# Perspectives on modelling micropollutants in wastewater treatment plants

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## ABSTRACT

Models for predicting the fate of micropollutants (MPs) in wastewater treatment plants (WWTPs) have been developed to provide engineers and decision-makers with tools that they can use to improve their understanding of, and evaluate how to optimize, the removal of MPs and determine their impact on the receiving waters. This paper provides an overview of such models, and discusses the impact of regulation, engineering practice and research on model development. A review of the current status of MP models reveals that a single model cannot represent the wide range of MPs that are present in wastewaters today, and that it is important to start considering classes of MPs based on their chemical structure or ecotoxicological effect, rather than the individual molecules. This paper identifies potential future research areas that comprise (i) considering transformation products in MP removal analysis, (ii) addressing advancements in WWTP treatment technologies, (iii) making use of common approaches to data acquisition for model calibration and (iv) integrating ecotoxicological effects of MPs in receiving waters.

**Key words** | ecotoxicology, experimental design, micropollutant fate, removal mechanism, trace chemicals, uncertainty

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## INTRODUCTION

Wastewaters entering treatment plants contain numerous inorganic and organic micropollutants (MPs) defined as trace chemicals present at concentrations from μg/L to pg/L. They can be grouped according to their application (e.g., pharmaceuticals and personal care products (PPCPs), pesticides), their molecular similarity (e.g., polyfluorinated compounds, metals) or biochemical activity (e.g., hormones) (Ternes & Joss 2006). MPs can also be classified according to their regional occurrence as defined in the lists of priority substances proposed in ongoing regulation reinforcement

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initiatives in both North America and Europe (Environment Canada 2004; European Community 2000, 2008).

Conventional wastewater treatment plants (WWTPs) were designed for the elimination of organic matter and nutrients. Therefore, most MPs are only partially removed with waste activated sludge, transformed or volatilized, whereas others are not altered by treatment (Clara *et al.* 2005a; Joss *et al.* 2005; Choubert *et al.* 2011; Martin-Ruel *et al.* 2011). MP modelling provides engineers and decision-makers with tools that can evaluate the fate of, and optimize, MP removal in WWTPs, thereby minimizing their impact on receiving waters.

The paper extends the discussion paper written by Plósz *et al.* (2013) with the objective of discussing models that are used to identify the conditions that maximize MP removal in WWTPs, and acknowledging the role that models play in the context of regulation, engineering practice and research by responding to the following questions.

1. **What is the purpose of MP modelling?** Modelling has become an integral part of WWTP design and operation, and is an important tool for assessing and regulating contaminant emission into the environment.
2. **What is the current status of MP modelling?** The MP fate models currently being developed differ in the number and definition of state variables and processes. One of the key issues is the question of the 'optimum complexity' of process models, i.e., the simplest model structure that allows solving the problem to be addressed.
3. **How should MP modelling evolve in the future?** Modellers are facing several challenges, such as evolving knowledge about MPs and evolving wastewater treatment technologies and regulatory targets.

## WHAT IS THE PURPOSE OF MP MODELLING?

The purposes of mathematical models are to understand processes (diagnostic), predict performance/behaviour (prognostic) and communicate scientific results (education) (Hug *et al.* 2009). While models are commonly used to design and optimize WWTPs, they are now more and more applied to support regulatory decisions. Models are also useful tools in research, education and consulting, for both understanding mechanisms and communicating knowledge. This section discusses aspects of regulatory control, engineering approaches to optimizing MP removal mechanisms in WWTPs and research needs in MP model development.

### Regulatory aspects

#### Australia

Water reuse is of great concern in Australia, and some guidelines exist that limit the concentration of some MPs in the treated water (sewage and stormwater) that is used to augment drinking water supplies (NRMMC-EPHC-NHMRC 2008). According to the Australian legal system these guidelines can then be adopted into regulation by the states. To date, there are no general guidelines for secondary effluent discharge of MPs in the environment.

#### North America

In the USA, MPs are largely unregulated at the federal level; instead, a patchwork of regulations at state and municipal levels exist to control MPs at the source rather than at the end of pipe, favouring source control (IJC 2009). Sometimes, control of specific metal and volatile organic MPs is implemented through municipal sewer ordinances. In Canada, the management and control of chemical substances is regulated at the federal level through the risk-based Canadian Environmental Protection Act, with provincial programmes that focus on end-of-pipe measures (Environment Canada 2004).

#### Europe

The European Parliament Directive 2008/105/EC defined environmental quality standards for 33 priority substances for receiving waters in the European Community (European Community 2008). These thresholds are maximal concentrations tolerated in receiving bodies, and define the good 'chemical status' as specified by the European Commission (European Community 2000). Few new MPs have been recently added to the list of priority substances (European Commission 2012). These are not linked to any municipal standard for discharging treated WWTP effluents, but they have led some European countries to improve their WWTPs. As an example, new legislation plans in Switzerland have been laid out for upgrading approximately 100 WWTPs with enhanced MP removal (OFE 2012). Additional regulations, such as the European Union's Registration, Evaluation, and Authorization of Chemicals (REACH) legislation, are changing the way chemicals in everyday products are handled. Indeed, data on chemical toxicity and uses are now required, as well as preventive action for classes of high concern chemicals.

### Future development

There are many types of regulations concerning MPs, but there is a lack of regulations for controlling specific MPs discharged from WWTPs. The thrust of environmental quality control to date has led to the ban of only a few of the many thousands of MPs (WEF 2007). From a modelling perspective, the lack of clear effluent limits in regulations is a challenge as it is difficult to define an effluent target for model-based process optimization of MP removal in WWTPs. In the absence of regulations, nevertheless, measured and predicted environmental concentrations, and predicted no effect concentrations can be considered. Finally, regulations may consider the assessment of ecotoxicological effects rather than concentrations of suspected MPs (WEF 2007). Then, the current-day models that are based on estimating the concentrations of individual MPs through the WWTP need to be extended to provide a composite biological toxicity index.

## Engineering aspects

### State-of-the-art

Engineers use models mainly to select the best process configuration for given wastewater compositions and effluent discharge requirements, to evaluate the efficiency of a design configuration under dynamic conditions and to find optimal operating conditions (e.g., aeration levels, sludge concentration). Therefore, mathematical models are a potential means for improving MP removal in WWTPs (Gernaey *et al*. 2004), either with existing infrastructure or by identifying additional treatment stages (tertiary treatment, enhanced sludge treatment, etc.). Considerable efforts are on going worldwide to compare and benchmark treatment technologies related to MP removal or transformation (Choubert *et al*. 2011; Pileggi *et al*. 2011; Cloutier *et al*. 2012; Pomiès *et al*. 2013). Comprehensive databases based on literature reports have been developed (e.g., Miège *et al*. 2009; USEPA 2010) and may provide additional insight into which process configurations demonstrate enhanced removal for different classes of MP compounds.

However, these databases have severe limitations for modellers in the sense that important process data that may be critical in predicting MP fate are not consistently provided. For example, many of the early experimental papers that reported on MP fate did not provide enough information about operational parameters, such as solids and hydraulic retention times. The loss of some MPs was correlated with changes in solids retention time (SRT) across a range of treatment configurations (Clara *et al*. 2005b). For other MPs, e.g., diclofenac, carbamazepine, SRT proved to be an insufficient predictor of MP fate (Strenn *et al*. 2004; Suarez *et al*. 2010). More recently, research on the role of heterotrophic bacteria versus ammonia-oxidizing autotrophic bacteria on the fate of selected MPs has shown that these groups of bacteria probably play different roles in defining MP fate (Khunjar *et al*. 2011a; Love *et al*. 2012). Therefore, a lack of correlation with SRT may be more owing to a lack of knowledge about the physiological condition of various ecological groups that are present in biological processes. Given the difficulty to obtain experimental data, mechanistic models are preferred to empirical ones (Melcer *et al*. 1988).

### Future development

Modellers have made significant progress in developing mathematical structures for deterministic models that predict the fate of MPs through various processes in WWTPs, particularly in biological treatment processes. However, a certain degree of complexity has to be reached if models are to be used to improve the prediction of MP removal in WWTPs, and the level of knowledge of removal mechanisms and chemical interactions currently precludes the application of models for designing and improving operational strategies of treatment processes. The fate of an increasingly larger range of MPs is being characterized and, thus, the improved understanding of the mechanisms underlying MP fate will probably result in process models able to predict effluent concentrations of MPs from WWTPs. While this carries the promise that such models will find their way into day-to-day engineering practice, considerable efforts are still needed.

## Research aspects

### State-of-the-art

In the field of MP modelling, research focusses on estimating parameters of existing models, as well as identifying new model structures. Some of the key issues that modellers are facing are the fate of MPs owing to the very low concentrations at which they occur, the large number of MPs to be considered, with a wide range of properties, and their behaviour in the complex environment of WWTP systems. Model calibration and validation are only as good as the data used. Consequently, model development is often hindered because water quality sampling strategies (frequency, location) are often insufficient to capture true patterns in

WWTPs, which can be highly dynamic (Ort *et al.* 2010a). To reduce costs when collecting data, some researchers are proposing the use of surrogates that serve to represent classes of MPs, and to use the fate of these surrogates to predict the fate of a broader range of compounds (Drewes *et al.* 2009).

### Future development

Researchers in MP modelling need to determine the most helpful information required to upgrade predictive models and thus improve the ability to predict the fate of MPs through WWTPs. For this purpose, the following problems need to be addressed: How can the co-metabolic biotransformation of MPs be described mathematically? What microorganisms are involved in MP biotransformation and how does microbial acclimation affect the biotransformation? Does retransformation of parent chemicals explain the fact that concentrations in the effluent are higher than in the influent? Do biotransformation pathways involve the sorbed or soluble MP fraction? How shall the potential influence of organic and inorganic fractions in the sludge on MP sorption be modelled?

## WHAT IS THE CURRENT STATUS OF MP MODELLING?

This section first discusses some problems identified for certain mechanisms involved in MP fate in WWTPs and then addresses some problems with overall fate models. The impact of data quality on the model structure, as well as the model uncertainty, is also reviewed. Finally, an illustration of what can be done with MP fate models is presented.

### MP fate in WWTPs

#### State-of-the-art

In WWTPs, the fate of MPs is controlled by physico-chemical and biological processes (Rogers 1996) (Figure 1). The distribution of the numerous MPs present in wastewaters between environmental compartments depends on the physico-chemical and biological properties that are relevant to each MP and process. Photolysis is a relevant removal mechanism of MPs in stabilization ponds (solar radiation) (e.g., Moreno *et al.* 2003) and in treatment units that employ ultraviolet (UV) disinfection (Pereira *et al.* 2007; Rosenfeldt *et al.* 2007). Volatilization due to

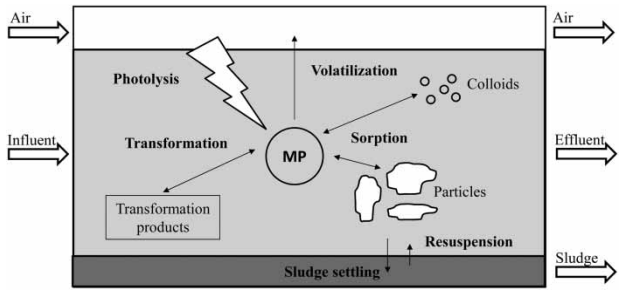


**Figure 1** | Processes controlling the fate of MPs during wastewater treatment.

diffused aeration, mechanical aeration and mixing can be another significant removal process in WWTPs for some MPs. Sorption and desorption onto suspended colloids and particles present in wastewaters induce the removal of sorbed MPs via waste sludge. Biotransformation is used to refer broadly to biologically-mediated chemical modifications, and includes the formation of metabolites (transformation products) or the complete mineralization (formation of carbon dioxide) of the compound. Chemical transformation occurs in advanced WWTPs equipped with a tertiary oxidation process that uses ozone, UV radiation/titanium dioxide or hydrogen peroxide in order to produce hydroxyl radicals, one of the strongest oxidants (e.g., Esplugas *et al.* 2007).

#### Photolysis

Direct photolysis occurs when light is absorbed by the MP, while indirect photolysis refers to processes initiated through the absorption of light by intermediary compounds (Schnoor 1996). Photolysis is affected by the absorbance characteristics of the MP and the suspended solids concentration which, combined with the natural attenuation of incoming sunlight by water itself, limits the penetration of light. The GCSOLAR program (USEPA) can calculate the photolysis half-lives of different pollutants as a function of the season, latitude, time of day, depth of water and ozone layer thickness (Zepp & Cline 1977).

#### Volatilization

The partition between the gas and the water phase occurs until equilibrium between the two phases is reached (Roberts *et al.* 1984) and is described by Henry's Law. Because of the very low concentration of MPs in the atmosphere, the transfer can be assumed to only occur from the

wastewater to the atmosphere. The Henry's Law constants can be used to predict the behaviour of a compound at the interface between air and water. Although most MPs have Henry's Law constants that suggest a low propensity to volatilize, volatilization can be a relevant process for some MPs in treatment trains with large surface areas (e.g., waste stabilization ponds) or with high aeration rate (e.g., membrane bioreactors).

## Sorption

Using the standardized notation proposed in Corominas *et al.* (2010), the partitioning of MP by sorption and desorption processes onto suspended solids, $X_{TSS}$ [g $L^{-1}$ as total suspended solids (TSS)] (sometimes expressed as volatile suspended soilds), can be characterized by assuming an equilibrium state between the concentrations of the dissolved MP, $S_{MP}$[g $L^{-1}$], and the solid phase, $X_{MP}$ [g $L^{-1}$]:

$$K_D = \frac{X_{MP}}{X_{TSS} \cdot S_{MP}}$$

where the partitioning or sorption coefficient is denoted as $K_D$ [L g$X_{TSS}^{-1}$].

Equilibrium partitioning can also be characterized with the ratio $k_{Sor}/k_{Des} = K_D$, where $k_{Sor}$ and $k_{Des}$ are the sorption and desorption rate coefficients respectively (e.g., Joss *et al.* 2006; Lindblom *et al.* 2009). Sorption and desorption can be assumed to be in close equilibrium if the sorption substance mass flux is about 10 times higher than the biodegradation flux (Ternes & Joss 2006).

A common procedure to determine $K_D$ consists of dosing a specific MP to inhibited biological sludge and then measuring the equilibrium concentrations in the liquid and solid phases. In targeted sorption experiments, biotransformation can be inhibited using one of a range of methods: thermal sterilization (De Gusseme *et al.* 2009); gamma radiation (Melo *et al.* 2008); chemical agents, such as mercury chloride (Maurer *et al.* 2008); and sodium azide (Barbot *et al.* 2010). However, these methods may influence sludge properties (see detailed assessment by Maurer *et al.* (2008)), and both the properties of the MP and those of the sludge that are relevant to sorption behaviour (e.g., Khunjar & Love 2011b; Hyland *et al.* 2012).

It is important to consider colloids when measuring $K_D$ because a significant amount of sorption can occur on colloids (Holbrook *et al.* 2004). Unfortunately, there is a lack of consensus about the definition of colloidal material in wastewater. For example, Rickert & Hunter (1971) define the colloidal size to be 0.001–1 μm, while Levine *et al.* (1985) defined colloid size to be 0.08–1 μm. Most often, water quality analysis consists of filtration through a 0.45-μm porous membrane to separate suspended solids from colloidal and soluble matter (APHA 2012). Therefore, the influence of colloids on sorption is not differentiated in most published cases.

Several MPs, such as most of the PPCPs found in municipal wastewater, are ionizing substances, i.e., anionic, cationic or zwitterionic; therefore, their partitioning behaviour is affected by pH and ionic interactions. One way to account for the impact of pH on partitioning behaviour is to use different $K_D$ values estimated under typical pH conditions prevailing in aerobic and anoxic reactors (Plósz *et al.* 2012).

## Biotransformation

Different hypotheses exist concerning whether biotransformation occurs in the dissolved or sorbed fraction compartment. However, the experimental evidence related to the biotransformation of sorbed fractions is limited, as shown by Delgadillo-Mirquez *et al.* (2011). In the case when dissolved MP biotransformation is favoured, kinetic constants are determined by measuring the change in dissolved MP concentrations over time. Furthermore, there is very limited to no knowledge about how the micro-organisms present in biological systems evolve or adapt to the presence of MPs.

Kinetic constants are mainly available for aerobic conditions, for example polycyclic aromatic hydrocarbons (PAHs), surfactants and a few pharmaceutical compounds (Urase & Kikuta 2005; Joss *et al.* 2006). A few researchers studied the effect of redox conditions on the transformation rates of trace or industrial chemicals (Zitomer & Speece 1993). Plósz *et al.* (2010a), and Suarez *et al.* (2010) assessed biotransformation under aerobic and anoxic conditions, and showed that the biotransformation rate can vary significantly under different redox conditions. This is most likely attributable to the different MP biotransformation capacity of reactions catalysed by heterotrophic bacteria under aerobic and anoxic conditions, and owing to differences in the relative capacity of heterotrophs and ammonia-oxidizing bacteria (AOB) to oxidize compounds under aerobic versus anoxic conditions. For instance, Khunjar *et al.* (2011a) showed that AOB degraded 17$\alpha$-ethinylestradiol (EE2) approximately five times faster than heterotrophic bacteria under aerobic conditions.

Numerous papers have reported that the biotransformation of MPs is only possible in the presence of another compound used as carbon and energy source (Criddle 1993; Clara *et al.* 2005b), and that the process is co-metabolic. Under this condition, the removal of MPs would not produce biomass growth, i.e., the biomass yield attributed to MP degradation is insignificant. Conversely, it has also been shown that readily biodegradable growth substrates can competitively inhibit MP transformation by limiting access to the non-specific enzyme sites (Chang & Alvarez-Cohen 1995).

## Modelling MP fate in WWTPs

### State-of-the-art

The development of models that can predict the fate of MPs in WWTPs started in the 1980s, after the fugacity concept was published (Mackay 1979). Several models were then created, most notably SimpleTreat (Struijs *et al.* 1991), WWTREAT (Cowan *et al.* 1993), Water9 (USEPA 1994) and TOXCHEM (Melcer *et al.* 1994). Meanwhile, activated sludge models (ASM) were proposed (Henze *et al.* 1987), and various add-on models or ASM-based models were created for both bulk pollutants and specific MPs (e.g., Monteith *et al.* 2008; Plósz *et al.* 2010a). Although most categories of MPs have been modelled before, it appears that volatile organic carbons, surfactants and priority metals (cadmium, lead and nickel) have been the most studied over the last 30 years (e.g., Lee *et al.* 1998; Byrns 2001; Dionisi *et al.* 2008). PAHs (regulated in the Water Framework Directive), bisphenol A and some pesticides (e.g., dichlorodiphenyltrichloroethane dieldrin, lindane) are referenced in a few models (Lee *et al.* 1998; Byrns 2001; Urase & Kikuta 2005; Lindblom *et al.* 2009). More recently, models for pharmaceutical and personal car products have appeared in the literature (Urase & Kikuta 2005; Plósz *et al.* 2012).

### Photolysis and volatilization

A possible modelling approach for photolysis is described in Vezzaro *et al.* (2009). Volatilization is modelled along with air stripping using a kinetic parameter that is proportional to the $k_L a$ value estimated for oxygen (Lee *et al.* 1998). This assumption is valid for MPs with a Henry's coefficient higher than 0.04 (unitless). Models assume that the fraction of MP sorbed to TSS is not available for mass transfer across the water/air interface (Byrns 2001).

### Sorption

Several models have been intensively used in the literature to describe adsorption (Limousin *et al.* 2007). The most famous ones are two-parameter semi-empirical models (e.g., Langmuir, Freundlich models). Some three parameter-models have also been used for better fitting performances (e.g., Brunauer–Emmett–Teller models). However, for most environmental applications, the use of a simple linear one-parameter model, linking equilibrium concentrations in soluble and particulate phases by a distribution coefficient $K_D$ gives simulation results in accordance with experiments (Joss *et al.* 2006; Ternes & Joss 2006). A major limitation in the simple linear sorption models is the existence of a variety of protocols to determine $K_D$. Therefore, there is a clear need to develop a reproducible and reliable standard test for measuring $K_D$ in a way that considers all prevailing factors that influence sorption. Also, there is a need to consider adsorption kinetics, and to know the time required for adsorption to be completed.

### Biotransformation

Biotransformation of MPs can be modelled either by assuming that a fraction of the biomass metabolizes MPs at a slow maximum specific growth rate (Lindblom *et al.* 2009; Clouzot *et al.* 2012a) or by considering a first-order reaction (Byrns 2001) or a pseudo-first order reaction proportional to $X_{TSS}$ (e.g., Joss *et al.* 2006). Some MP models also consider biotransformation in both dissolved and sorbed fraction compartments (Lee *et al.* 1998; Byrns 2001; Peev *et al.* 2004). Recently, Delgadillo-Mirquez *et al.* (2011) used existing co-metabolism kinetic models (Criddle 1993; Chang & Alvarez-Cohen 1995) in a four-compartment (gas, aqueous, suspended solids and colloidal matter) dynamic model to describe the fate of PAHs during anaerobic digestion, and demonstrated that biotransformation was predominantly governed by aqueous-phase MP concentrations.

### Tertiary treatment processes

A model for MP oxidation by ozone and hydroxyl radicals for drinking waters was originally described by von Gunten (2003) and recently tested on a WWTP ozone reactor by Zimmermann *et al.* (2011). Finally, several models exist to describe the adsorption process on activated carbon (surface diffusion, pore diffusion, pore-surface diffusion, film-pore

diffusion, film-surface diffusion) (Valderrama *et al.* 2007; Fontecha-Cámara *et al.* 2008).

## Data for modelling

Experimental data used for model development, calibration and validation are directly related to model uncertainty. Therefore, optimal experimental design is important to infer data representative of real systems. For example, most studies on MP modelling employ batch experimental data obtained using doses of reference substances but MP removal in real WWTPs is much more complex: (i) MPs can occur in the form of human metabolites, some of which can retransform to the parent compound in the sewer and WWTP; (ii) total re-transformable chemical concentrations can be equal or higher than the measured parent compound concentration (e.g., for diclofenac: Pérez & Barceló (2008)); and (iii) biotransformation can be affected by growth on substrates for some compounds (e.g., Chang & Alvarez-Cohen 1995). One way to obtain more realistic data is to carry out measurements using the indigenous MP content of pre-clarified municipal wastewater (Plósz *et al.* 2010a).

Influent and effluent MP load data are needed for each relevant treatment step to build models that will predict the overall ability of a WWTP to remove MPs. However, the frequency of data collected during full-scale experiments is often inadequate for model calibration and validation, and does not capture the variability of MPs present in wastewater. This occurs because MP analysis requires expensive analytical equipment, complex procedures with costly consumable supplies, and analysts with significant knowledge about matrix effects when analysing MPs (Richardson 2012). As an example, Ort *et al.* (2010b) proposed a step-by-step sampling guide for assessing MPs in WWTPs depending on the questions being addressed. The primary goal is to minimize sampling uncertainty by using a non-biased sampling mode (i.e., flow-proportional, or at least volume-proportional) with a sampling frequency that is sufficiently high to capture the relevant dynamics. Hydraulic properties, in combination with size of the catchment and the frequency of occurrence of a MP, determine how samples have to be collected to ensure they are representative.

Different temporal resolutions and sampling approaches have been proposed in the past to better understand influent variability and its effect on the performance of treatment systems (e.g., Joss *et al.* (2005): three 8-h composites, 1 day, volume-proportional; Plósz *et al.* (2010b): 3 days, flow-proportional). Recently, samples were collected at higher temporal resolution (e.g., Gerrity *et al.* (2011): 30-min composites, two 12-h periods, continuous time-proportional) versus a sampling approach with a lower temporal resolution that was designed to reliably determine average removal rates by averaging influent loads over longer periods (e.g., Majewsky *et al.* (2011): 4-consecutive-day influent composite and 1-day effluent composite).

In conclusion, there is no 'one-fits-all' sampling and analysis strategy; indeed, the sampling strategy depends on inflow variability (determined by the catchment size and the occurrence of individual MPs) and the expected, relevant rate constants (determined by the processes under investigation, the hydraulic residence times and the properties of the MP that is being considered). The degree of spatial-temporal resolution achieved during sampling will depend upon whether the sampling campaign is being conducted to address compliance requirements or design needs.

## Model application

The existing models developed for MPs are useful tools to help the understanding of the mechanisms underlying MP fate in WWTPs and thus provide a measure of the efficiency of different treatment technologies. An example of the results that can be obtained from a pure simulation study based on parameters found in the literature using the MP fate process modelling approach of Vezzaro *et al.* (2009) is given by Cloutier *et al.* (2012), who modelled the removal efficiencies of three MPs characterized by various properties using five different wastewater treatment technologies (Table 1). In that study, the following processes were modelled: high rate conventional activated sludge (CAS), which removes only organics; nitrifying activated sludge (NAS), which also removes ammonium through nitrification; biological nutrient removal (BNR), which includes denitrification in the removal processes; CAS with sand filtration (CAS + SF), and enhanced primary clarification directly followed by an ozonation process (EPC + $O_3$).

On the one hand, the simulation results showed that trichloroethylene (TCE) (volatilized) and bis (2-ethylhexyl) phthalate (DEHP) (sorbed and transformed) are easily removed in all treatment trains studied. On the other hand, EE2 is mostly removed by sorption to sludge. However, at the long sludge retention times that allowed growth of nitrifying bacteria, that is 10 days for the NAS system and 20 days for the BNR system, the EE2 removal by co-metabolic biotransformation by nitrifiers increases. The results also suggest that the addition

**Table 1** | Removal efficiencies of three MPs in different wastewater treatment trains (from Cloutier *et al.* (2012))

| | | CAS | NAS | BNR | CAS + SF | EPC + $O_3$ |
|---|---|---|---|---|---|---|
| EE2 | Sorption (%) | 47 | 44 | 45 | 49 | 69 |
| | Volatilization (%) | 0 | 0 | 0 | 0 | 0 |
| | Transformation (%) | 0 | 8 | 9 | 0 | 30 |
| | Total (%) | 47 | 52 | 54 | 49 | 99 |
| TCE | Sorption (%) | 4 | 4 | 4 | 4 | 7 |
| | Volatilization (%) | 96 | 96 | 95 | 95 | 10 |
| | Transformation (%) | 0 | 0 | 0 | 0 | 65 |
| | Total (%) | 100 | 100 | 99 | 99 | 82 |
| DEHP | Sorption (%) | 64 | 59 | 60 | 64 | 80 |
| | Volatilization (%) | 2 | 6 | 5 | 2 | 0 |
| | Transformation (%) | 32 | 33 | 33 | 33 | 15 |
| | Total (%) | 98 | 98 | 98 | 99 | 95 |

of a tertiary treatment process, such as ozonation, can significantly increase the removal of EE2. This is consistent with what has been seen in the literature for other MPs (Ternes *et al.* 2003; Hollender *et al.* 2009).

## HOW SHOULD MP MODELLING EVOLVE IN THE FUTURE?

### Adaptation to evolving knowledge

The model developer and the experimenter collecting data are not always the same person, and, as a consequence, a lot of valuable information may not always be collected. Scientific communities that are focussed on understanding and predicting MP fate would benefit from a coordinated research approach to ensure that each group is contributing the most important information to advancing MP model development. Modellers have to carefully scrutinize which experimental results to use in structuring and calibrating their models. Additionally, experiments have to be performed at environmentally relevant concentrations. Furthermore, a subset of experiments that attribute mechanistic factors to MP fate can help in defining modelling approaches that are needed for various classes of MPs. Overall, modellers need consistency across experimental procedures from system to system and between research groups. Therefore, agreement on standardized experimental protocols (fate experiment setup, analytical chemistry methods, and sampling procedures) will allow experiments conducted across different systems and research groups to be compared. Even if standardized protocols may block innovation, they are useful to reliably compare different results.

There is some, but not enough, information on the important transformation products generated during wastewater treatment, and their physico-chemical, biotransformation and eco-toxicological characteristics (e.g., Schulz *et al.* 2008; Escher & Fenner 2011; Khunjar *et al.* 2011a). Identifying transformation products involves complicated analytical techniques, and a large amount of time for their development that often cannot be rendered on full-scale systems. However, high resolution mass spectrometry tools are increasingly being proposed to identify and quantify low concentrations of transformation products, and will, undoubtedly, be useful in MP research (Prasse *et al.* 2011). Indeed, the impact of transformation byproducts and retransformable chemicals should be considered when interpreting removal. Adaptation (acclimation) to MPs is also important to model and predict WWTP shutdown periods or new chemical plant start-ups.

### Adaptation to future wastewater treatment technologies

Thinking beyond current-day WWTP technologies, there are drastic changes underway in the wastewater treatment industry that are motivated by a desire to develop strategies for wastewater management that are more cost effective, acceptable by society and have less of an environmental impact (e.g., Guest *et al.* 2009).

In this vein, many innovative biotechnologies are being actively researched and developed that are able to recover resources from wastewater (e.g., bio-electrolysis systems, suspended culture anaerobic technologies for mainstream

treatment, anaerobic ammonia oxidation (anammox)-based technologies for mainstream or side-stream treatment). An interesting feature of many new biotechnologies is that they are mostly or fully anaerobic. The fate of some MPs has been evaluated under anaerobic conditions (Carballa *et al.* 2007; deGraaff *et al.* 2011), but to a much lesser degree than for aerobic environments. Furthermore, the historical knowledge about anaerobic pathways for biotransformation of xenobiotic compounds suggests that transformation products would be different under anaerobic conditions (Heider & Fuchs 1997). As these technologies develop and move toward full-scale implementation, both experimental and modelling research will be needed to elucidate how well MPs are removed and transformed, and their contribution to eco-toxicological risk.

Oxidation processes will also play an important role in future. For instance, approximately 100 WWTPS are likely to be equipped with an additional treatment step to remove MPs (OFE 2012), and many of those WWTPs will be upgraded with an ozonation process (Hollender *et al.* 2009; Zimmermann *et al.* 2011).

### Adaptation to regulatory targets

Regulation is more oriented towards the overall biological effect of MPs than concentrations of every suspected MP. Indeed, ecological risk assessment is widely used by decision-makers to quantify potential adverse effects of anthropogenic activities on various ecosystems (Newman & Unger 2003). In WWTPs, there is limited knowledge of the degree to which transformation products that have eco-toxicological relevance are created, and therefore no current MP models consider the role that the WWTP biota plays in transforming MPs into eco-toxicologically relevant transformation products, and how WWTP design and operation can be modified to reduce the ecological risk imposed by the effluent. Models are already used to predict the impacts on receiving waters of WWTP discharges of organic matter and nutrients (e.g., QUAL2E, RWQM1, Reichert *et al.* (2001)). Different WWTP technologies, designs and operating strategies have been compared, based on their ecological impacts (e.g., Benedetti *et al.* 2010). 'Model-based benchmarking' is an approach used by the wastewater industry to compare the efficacy of treatment approaches by running realistic simulations (Spanjers *et al.* 1998). However, the capacity of treatment trains to mitigate the eco-toxicological impacts from the discharge of MPs in WWTP effluents has not been considered.

The eco-toxicological impacts of MPs released by WWTPs in receiving waters are a current research priority. Ecological risk assessment of MPs previously focussed on assessing impacts on individual organisms, but now ecological models that assess higher levels of organization are being increasingly used (Galic *et al.* 2010). Eco-toxicologists recognize the need to predict impacts on food webs and ecosystems, but the few existing food web and ecosystem models have been applied to metals and pesticides (e.g., Arnot & Gobas 2004; De Laender *et al.* 2008). A typical aquatic ecosystem model, including phytoplankton, zooplankton and fish, is being developed to predict the ecological effects of endocrine disrupters discharged in WWTP effluents by considering effects on individual aquatic organisms, as well as whole ecosystem responses that occur through ecological interactions, such as feeding and competition (Clouzot *et al.* 2012b).

Model simulations already provide benchmark criteria for energy use, effluent quality and greenhouse gas emissions (Flores-Alsina *et al.* 2011). A simulation benchmark criterion for eco-toxicological impacts of MPs would be a useful and relevant addition. Indeed, the combination of fate models with ecological models (already used in ecological risk assessment) would allow evaluation of the capacity of different WWTP technologies to protect the ecological functions of receiving waters (Figure 2). The ecological benchmark criterion could be obtained with a single index, such as Simpson's index of diversity (Simpson 1949), that is deduced from the ecological modelling results.

It is important to highlight that two scientific communities are involved in developing models regarding MPs: on the one hand, models are built for predicting the fate of MP in WWTPs and, on the other hand, they are built for predicting the ecotoxicological effects once MPs are discharged to the environment. Therefore, a coordinated research approach would be key in making progress in the overall MP modelling field.

## CONCLUSION

The anticipated regulation of MPs is a driving force that can increase the use of models by engineers and decision-makers. The MP models in use today are an excellent tool to predict the fate of some MPs in WWTPs, but they are still limited in their ability to predict the fate of the numerous other MPs present in wastewaters and their impact on the receiving waters. Experimental methods that elucidate

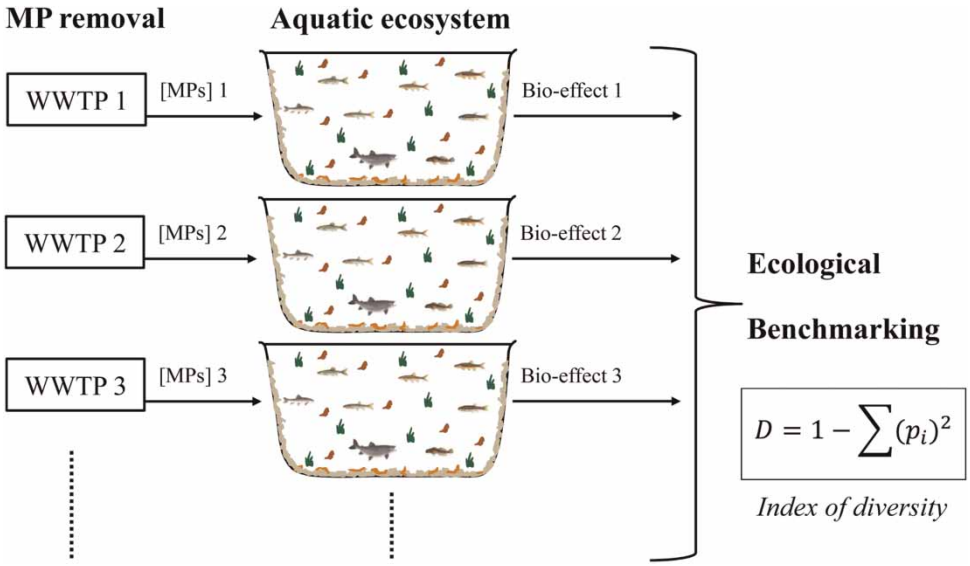


**Figure 2** | Ecological benchmarking of WWTP technologies regarding MPs.

the important mechanisms controlling MP fate are required to improve the ability to predict the performance of WWTPs that receive MPs. In preparation for regulation of MPs in WWTP discharges, researchers and modellers should consider the development of models based on classes of compounds (vs single compounds) that could be linked to their eco-toxicological effects. These models should also help determine how WWTPs might be able to achieve effluent requirements of differing complexity, ranging from monthly averages and daily maxima to annual average or never to be exceeded acute and chronic toxicity values. In addition, improved sampling approaches are required to advance more confidently in the development of computational MP fate models.

In the future, MP models should be developed considering the transformation products created in WWTPs and the evolving wastewater technology. In addition, ecological models should be seen as a means to support decision-making regarding modifications to wastewater treatment design.

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