern in the Ecological Status assessment (specified as specific pollutants).

The Urban Waste Water Treatment Directive (91/271/EEC) regulates: (i) domestic/urban wastewater collection and treatment (settlements areas and areas of economic activity); (ii) industrial wastewater pre-treatment; and (iii) sewage sludge disposal (also complementary legislation on agricultural use;). Notably, the 91/271/EEC directive does not consider MP removal via wastewater treatment, and the treatment objectives (biological) are set based on bulk pollutants removal – for non-sensitive areas: COD and biochemical oxygen demand (BOD_5); for sensitive areas (risk of eutrophication): COD, BOD_5, nitrogen and phosphorus. As to source control, complementary regulation (amended 2012) focuses on banning phosphate-containing detergents from EU markets.

North America

There are few (if any) operating permits which require treatment to specific concentrations or loadings of MPs (with the exception of metals and some industrial organics such as phthalate esters and chlorinated solvents).

Regulatory model use

In the future, if MPs become regulated in either effluents or residual wastewater solids (biosolids), modelling of these contaminants would become of greater importance to determine, for example, when elevated concentrations or loadings of MPs in treated effluents may be expected. The fate models may also be used to determine the distribution of the regulated MPs between solid, liquid and gas phases, so that monitoring for the contaminants can be done more efficiently. Many of the MPs of emerging interest tend to be of low volatility and monitoring and modelling of these compounds in the off-gases from aeration basins would thus be of limited value.

Applications of steady-state modelling might include estimation of average loadings of MPs in effluents discharged to water bodies, or the anticipated levels of accumulation of MPs in residual sludges or biosolids. Should regulatory limits be imposed, however, with maximum or 'never to exceed' effluent concentrations or loadings, dynamic modelling would be required to determine under what set of operating conditions compliance with the limits would be maintained (or alternatively under which conditions effluent limits might be exceeded, and for how long).

For model-based (regional) risk assessments (e.g. Ort *et al.* 2009), correlations between country-based consumption and chemical discharge data can be used. The effective prediction of the anthropogenic MP discharges from an urban catchment area, connected to WWTPs, thus is influenced by the error introduced by assuming e.g. even distribution of pharmaceutical use in a country, identical human drug metabolism. Additionally, MP sorption and biotransformation in sewer networks is mostly omitted in regional model-based assessments (e.g. Ort *et al.* 2009). Future research thus is required to assess model input uncertainty and optimal sewer and WWTP model complexity used for regulatory decision support.

SYSTEM MONITORING

Effective (model) prediction of the contaminant sources (point and network) and sinks (microbial degradation and accumulation in biosolids) is crucial to assess the output into the recipient, and the environmental impact to be avoided. The assessment of the MP removal performance

in wastewater treatment systems requires, in addition, an efficient chemical analysis method and an intensive sampling campaign using optimal resolution and precautious sample handling.

Sampling

The optimal set of sampling time resolution and sampling sites vary depending on the assessment of the behaviour of MPs in wastewater collection and treatment systems. Wastewater samples must be collected to provide realistic input data for MP fate models and their calibration and/or validation. Currently, analytical costs per sample are still relatively high. Hence, usually, composite samples are obtained, mostly with time-proportional sampling methods. When collecting samples from sewers – or influents to WWTPs – the sampling methods may in many situations lead to non-representative samples, because MP concentrations and loads can be subject to unknown, large short-term fluctuations (e.g. Ort & Gujer 2006; Ort *et al.* 2010a). However, sampling uncertainty can be greatly minimised and sampling artefacts avoided completely if an appropriate sampling mode and frequency are selected. The latter should be precautionarily high if no sound systems analysis for the specific location is carried out before sampling. A suggestion of a complete sampling protocol can be found in Ort *et al.* (2010b). Representative samples are the essential basis to understand occurrence and fate of MPs (field measurements) and to derive meaningful parameters (modelling) instead of interpreting and mimicking sampling artefacts.

Analysis

There is an extensive choice of analytical options available depending on the MPs of interest. Methods are optimised depending on the analytes of interest. Aqueous phase samples are generally extracted and pre-concentrated by solid phase extraction and solid phase matrices extracted with solvent. Methods are optimised depending on the analytes of interest. Limits of detection can be a limiting factor for some trace MPs.

For targeted analysis and quantification of specific non-volatile, water soluble analytes, liquid chromatography–mass spectrometry or tandem mass spectrometry (LC/MS or LC/MS/MS) may be an option (Viglino *et al.* 2007). For more volatile compounds, gas chromatography–mass spectrometry (GC/MS) may be more suitable. Wastewater is a complex sample matrix with many potential interfering compounds. LC/MS is often more susceptible to matrix interference, although matrix matched calibration standards, labelled internal standards and skilled analysts can go some way to overcome this issue. For robust reliable data, analytical methods must be validated and analyte recovery and suppression/enhancement must be quantified.

For the screening of 'unknown' compounds, or non-targeted analysis, LC or GC coupled to time-of-flight mass spectrometry (ToF-MS) can be powerful tools for qualitative analysis (e.g. Plósz *et al.* 2010a). ToF-MS analysis can be a useful tool highlighting or 'screening' for compounds of interest which can then be quantified. ToF-MS data are also useful for retrospective identification or for monitoring data fingerprints where coarse observation in changes in composition is helpful and for the identification of metabolites of quantified MPs.

CONVENTIONAL TREATMENT SYSTEM PERFORMANCE

In urban catchments, WWTPs are the most important means to reduce the environmental risk posed by point and centrally collected wastewater sources. Research (e.g. Joss *et al.* 2006) is demonstrating that the existing biological wastewater treatment processes can remove a broad array of MPs to a certain extent. Additionally, recent and ongoing research (Clara *et al.* 2005; Suarez *et al.* 2010) is also informing the profession on approaches to further improve the biological removal of, e.g. pharmaceuticals and contrast media using long solids retention time (SRT) in activated sludge systems. We note, however that increased SRT can have little or no effect on the biotransformation rate of some MPs, e.g. carbamazepine. However, there is a long list of MPs that are not efficiently removed during wastewater treatment and contaminate receiving water, potentially resulting in chronic toxic effects on aquatic organisms and humans. Although the individual concentrations may be low, the potential for enhancement of the toxic effect of chemicals with similar modes of action through interactions such as addition, synergism and antagonism is of great concern (Boxall *et al.* 2003). Of particular concern in this respect are pharmaceutically active compounds (PhACs) which are designed to be active at very low concentrations. A study by Pomati *et al.* (2006) showed that the combined effect of a mixture of thirteen PhACs at environmental levels significantly affected the growth of test human embryonic cells. Continued effort in identifying other groups of chemicals with similar mode of

action from the prioritised list of water chemicals is needed. Future work must also focus on better understanding of the biotic and abiotic processes underlying the environmental fate during various processes of the wastewater treatment system of surrogate chemicals representing such groups.

MODELLING MICRO-POLLUTANT FATE IN WASTEWATER

General considerations

In order to be able to improve the urban wastewater system, we first have to improve our understanding of how MP removal happens. This paper focuses on mathematical models, employing concentration-based rate equations. An alternative approach is to use fugacity capacity-based formulae (e.g. Mackay & Paterson 1981; Struijs *et al.* 1991; Seth *et al.* 2008). Because of the low volatility of MPs of emerging interest, volatilisation and stripping of MPs in WWTPs is not discussed in this paper. In Figure 1, we show a schematic representation of the underlying principles of factors influencing MP removal in wastewater.

Conventional models of xenobiotic organic MP fate in wastewater treatment (e.g. Melcer *et al.* 1994; Joss *et al.* 2006), summarising the current understanding, include a pseudo-first-order kinetic term for biotransformation of the parent compound as well as sorption and desorption

equations. In such a model, the biotransformation rate coefficient is identical under aerobic and anaerobic/anoxic conditions, and sorption onto solids is described using one partitioning coefficient. The model identification and calibration can be performed using experimental data obtained in batch experiments spiked with commercially available substances (Ternes *et al.* 2004; Joss *et al.* 2006). These conventional models can be limited in describing full-scale systems as demonstrated by Plósz *et al.* (2010c). The model inefficiencies can, in part, be explained by the fact that, in real systems, MP removal can be impacted by: (i) the presence of growth substrates, facilitating cometabolism (e.g. Grady *et al.* 1999); (ii) the potentially different biotransformation efficiencies under aerobic and anoxic conditions (Lindblom *et al.* 2009; Suarez *et al.* 2010; Plósz *et al.* 2010b); (iii) complexation with metal salts (iron, aluminium) dosed for phosphorus removal (Plósz *et al.* 2010c); and (iv) presence of an organism with required metabolic activity (Lindblom *et al.* 2009). Possible ways to account for some of these impacts in model identification and calibration procedures are discussed in the 'Use of models' section.

Sorption–desorption processes

In wastewater, MPs can sorb to solids as well as to dissolved and colloidal matter (DCM). MP fate throughout wastewater treatment systems strongly depends on their sorption behaviour (e.g. Song *et al.* 2006). Sorption of the chemical
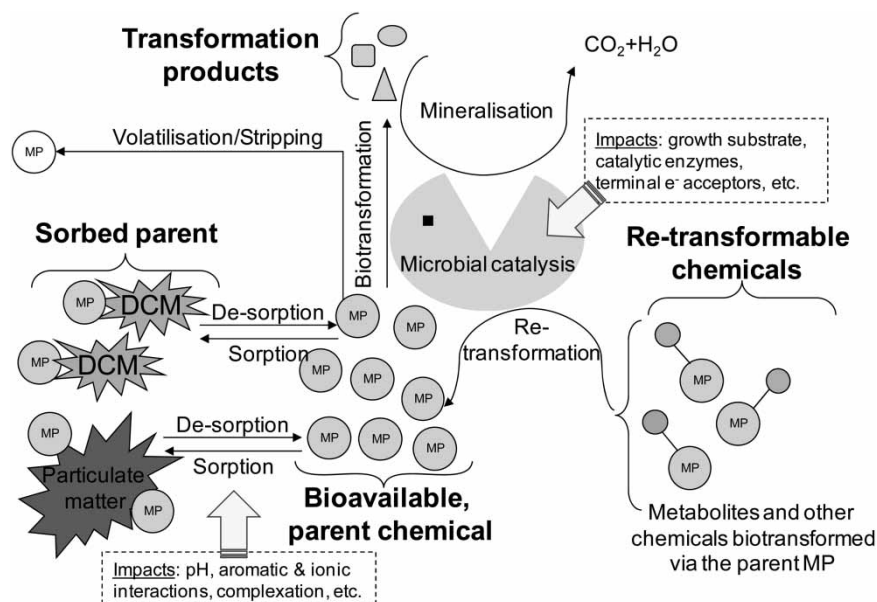

Figure 1 | Micro-pollutant (MP) fractions and processes, influencing MP removal in wastewater. Compiled based on studies by Criddle (1993); Alvarez-Cohen & Speitel (2001); Ternes & Joss (2006); Melcer *et al.* (2007); Monteith *et al.* (2008); Lindblom *et al.* (2009); Barret *et al.* (2010a); Plósz *et al.* (2010b,c). DCM: dissolved and colloidal matter.

influences their availability for biotransformation. From a general point of view, a sorbed organic MP is not available for biotransformation by microorganisms (Artola-Garicano *et al.* 2003). At lower MP concentration (caused by sorption) lower biotransformation rate can be achieved, based on reaction kinetics principles. Furthermore, hydrolysis of particulates during the biological process can transfer the compound from the sorbed (bioaccessible) to the aqueous phase (bioavailable) and influence the compound's transformation. To refine the assessment of bioavailable (dissolved) MPs, Barret *et al.* (2010a) present a three-compartment model (i.e. freely dissolved, sorbed-to-particles and sorbed-to-DCM) for MP sorption. Compared with most MP biotransformation rate values, sorption and desorption rates are significantly higher, and can be assumed to be in close equilibrium if the sorption substance mass flux is significantly higher than the biodegradation flux. Wang & Grady (1995) as well as Barret *et al.* (2010a) demonstrate that hydrophobic compounds have very quick sorption and desorption kinetics in biological treatment systems.

Sorption to DOC can significantly influence the fate of hydrophobic MPs during the wastewater treatment process (e.g. Song *et al.* 2006). For sorption of chemicals, Gustafsson *et al.* (2001) have classified the organic carbon (OC) in dissolved solids as including both colloidal organic carbon (COC) and DOC, where COC represents the OC fraction that is able to bind with hydrophobic MPs. Holbrook *et al.* (2004) concluded that OC with molecular weight less than 500 or 1,000 daltons (1 kDa) does not participate in COC sorption and can therefore be considered as DOC. A better characterisation of the influence of COC on the dynamics of hydrophobic MPs during municipal wastewater treatment processes and consideration of possible inclusion in fate models is needed. The partitioning behaviour of ionising MPs is altered by pH conditions. Thus, in WWTP process models, sorption of ionising contaminants cannot be accounted for by a single K_D value. Using a set of K_D values, defined for ranges of pH values typical of anoxic and aerobic bioreactor effluents, can partly alleviate this problem (Plósz *et al.* 2010b, c). MP sorption can additionally be impacted by aromatic and ionic interactions as well as complexation – a subject that is further discussed in the 'Use of models' section.

Biotransformation of MP parent compound

Most MPs cannot be utilised as growth substrate, and their oxidation occurs, mostly, on non-specific oxygenase enzyme sites at the net consumption of reductive forces of the cell (MPs as cometabolic substrate). The presence of growth substrates can affect, i.e. improve or competitively inhibit the cometabolic MP substrate oxidation process (Figure 1). Traditionally, cometabolic biotransformation kinetics is modelled using various approaches (Criddle 1993; Alvarez-Cohen & Speitel 2001), which may often become complex models, even when the growth substrate metabolism is modelled by first-order kinetics. In addition, a large number of kinetic parameters could complicate the modelling effort. These models, however, were originally identified and calibrated using contaminant concentrations in the mg L^{-1} range, which is significantly higher than the concentration at which MPs prevail in municipal wastewater. The applicability of such models to typical municipal wastewater may well be limited. This is because factors, such as, toxicity problems can be associated with high concentration ranges.

The applicability of cometabolic biotransformation models to an activated sludge WWTP was assessed for selected antibiotics (occurring in the <10 µg L^{-1} range) using a competitive inhibition relation for readily biodegradable substrates (Plósz *et al.* 2010b). Barret *et al.* (2010b) assessed first-order kinetics for cometabolism of polycyclic aromatic hydrocarbon (PAH) degradation for anaerobic digestion of contaminated sludge. The authors adopted the model by Criddle (1993), and considered the three-compartment model approach (i.e. MPs sorbed to particles, to colloidal matter and free dissolved). In contrast, readily biodegradable substrates were found to significantly increase the biotransformation rate estimated for the non-steroidal anti-inflammatory drug diclofenac and for the psycho-active drug carbamazepine (Tran *et al.* 2009). In order to account for these effects on cometabolic substrate degradation, a library, including functions and model parameter values describing the relation between parent compound biotransformation rate coefficients and readily biodegradable substrates should be developed in the future.

The cometabolism pathway could be the main mechanism of hydrophobic MP removal present at low concentration. Nevertheless, cometabolism degradation must be linked to the available biological potential such as the presence of a microbial community involved in the specific contaminant removal.

Retransformation/formation of MP parent compounds

Parent compounds can be retransformed/formed from other MP fractions, occurring in municipal wastewater, i.e. from

drug metabolites, other commercial chemicals (Plósz *et al.* 2010b, c) – see Figure 1. For selected antibiotic MPs, one state-variable can be used to account for the total retransformable chemical concentration, occurring in municipal wastewater (Plósz *et al.* 2010b, c). Additionally, it is shown that, in wastewater, the influent total retransformable antibiotic MP concentration effectively correlates with the parent MP concentration values. For a given sewer catchment area, the influent total retransformable MP concentration thus can be characterised with a ratio value calculated for the influent total retransformable and the parent MP concentrations. This can then be used to compile a dynamic concentration time-series.

Transformation products – daughter chemicals

The early publications on fate modelling (e.g. Monteith *et al.* 1995) assumed that biotransformation resulted in the disappearance/complete removal of contaminants. Since then, researchers have determined that biotransformation may not completely mineralise MPs, but instead transform the parent compound to transformation products – also referred to as daughter product chemicals (Figure 1). Transformation products and intermediary degradation products can have a different/higher toxicity or endocrine disrupting potential than the parent compound. Examples of the biotransformation of MPs include the stepwise reduction of the ethylene oxide chain in alkylphenol ethoxylates (Melcer *et al.* 2007) and the biotransformation of the estrogen 17-β-estradiol (E2) to estrone (E1) (Joss *et al.* 2004; Shi *et al.* 2004; Dytczak *et al.* 2006). Nonylphenol, an endocrine disrupter (listed in WFD) has been extensively studied (Angelidaki *et al.* 2001; Farré *et al.* 2002; Langford *et al.* 2005; Monteith *et al.* 2008; Soares *et al.* 2008). Several issues with respect to modelling MP daughter contaminant formation come to mind, namely: (a) what are the kinetic rate coefficients required for the various biotransformation steps?; (b) are different transformational pathways found under different pH and/or redox environments?; (c) are concentration and supporting operational data available to calibrate and validate the formation of metabolic intermediates?

USE OF MODELS

MP models can be used to evaluate treatment trains, to frame the problem at hand or to understand the mechanisms of the treatment processes. The scale of MP fate models spans from small (process level) to large (urban water systems). Some examples of model development and application are presented in this section.

Upstream of the WWTP

Looking at the issue of MPs with a broader perspective, the scientific objectives should be to identify the sources of MPs in urban areas, to identify and assess appropriate strategies for limiting their release from urban sources and for treating wastewater and stormwater containing them on a variety of spatial scales (Benedetti *et al.* 2009; Vezzaro *et al.* 2010). Furthermore, the aim should be to develop GIS-based spatial decision support tools for identification of appropriate emission control measures (Schowanek *et al.* 2001), to develop integrated dynamic urban-scale source-and-flux models that can be used to assess the effect of source control options on MPs' emissions and to optimise monitoring programmes, and assess the direct and indirect costs, the cost–effectiveness and the wider societal implications of source control strategies. The developed approaches, models and assessments could be used to formulate a set of appropriate emission reducing strategies. In this context, integrated, dynamic urban-scale source-and-flux models were developed in the context of the EU FP6 project Score-PP (www.scorepp.eu). The models are used for quantifying the release of MPs from urban sources and their fate within different wastewater treatment systems. These models – which can be linked to simple, river basin scale multimedia models used in ecological risk assessment (De Keyser *et al.* 2010) – enable 'what-if' scenarios to assess the effect of emission barriers as well as to evaluate their potential in enabling monitoring systems and sampling programmes to be optimised. An integrated, dynamic model is able to predict the dynamic fate of MPs and therefore it assesses the compliance with EQS (annual averages and peak concentrations) as shown by Gevaert *et al.* (2009).

WWTP – fate of hormones in activated sludge

Monteith *et al.* (2008) examined the role of WWTP operating conditions on the behaviour of the natural estrogenic hormones estrone (E1) and estradiol (E2), and the synthetic estrogen (EE2). Initial simulations used biotransformation rate coefficients documented by Ternes *et al.* (1999) from laboratory-scale aerated batch reactor studies. Predicted removal efficiencies of the hormones in the initial modelling results (particularly the estimated contribution of

biotransformation to overall removal) were very high for E1 and E2 at 99.8 and 97.5%, respectively, when compared to literature results. As a result, the values of the biotransformation coefficients for E2 and E1 were calibrated downward to more closely match the ranges of removal efficiencies typically observed in the technical literature. The estimated removal efficiency for EE2 was consistent with literature results, so no adjustment of the EE2 biotransformation rate coefficient was deemed necessary.

Following re-calibration of the biotransformation rate coefficients, the model results indicated that the masses of E1 and EE2 remaining in the treated effluent were similar (29–31% of the input mass), while the effluent mass of E2 was substantially lower at 10% of the input mass. Biotransformation of E2 and E1 were very similar, i.e. 51–52% of the influent mass, with biotransformation of EE2 at 41% of the input mass. More of the E2 and EE2 masses were associated with the primary solids than was E1. The model suggested that sorption of the hormones to secondary solids was slight, and would not provide as significant a removal mechanism as sorption to primary solids.

Validation of the model was conducted with operating data for the three biological nutrient removal treatment plants published in Drewes *et al.* (2005). The agreement of reported and predicted concentrations of the three estrogens in the effluents of two plants was good, especially for E1. The predicted effluent concentration of E2 at one of these two plants was higher. There was significant deviation between the modelled effluent hormone concentrations and concentrations reported for the third plant. Calibration of the model of this plant was the most difficult of the three due to difficulties in matching the reported SRT of 10 d with the mixed liquor suspended solids concentration of 3,660 mg/L.

The importance of design and operating parameters on the fate of the three estrogens in wastewater treatment was assessed by sensitivity analysis in the simulator. Salient observations revealed by the sensitivity analysis were: (i) below approximately 9–11 °C, biotransformation of the three hormones effectively stops, leaving sorption to primary and waste biological sludge solids as the only significant removal mechanism; (ii) at wastewater temperatures of 20 °C and higher, SRT values greater than 5 d had little effect on reducing effluent hormone concentrations; (iii) at 10 °C, when biotransformation kinetics are becoming minimal, the effect of increasing SRT becomes more significant, with E2 being the most affected of the three hormones; and (iv) at 20 °C, simulated effluent concentrations of E1 and EE2 rose quickly when the hydraulic retention time

(HRT) of the bioreactor was less than 5–6 hours, which is typical of many operations. During wet weather operations, HRT values can be much shorter, resulting in reduced efficiency of biotransformation. As wastewater temperature declines towards 10 °C, effluent hormone concentrations increase rapidly when the bioreactor HRT is less than 6–7 hours. Below 10 °C negligible biotransformation of the hormones occurs, even at HRTs extending well beyond 7 hours.

WWTP – Modelling framework for xenobiotic micro-pollutants in activated sludge (ASM-X)

Plósz *et al.* (2010b,c,d) present a methodology for model identification, calibration and evaluation as well as for the characterisation of MP fractions and diurnal variation of MP occurrence in municipal wastewater. A novel method was developed to infer process rate, sorption, and correction factor parameter values from batch experimental results obtained under aerobic and anoxic conditions. Instead of spiking the batch reactors with reference substances, measurements were made using the organic MP content (antibiotics: sulfamethoxazole, tetracycline, ciprofloxacin (CIP)) of preclarified municipal wastewater. The developed process model, ASM-X, distinguishes between aerobic and anoxic sorption as well as parent compound formation and biotransformation processes. The rate equations identified for biotransformation processes (parent compound formation/re-transformation and biotransformation), include pseudo-first order kinetics terms, terms for growth substrate cometabolism and switching/inhibition functions for oxygen (aerobic–anoxic). The ASM-X methodology is an example of generating knowledge for more mechanistic model development, including identification, calibration and evaluation/validation.

Based on existing environmental data from the literature and toxicity data, a Norwegian environmental risk assessment study by Grung *et al.* (2008) assessed risk quotients for eleven pharmaceuticals. The authors showed that the release of the antibiotic CIP from WWTPs may potentially be of environmental concern in Norway. Combination of dynamic modelling and independent full-scale measurement data were then used to identify factors that can influence the zwitterionic CIP removal in wastewater treatment (Plósz *et al.* 2010b). It is shown that WWTP effluent quality can intermittently significantly deteriorate (increase from 6–7 to 20 µg L^{-1}). It was hypothesised that the iron-(II)-salt dosing into the sludge recirculation line can influence ionic strength and cation-bridging in the sewage, which may explain the decreased sorption capacity of activated

sludge. Additionally, pH conditions, prevailing in the bio-reactors, were identified as factors that can significantly affect zwitterionic speciation on solids. Subsequently, targeted sorption experiments with CIP were carried out and results obtained were used to explain the possible impacts on CIP removal in the WWTP (Plósz *et al.* 2011c). The CIP sorption experimental data show that partitioning can be influenced by ionic interactions between sludge components and dissolved Fe-ions or bonding between cations and charged parent compound molecules. Results additionally show that the impact of Fe-salt dosed in the WWTP (chemical phosphorus precipitation) can vary under aerobic, anoxic and anaerobic conditions, and that the presence of nitrate can significantly influence CIP partitioning under aerobic conditions. The possible depletion of nitrate in the pre-anoxic effluent can additionally deteriorate the sorption capacity, in the presence of Fe(II). This combined experimental and dynamic modelling work can provide a means for decision support to optimise WWTP retrofitting solutions in the future.

WWTP – Anaerobic digestion

Delgadillo-Mirquez *et al.* (2011) developed a model for laboratory-scale anaerobic digesters at equilibrium state. Hydrophobic compounds, such as PAHs, were distributed in four compartments (gas concentration, sorbed to

dissolved/colloidal matter, sorbed to particles and free dissolved) with three equilibrium constants. Furthermore, the model includes hydrolysis of particles (as the rate-limiting step of anaerobic digestion) and a cometabolism kinetic (Criddle 1993). This subsequently influences the distribution and the availability of pollutants for biotransformation. In this study, the modelling approach validated the accepted assumption that the aqueous phase is bioavailable and presented the cometabolism pathway as the main PAH degradation mechanism. Besides, the model includes three cometabolism parameters for each compound. These estimated parameter values can explain the different degradation rate between PAHs, between digesters and between bioaugmentation strategies developed for optimisation of the pollutant removal. The model proposed is potentially useful to better understand the pollutant distribution and degradation and to test scenarios for PAH removal optimisation.

Integrated urban wastewater system (IUWS)

The model of the case study on IUWS consists of a rural catchment, three urban sewer catchments connected to an intercepting combined sewer system, an activated sludge plant including primary settling, two aerated tanks and secondary settling (Figure 2). The treatment plant and the overflow structures at the three urban catchments discharge
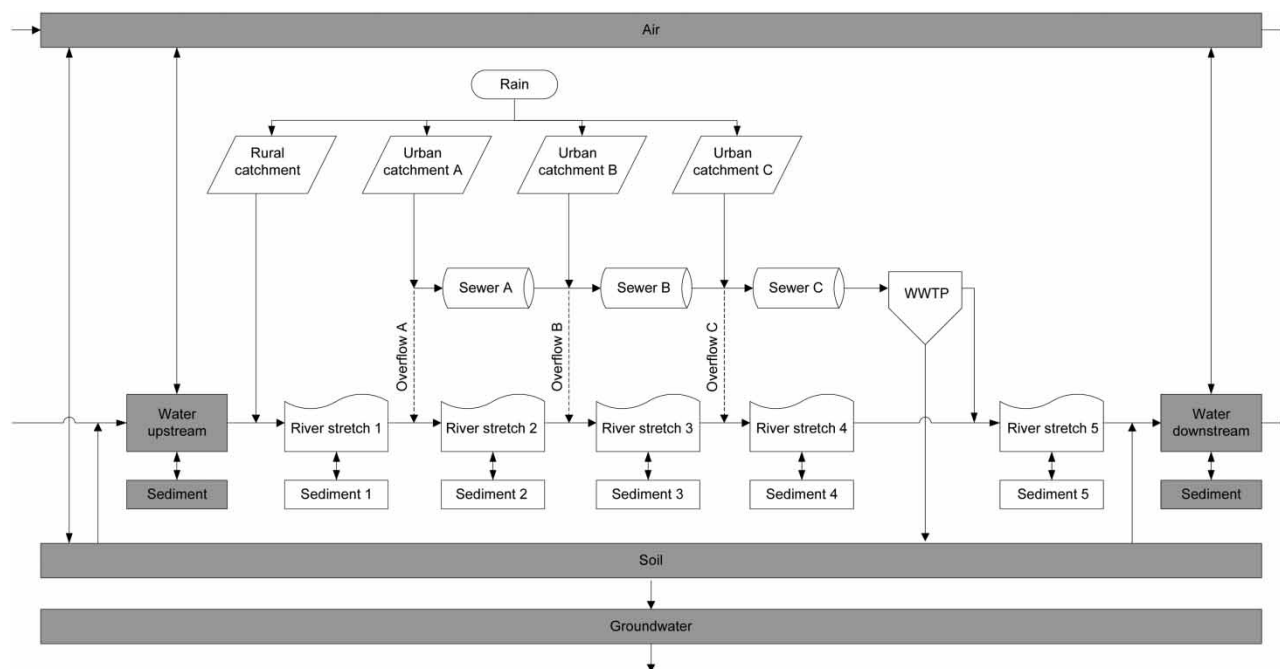

Figure 2 │ Schematic representation of the integrated environmental model (IUWS model (white blocks) and MFTM (grey blocks)).

to a river modelled as a series of five stretches, each of them in contact with river sediment. That model is linked to a multimedia fate and transport model (MFTM) to receive inputs from the surrounding area and to evaluate the impact of its outputs to the different environmental media (air, water, sediment, soil). The parameter values were adapted to simulate the fate of bis(2-ethylhexyl) phthalate (DEHP) in the integrated system. More details on the model can be found in De Keyser *et al.* (2010). With the model, a number of scenarios were evaluated. In the reference scenario, an upstream MFTM water compartment provides the input to the IUWS river model, a downstream MFTM water compartment receives the IUWS river water and primary and secondary waste wastewater sludge is conveyed to the MFTM soil compartment after treatment in a thickener. A combined sewer system was implemented with treatment in the WWTP before discharge into the surface water. In the second scenario the sewer system is separated, sending wastewater to the WWTP and stormwater to infiltration ponds considered as best management practice (BMP), with volatilisation and infiltration processes occurring.

Wet and dry deposition, as well as diffusion, are considered as exchange processes between the compartments air and soil in the multimedia model, but similar links between the air and the urban catchments were neglected because the surface area of the urban catchments causes the fluxes to be a factor 1,000 smaller than the assumed emissions onto the urban surface. The dynamic simulation results shown in Figure 3 indicate that the installation of stormwater infiltration ponds helps avoid DEHP peak discharges into the surface water originating from the stormwater. On the other hand, data plotted in Figure 3 also shows that the stormwater infiltration ponds reallocate the DEHP flows to groundwater and air. The increased air concentrations are transient due to photochemical breakdown and advective transport out of the modelled system, whereas the accumulation of DEHP in the groundwater compartment could potentially cause long-term problems.

Discussion

Based on the above examples on model use, here we discuss some of the important attributes that may be relevant to future model development. First, MP biotransformation is not considered in most of the models of sewer systems and/or recipient water bodies. Second, for WWTP modelling in catchment-scale simulation tools, often simple heuristic sink terms (i.e. fraction of MP eliminated) are used to approximate MP removal. Third, MP removal, for example, in WWTPs, is mostly assessed based on loads calculated using the influent and effluent parent compound
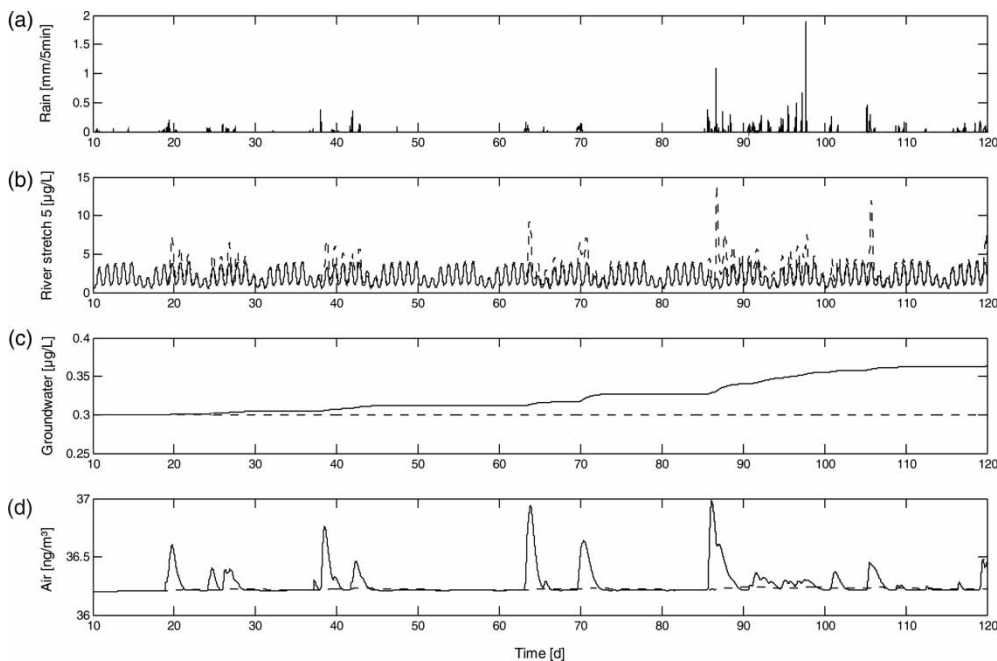

Figure 3 │ Input rainfall series (a) and simulated DEHP concentration in the two modelled scenarios (basic scenario in dotted line, scenario with sewer separation and infiltration ponds in solid line) in the last river stretch of the IUWS model (b), in the groundwater compartment of the MFTM (c) and in the air compartment of the MFTM (d); installation of the ponds occurs at day 10.

concentrations. The impact of parent compound retransformation from other chemicals (e.g. human metabolites) thus has been mostly overlooked – a factor that can significantly affect the calculated MP removal efficiency rate. Fourth, in literature studies, the selection of MPs for modelling is often just an arbitrary decision. Future MP modelling studies should prioritise chemicals according to the rankings obtained in regional risk assessments, e.g. in the context of the WFD.

LIFE CYCLE ASSESSMENT (LCA) FOR ADVANCED TREATMENT TECHNOLOGIES

Life cycle assessment (LCA) is a holistic accounting method to assess potential environmental impacts of human activities involved in providing a product or service (e.g. wastewater treatment) described and quantified in the functional unit (e.g. one cubic metre wastewater) to which all impacts are related. The implementation of MP models in LCA studies can improve the assessment of retrofitting needs by providing an in-depth assessment of the MP occurrence and removal in biological wastewater treatment. With the aim of choosing the most environmentally sustainable wastewater treatment technology for MP removal, LCA may be used as a decision support tool.

By normalising and eventually weighting the impact potentials it becomes possible to compare different ways (e.g. technologies) of providing the same service (e.g. removal of MPs). In its most comprehensive form, LCA includes all exchanges, i.e. emissions and resource consumptions (e.g. from building, running and demolishing the treatment facilities), in the whole life cycle of the service, from extraction of raw materials to final disposal ('cradle to grave'). In the recently finished EU FP6 project NEPTUNE (www.eu-neptune.org), LCA was actually used for assessing the relative environmental sustainability of different 'new' wastewater treatment technologies for MP removal. The principle used was to compare the induced impacts (from building, running and demolishing the polishing step) with the avoided impacts due to the removal of MPs (i.e. avoided impact in the recipient). By subtracting the total induced impact from the total avoided impact, an indicator of the relative sustainability is achieved – the higher the value, the higher the relative sustainability. In the NEPTUNE project the following technologies/systems on MP removal were assessed (Larsen *et al.* 2010); ozonation, sand filtration, pulverised activated carbon (PAC) addition in biology, ozonation followed by sand filtration and PAC addition to effluent followed by sand filtration. Among these treatment systems ozonation combined with post sand filtrations seems to be the most optimal solution when looking at environmental sustainability. PAC addition to effluent combined with post sand filtration did not show as good a sustainability profile as the one for ozonation combined with sand filtration – mainly due to the high potential impact from the production of PAC. When looking at cost/efficiency, i.e. the obtained reduction in potential environmental impact per Euro spent, the value for ozonation combined with sand filtration is about three times higher for ozonation combined with sand filtration than for PAC addition to effluent combined with post sand filtration. Due to the lack of measured data, the number of MPs included in the sustainability assessments were (only) about 30. Increasing this number by sensible MP fate modelling would most probably enhance the comprehensiveness and the reliability of the results.

CONCLUSIONS AND RECOMMENDATIONS

To conclude, as to the environmental risk posed by MPs, we are currently in the denial phase where the benefits of control are uncertain and the costs are judged to be high. To assess the environmental risk, given the large number of chemicals, MPs should be prioritised for monitoring, e.g. in the context of the European Union's Water Framework Directives. These EU directives do not consider yet MP removal via wastewater treatment. If MPs become regulated in wastewater, more mechanistic modelling of these contaminants would become of greater importance. This can contribute to improved assessment of WWTP retrofitting needs by regulators and stakeholders. Should regulatory limits be imposed with maximum or 'never to exceed' effluent concentrations or loadings, dynamic modelling would be required.

Recently, integrated, dynamic urban-scale source-and-flux models were developed for quantifying the release of MPs from urban sources and their fate within different wastewater treatment systems. These models can be linked to simple, river basin scale multimedia models used in ecological risk assessment. For WWTPs, more mechanistic models were developed for hormones and antibiotics MPs in activated sludge and PAHs in anaerobic digestion processes. Integrated urban water system models were evaluated, including rural catchment, sewer networks, WWTPs, overflow structures connected to a river model.

A few recommendations are additionally provided to improve MP fate and transport models, and to increase their acceptance and use:

- In the future, more data are needed that can be used in mass balance calculations, i.e. reported concentration values should be representative of the flow conditions prevailing in a given system. Future MP modelling studies should prioritise chemicals that are top ranked in regional risk assessments.
- Besides detectable parent compounds, emission assessments should additionally account for human drug metabolites and other contaminant fractions in wastewater (sorbed or conjugated), which can be retransformed via the parent compound – some of which can only be assessed using model-based evaluations.
- Thanks to the considerable development relevant areas went through in the last decade, e.g. analytical methods, drug metabolism research, monitoring techniques, relatively low uncertainty levels in measured concentration data can be achieved. Heuristic and other conventional fate models can and should thus be replaced with more mechanistic approaches. In the future, a systematic modelling framework is required for predicting MP removal in WWTPs.
- Further research is still required to assess biotransformation parameter values for a high number of MPs under different redox and pH conditions, typical of WWTPs. Additionally, factors that can affect MP removal in WWTPs (e.g. readily biodegradable substrates, metals salts) should be evaluated, and accounted for in process models. In WWTPs, the impact of cyclic (diurnal) contaminant mass load on removal efficiency should be assessed using dynamic models.
- The conditions of microbial adaptation at higher SRT and thus the enhanced biotransformation capacity of MPs require further research. The assessment of specific microbial strains and enzymatic reactions responsible for MP biotransformation in wastewater are important examples for the focus of future studies.
- In process models used for decision making (e.g. WWTP retrofitting), besides accounting for anoxic/anaerobic and aerobic growth conditions, advanced chemical and physical–chemical removal processes should additionally be included. This requires more mechanistic knowledge and thus model development.
- LCA is a comprehensive method that can support choosing the most environmentally sustainable wastewater treatment technology for MP removal. It can be used to get the net benefit of a technology, by comparing the induced impacts (from installing the new technology) to the avoided impacts thanks to the removal of MP.
- Experience should be gained by realising more case-studies and this should show the benefits of MP-modelling.

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REFERENCES

Alvarez-Cohen, L. & Speitel Jr., G. E. 2001 Kinetics of aerobic cometabolism of chlorinated solvents. *Biodegradation* **12** (2), 105–26.

Angelidaki, I., Mogensen, A. S. & Ahring, B. K. 2001 Degradation of organic contaminants found in organic waste. *Biodegradation* **11**, 377–383.

Artola-Garicano, E., Borkent, I., Damen, K., Jager, T. & Vaes, W. H. J. 2003 Sorption kinetic and microbial biodegradation activity of hydrophobic chemical in sewage sludge: model and measurements based on free concentration. *Environmental Science and Technology* **37** (1), 116–122.

Barret, M., Patureau, D., Latrille, E. & Carrère, H. 2010a A three-compartment model for micropollutants sorption in sludge: Methodological approach and insights. *Water Research* **44** (2), 616–624.

Barret, M., Carrère, H., Latrille, E., Wisniewski, C. & Patureau, D. 2010b Micropollutant and sludge characterization for modeling sorption equilibria. *Environmental Science and Technology* **44** (3), 1100–1106.

Benedetti, L., Vezzaro, L., Gevaert, V., De Keyser, W., Verdonck, F., De Baets, B., Nopens, I., Vanrolleghem, P. A. & Mikkelsen, P. S. 2009 Dynamic transport and fate models for

micropollutants in integrated urban wastewater systems. *In: Proceedings of WEFTEC2009*. Orlando, FL, USA, 10–14 October 2009.

Boxall, A. B. A., Kolpin, D. W., Halling-Sørensen, B. & Tolls, J. 2003 Are veterinary medicines causing environmental risks? *Environmental Science and Technology* **37** (15), 286–294.

CEC 2000 Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for the Community action in the field of water policy.

Clara, M., Kreuzinger, N., Strenn, B., Gans, O. & Kroiss, H. 2005 The solids retention time – a suitable design parameter to evaluate the capacity of wastewater treatment plants to remove micropollutants. *Water Research* **39**, 97–106.

Criddle, C. S. 1993 The kinetics of cometabolism. *Biotechnology and Bioengineering* **41**, 1048–1056.

De Keyser, W., Gevaert, V., Verdonck, F., Nopens, I., De Baets, B., Vanrolleghem, P. A., Mikkelsen, P. S. & Benedetti, L. 2010 Combining multimedia models with integrated urban water system models for micropollutants. *Water Science and Technology* **62** (7), 1614–1622.

Delgadillo-Mirquez, L., Lardon, L., Steyer, J. P. & Patureau, D. 2011 A new dynamic model for bioavailability and cometabolism of micropollutants during anaerobic digestion. *Water Research* **45**, 4511–4521.

Drewes, J. E., Hemming, J., Ladenburger, S. J., Schauer, J. & Sonzogni, W. 2005 An assessment of endocrine disrupting activity changes in water reclamation systems through the use of bioassays and chemical measurements. *Water Environment Research* **77** (1), 12–23.

Dytczak, M. A., Londry, K. L. & Oleszkiewicz, J. A. 2006 Transformation of estrogens in nitrifying activated sludge under aerobic and alternating anoxic/aerobic conditions. In: *Proceedings of WEFTEC2006*. Dallas, TX, USA, 22–25 October 2006.

Farré, M., Kloter, G., Petrovic, M., Alonso, M. C., de Alda, M. J. L. & Barceló, D. 2002 Identification of toxic compounds in wastewater treatment plants during a field experiment. *Analytical Chimica Acta* **456** (1), 19–30.

Gevaert, V., Verdonck, F., Benedetti, L., De Keyser, W. & De Baets, B. 2009 Evaluating the usefulness of dynamic pollutant fate models for implementing the EU Water Framework Directive. *Chemosphere* **79**, 27–35.

Grady Jr., C. P. L., Daigger, G. T. & Lim, H. C. 1999 *Biological Wastewater Treatment*. Marcel Dekker, New York, USA.

Grung, M., Källqvist, T., Sakshaug, S., Skurtveit, S. & Thomas, K. V. 2008 Environmental assessment of Norwegian priority pharmaceuticals based on the EMEA guideline. *Ecotoxicology and Environmental Safety* **71** (2), 328–340.

Gustafsson, O., Nilsson, N. & Bucheli, T. D. 2001 Dynamic colloid-water partitioning of pyrene through a coastal Baltic spring bloom. *Environmental Science and Technology* **35** (20), 4001–4006.

Holbrook, R. D., Love, N. G. & Novak, J. T. 2004 Investigation of sorption behavior between pyrene and colloidal organic carbon from activated sludge processes. *Environmental Science and Technology* **38**, 4987–4994.

Joss, A., Andersen, H., Ternes, T. A., Richle, P. A. & Siegrist, H. 2004 Removal of estrogens in municipal wastewater treatment under aerobic and anaerobic conditions: consequences for plant optimization. *Environmental Science and Technology* **38** (11), 3047–3055.

Joss, A., Siegrist, H. & Ternes, T. A. 2008 Are we about to upgrade wastewater treatment for removing organic micropollutants. *Water Science and Technology* **57** (2), 251–255.

Joss, A., Zabczynski, S., Göbel, A., Hoffmann, B., Löffler, D., McArdell, C. S., Ternes, T. A., Thomsen, A. & Siegrist, H. 2006 Biological degradation of pharmaceuticals in municipal wastewater treatment: proposing a classification scheme. *Water Research* **40** (8), 1686–1696.

Langford, K. H., Scrimshaw, M. D., Brikett, J. W. & Lester, J. N. 2005 Degradation of nonylphenolic surfactants in activated sludge batch tests. *Water Research* **39**, 870–876.

Larsen, H. F., Hansen, P. A. & Boyer-Souchet, F. 2010 Decision support guideline based on LCA and cost/efficiency assessment. *Deliverable 4.3. EC Project 'NEPTUNE'*, contract No.: 036845. www.eu-neptune.org

Lindblom, E., Press-Kristensen, K., Vanrolleghem, P. A., Mikkelsen, P. S. & Henze, M. 2009 Dynamic experiments with high bisphenol-A concentrations modelled with an ASM model extended to include a separate XOC degrading microorganism. *Water Research* **43** (13), 3169–3176.

Mackay, D. & Paterson, S. 1981 Calculating fugacity. *Environmental Science and Technology* **15** (9), 1006–1014.

Melcer, H., Bell, J. P., Thompson, D. J., Yendt, C. M., Kemp, J. & Steel, P. 1994 Modeling volatile organic contaminants fate in waste-water treatment plants. *Journal of Environmental Engineering-ASCE* **120** (3), 588–609.

Melcer, H., Klecka, G., Monteith, H. & Staples, C. 2007 Fate of nonylphenol ethoxylate surfactants in wastewater treatment plants. In: *Proceedings of WEF Specialty Conference on Compounds of Emerging Concern*. Providence, RI, USA, 29–30 July 2007.

Monteith, H., Andres, H., Snowling, S. & Schraa, O. 2008 Modeling the fate of estrogenic hormones in municipal wastewater treatment. In: *Proceedings of WEFTEC2008*. Chicago, IL, USA, 18–22 October 2008.

Monteith, H. D., Parker, W. J., Bell, J. P. & Melcer, H. 1995 Modeling the fate of pesticides in municipal wastewater treatment. *Water Environment Research* **67**, 964–970.

NORMAN 2011 Network of reference laboratories and related organisations for monitoring and bio-monitoring of emerging environmental pollutants. www.norman-network.net.

Ort, C. & Gujer, W. 2006 Sampling for representative micropollutant loads in sewer systems. *Water Science and Technology* **54** (6–7), 169–176.

Ort, C., Hollender, J., Schaerer, M. & Siegrist, H. 2009 Model-based evaluation of reduction strategies for micropollutants from wastewater treatment plants in complex river networks. *Environmental Science and Technology* **43** (9), 3214–3220.

Ort, C., Lawrence, M. G., Reungoat, J. & Mueller, J. F. 2010a Sampling for PPCPs in wastewater systems: a comparison of

different sampling modes and optimization strategies. *Environmental Science and Technology* **44** (16), 6289–6296.

Ort, C., Lawrence, M. G., Rieckermann, J. & Joss, A. 2010b Sampling for PPCPs and illicit drugs in wastewater systems: are your conclusions valid? A critical review. *Environmental Science and Technology* **44** (16), 6024–6035.

Plósz, B. G., Langford, K. H., Heiaas, H. H., Macrae, K., Liltved, H., Lopez, A. & Vogelsang, C. 2010a The BIOZO process – a biofilm system combined with ozonation: Occurrence of xenobiotic organic micropollutants in and removal of polycyclic aromatic hydrocarbons and nitrogen from landfill leachate. *Water Science and Technology* **61** (12), 3188–3197.

Plósz, B. G., Leknes, H. & Thomas, K. V. 2010b Impacts of competitive inhibition, parent compound formation and partitioning behaviour on antibiotic micropollutants removal in activated sludge. *Environmental Science and Technology* **44** (2), 734–742.

Plósz, B. G., Lehnberg, K., Dott, W. & Thomas, K. V. 2010c An activated sludge model for xenobiotic organic micropollutants (ASM-X): Factors influencing the solid-liquid partitioning in wastewater treatment. In: *Proceedings of the 2nd IWA/WEF Wastewater Treatment Modelling Seminar.* Mont-Sainte-Anne, Quebec, Canada, 28–31 March 2010.

Plósz, B. G., Leknes, H., Liltved, H. & Thomas, K. V. 2010d Diurnal variations in the occurrence and the fate of hormones and antibiotics in activated sludge wastewater treatment in Oslo, Norway. *Science of the Total Environment* **408** (8), 1915–1924.

Pomati, F., Castiglioni, S., Zuccato, E., Fanelli, R., Vigetti, D., Rossetti, C. & Calamari, D. 2006 Effects of a complex mixture of therapeutic drugs at environmental levels on human embryonic cells. *Environmental Science and Technology* **40** (7), 2442–2447.

Seth, R., Mackay, D. & Webster, E. 2008 Continued development of a mass balance model of chemical fate in a sewage treatment plant. *Water Research* **42**, 595–604.

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 Research* **38**, 3223–2330.

Schowanek, D., Fox, K., Holt, M., Schroeder, F. R., Koch, V., Cassani, G., Matthies, M., Boeije, G., Vanrolleghem, P. A., Young, A., Morris, G., Gandolfi, C. & Feijtel, T. C. 2001 GREAT-ER: a new tool for management and risk assessment of chemicals in river basins. Contribution to GREAT-ER # 10. *Water Science and Technology* **43** (2), 179–185.

Soares, A., Guieysse, B., Jefferson, B., Cartmell, E. & Lester, J. N. 2008 Nonylphenol in the environment: a critical review on occurrence, fate, toxicity and treatment in wastewaters. *Environmental International* **34** (7), 1033–1049.

Song, M., Chu, S., Letcher, R. J. & Seth, R. 2006 Fate, partitioning and mass loading of polybrominated diphenyl ethers (PBDEs) during the treatment processing of municipal sewage. *Environmental Science and Technology* **40** (20), 6241–6246.

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 Research* **25** (7), 891–900.

Suarez, S., Lema, J. M. & Omil, F. 2010 Removal of Pharmaceutical and Personal Care Products (PPCPs) under nitrifying and denitrifying conditions. *Water Research* **44** (10), 3214–3224.

Ternes, T. A. & Joss, A. 2006 *Human Pharmaceuticals, Hormones and Fragrances – The Challenge of Micropollutants in Urban Water Management*. IWA Publishing, London, UK.

Ternes, T. A., Keckel, P. & Mueller, J. 1999 Behavior and occurrence of estrogens in municipal sewage treatment plants. II. Aerobic batch experiments with activated sludge. *Science of the Total Environment* **225** (1–2), 91–99.

Ternes, T. A., Herrmann, N., Bonerz, M., Knacker, T., Siegrist, H. & Joss, A. 2004 A rapid method to measure the solid-water distribution coefficient (K-d) for pharmaceuticals and musk fragrances in sewage sludge. *Water Research* **38**, 4075–4084.

Tran, N. H., Urase, T. & Kusakabe, O. 2009 The characteristics of enriched nitrifier culture in the degradation of selected pharmaceutically active compounds. *Journal of Hazardous Materials* **171** (1–3), 1051–1057.

Vezzaro, L., Eriksson, E., Ledin, A. & Mikkelsen, P. S. 2010 Dynamic stormwater treatment unit model for micropollutants (STUMP) based on substance inherent properties. *Water Science and Technology* **62** (3), 622–629.

Viglino, L., Aboulfadl, K., Daneshvar Mahvelat, A., Prévost, M. & Sauvé, S. 2007 On-line solid phase extraction and liquid chromatography/tandem mass spectrometry to quantify pharmaceuticals, pesticides and some metabolites in wastewaters, drinking, and surface waters. *Journal of Environmental Monitoring* **10**, 482–489.

von der Ohe, P. C., Dulio, V., Slobodnik, J., De Deckere, E., Kuhne, R., Ebert, R. U., Ginebreda, A., De Cooman, W., Schüürmann, G. & Brack, W. 2011 A new risk assessment approach for the prioritization of 500 classical and emerging organic microcontaminants as potential river basin specific pollutants under the European Water Framework Directive. *Science of the Total Environment* **409** (11), 2064–2077.

Wang, X. & Grady Jr., C. P. L. 1995 Effects of biosorption and dissolution on the biodegradation of di-*n*-butyl phthalate. *Water Environment Research* **67**, 863–871.