



HAL
open science

Are we about to reliably predict the fate of micropollutants through wastewater treatment plants?

L. Clouzot, F. Cloutier, N. Love, H. Melcer, C. Ort, Dominique Patureau, B.G. Plósz, M. Pomiès, P.A. Vanrolleghem, J.M. Choubert

► To cite this version:

L. Clouzot, F. Cloutier, N. Love, H. Melcer, C. Ort, et al.. Are we about to reliably predict the fate of micropollutants through wastewater treatment plants?. WWTmod 2012, Feb 2012, Mont st Anne, Canada. p. 299 - p. 312. hal-00697063

HAL Id: hal-00697063

<https://hal.science/hal-00697063>

Submitted on 14 May 2012

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Are we about to reliably predict the fate of micropollutants through wastewater treatment plants?

Ludiwine Clouzot¹, Frédéric Cloutier¹, Nancy Love², Henryk Melcer³, Christophe Ort⁴, Dominique Patureau⁵, Benedek G. Plósz⁶, Maxime Pomiès⁷, Peter A. Vanrolleghem¹ and Jean-Marc Choubert⁷

¹ modelEAU, Département de génie civil et de génie des eaux, Université Laval, 1065 avenue de la médecine, G1V 0A6 Québec, Québec, Canada (Emails: *ludiwine.clouzot.1@ulaval.ca*; *frederic.cloutier.1@ulaval.ca*; *peter.vanrolleghem@gci.ulaval.ca*)

² University of Michigan, 183 EWRE Building, 1351 Beal Avenue, Ann Arbor, MI 48109, USA (Email: *nglove@umich.edu*)

³ Brown & Caldwell, 701, Pike Street, Suite 1200, Seattle 98101, WA, USA (Email: *hmelcer@brwncald.com*)

⁴ Eawag, Swiss Federal Institute of Aquatic Science and Technology, Urban Water Management, CH-8600 Dübendorf, Switzerland (Email: *christoph.ort@eawag.ch*)

⁵ INRA, UR50, Laboratoire de Biotechnologie de l'Environnement, Avenue des Etangs, F-11100 Narbonne, France (Email : *dominique.patureau@supagro.inra.fr*)

⁶ Department of Environmental Engineering (DTU Environment), Technical University of Denmark, Miljøvej, Building 113, DK-2800, Kgs. Lyngby, Denmark (Email: *beep@env.dtu.dk*)

⁷ Irstea, UR MALY, Wastewater treatment & Modelling Research Group, 3 bis quai Chauveau - CP 220, F-69336 Lyon, France (Emails: *maxime.pomies@irstea.fr*; *jean-marc.choubert@irstea.fr*)

Abstract

Models for micropollutants (MPs) are required to provide engineers and decision-makers with reliable tools that will help increase MP removal through wastewater treatment plants (WWTPs) and minimize their impact on the receiving waters. This paper aims at identifying the modelling needs of research (fundamental) vs. practice (design) vs. regulation (compliance) with a focus on the interactions. Different model developments that have occurred recently are first presented with a discussion on the key-question of the 'optimum complexity'. Sampling strategies are also discussed since they influence the model uncertainty. Finally, the paper proposes suggestions for how models might be modified to incorporate our evolving knowledge about MP fate to improve model utility into the future. For instance, the relative role of heterotrophic bacteria versus ammonia oxidizing autotrophic bacteria towards the fate of MPs should be addressed, and the elaboration of a unified agreement on experimental protocols would be necessary to advance model calibration. The degree to which by-products that have ecotoxicological relevance are created during treatment is also a key issue that needs to be considered in future model as well as the use of ecological models as a means to benchmark modifications to wastewater treatment.

Keywords

Ecological Risk Assessment, Emerging contaminants, Metabolism, Modelling, Regulation, Uncertainty

INTRODUCTION

Conventional wastewater treatment plants (WWTPs) were not designed for the elimination of micropollutants (MPs). Thus, only some of them are eliminated, transferred to sludge or biotransformed, whereas others are not altered by treatment (Clara *et al.*, 2005a; Joss *et al.*, 2005; Choubert *et al.*, 2011; Martin-Ruel *et al.*, 2011). Upcoming regulations will be more and more stringent towards the release of MPs to the aquatic environment, especially since, among others, the publication of the European Water Framework Directive (WFD; EC, 2000, 2008), and also on-going projects of regulation reinforcement (e.g. list of priority substances, sludge use for agriculture, etc.).

A more mechanistic knowledge, structured in mathematical models, is a potential means for optimizing treatment (Gernaey et al., 2004), either with existing infrastructure or by identifying additional treatment stages (tertiary treatment, sludge treatment). However, several gaps still remain and are ongoing topics of research all over the world: good quality data (with associated uncertainty), new concepts (e.g. co-metabolism), detailed data capturing time-dependent inputs, new inputs (organic matter and micro-organism characterization), etc. MP modelling is required to improve our knowledge but also to provide engineers and decision-makers with reliable tools that will help increase MP removal in WWTP and minimize their impact on receiving waters.

The present paper aims at identifying the modelling needs to reliably predict the fate of MP through WWTPs with a focus on the interactions between regulation, engineering practice and research. Different developments that have occurred recently are first presented with a discussion on those that hold the greatest promise for inclusion in future fate models (model structure, processes, calibration and validation). One of the key issues is the question of the ‘optimum complexity’ of process models. Sampling strategies are also discussed since they influence model uncertainty. Finally, the paper proposes a new modelling approach considering ecotoxicological characteristics of WWTP effluents to respond to the regulatory targets.

The main messages and questions raised in this paper are:

- (1) Modelling is required for assessing MP emission into the environment and for optimizing WWTP design and operation. Improving MP modelling will increase the models’ reliability and thus, their use by engineers and decision-makers.
- (2) Different MP fate models are currently being developed with various definitions of terms and levels of detail regarding the variables and concepts. They concern regulated MPs and also ones of new concern like pharmaceuticals and personal care products. The model complexity (as evidenced by the number of parameters) and the data uncertainty influence the model calibration and its reliability. Do we need to go in further detail or do we need to simplify our models?
- (3) What are the next steps in MP modelling? What about innovative and adaptive approaches?

WHAT SHOULD WE EXPECT FROM MP MODELLING?

Regulatory point of view

There are many types of regulations concerning MPs that address chemical production, inventory assessment, source control, monitoring, and environmental quality standards. The thrust of environmental quality control to date in both North America and Europe has been the development of water quality criteria to protect flora and fauna in receiving waters. A consequence of the environmental quality focus is that it has led to the ban of only a few of the many thousands of MPs. For example, a ban exists in California on the penta-, octa- but not deca- forms of polybrominated diphenyl ethers (PDBE) in consumer products. In Connecticut, industry is required to stop the use of products containing alkylphenol ethoxylates, which have also been banned by the European Union and Canada (WEF, 2007). It has not, however, led to the widespread development of regulations concerned with MP control in discharges from WWTPs, with some notable

exceptions such as the control of organic MPs in the U.S. organic chemical and petroleum refining industries through the limits set on benzene as a surrogate for other organic MPs.

In general, there is an absence of nationwide or statewide regulations for controlling MPs from WWTPs, which, from a modeling prospective, is a challenge since it is difficult to define an effluent target for the simulation of MPs in WWTPs. In the U.S., MPs are largely unregulated at the federal level; instead, a patchwork of regulations at the State and municipal levels exist to control MPs at source rather than at the end of pipe (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 programs that focus on end of pipe measures (Anon, 2004). In Europe, the European Parliament Directive 2008/105/EC defined environmental quality standards for 33 priority substances for receiving waters in the European Community (EC, 2008). These thresholds are targeted concentrations to reach in receiving bodies, and that define the good 'chemical status'. However, these are not linked to any EC member country or municipal standard for discharging treated WWTP effluents.

The approach to MP control to date has largely focused on individual compounds. However, MPs rarely occur in isolation, making it difficult to determine the specific chemicals responsible for endocrine disruption or other effects (North, 2006). Aquatic organisms are exposed to numerous compounds that individually may have no noticeable effect, but, when present in mixtures, may have observable effects. Because organisms are not exposed to a single chemical stressor at a time, emphasis could shift to developing regulations based on biological effects rather than concentrations of suspected MPs. New regulations could also shift towards regulating MP as a class, based on a common mechanism for toxicity (i.e., endocrine disruption) or similar chemical structure, rather than by individual compound (WEF, 2007).

Nevertheless, there is a renewed commitment to the prevention of chemicals of concern. Numerous drivers are changing the way governments and industry think about chemicals in everyday products. Regulations such as the European Union's *Registration, Evaluation, and Authorization of Chemicals* (REACH) legislation are inducing a cultural shift in industrial chemicals management by requiring data on chemical toxicity and uses, requiring preventive action for classes of chemicals, and shifting the burden of proof to industry to demonstrate safety for high concern chemicals. In preparation for when this initiative results in WWTP discharge regulations that specify effluent requirements for specific MPs, researchers and modelers should continue the development of information that improves our understanding of the mechanism of MP removals in WWTPs and how the plants 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 values.

Engineering point of view

Engineering practice uses models mainly to select the best process configuration for certain wastewater composition and effluent discharge requirements, to evaluate the efficiency of a design configuration under dynamic conditions and to find optimal operating conditions (aeration, sludge concentration), especially in North-America. As the understanding of the profession increases regarding MP fate and behaviour in different types of unit processes, a clear demand is coming from engineering practice to be able to tap into this knowledge through its incorporation in process models. Very important problems remain to be solved before these models will be usable in day-to-

day practice. This is due to the variety of micropollutants to be considered, their variety in properties and the lack of knowledge regarding their behaviour in the complex systems that wastewater treatment plants are. However, models can already now help the design and optimization process, as they can already go beyond the use of empirical knowledge and rules in use today.

Considerable efforts are ongoing worldwide to compare/benchmark treatment technologies (Choubert et al., 2011; Pileggi et al., 2011) and these give considerable insights in the strengths and weaknesses of certain treatment trains with respect to removal of (classes of) MPs. The comprehensive databases that have been developed (Miège et al., 2009) are currently being mined to support model development in order to generalize beyond the particularities of individual treatment plants (Cloutier et al., accepted). It can be expected that in the near future an important increase will be achieved in available unit process models adapted to predict MP fate. The fate of an increasingly wide range of MPs is being characterized thanks to the important measuring programs in place today. While this carries the promise that these models will find their way in engineering practice, considerable research efforts are still needed to reach the stage where engineering practice will have the confidence in models similar to the confidence that practicing engineers now have in nutrient removal models.

Research point of view

In the field of MP modelling, research questions focus on the determination of the suitable mechanistic knowledge, i.e. concepts and equations involved in structured mathematical models. In the academic context, process modelling is useful to test hypothesis, and is a means to identify the right process. One of the key issues is the fate of MPs due to the very low concentration level at which they occur: is co-metabolism a key process to be included in MP models, or is the concept of growth and decay of biomass sufficient? Other questions deal with the biotransformation pathways involved: Is an initiating adsorption step onto sludge necessary? Or does biotransformation occur directly from the soluble fraction? Finally, the consideration of bioavailability of MPs in biokinetic models and prediction of the generation of by-products remain unclear.

Sampling strategies (frequency, location) remain an important issue that draws attention by engineers and is important considering the requirements of regulators. Research work in academia should pursue progress in how to consider modelling results, and how to compare them with threshold values given their overall inaccuracy (sampling + analysis). The importance of sample analysis at higher temporal resolution should be considered to better understand the influent variability, and thus predict the performance of treatment systems.

HOW DO WE CURRENTLY MODEL MP FATE THROUGH WWTPs?

State-of-the-art and limits of existing models

Biotic and abiotic phenomena influence the distribution and the fate of MP throughout the treatment system. This distribution/fate is governed by the physicochemical properties of the pair MP and matrix, together with the process design and operating conditions of the treatment plant. MPs are removed from WWTPs by various processes such as volatilization, biodegradation, sorption, air stripping, photolysis, etc. (Rogers, 1996). State-of-the-art models use the chemical and physicochemical properties of MPs that are relevant to each process in order to assess their fate in

WWTPs. A certain degree of complexity has to be reached if models are to be used as a tool to increase the removal of MPs in WWTPs.

The development of models that can predict the fate of MPs in WWTPs started in the 80's, after the development of the fugacity concept (Mackay, 1979). Several models were then created, most notably SimpleTreat (Struijs *et al.*, 1991), WW-TREAT (Cowen *et al.*, 1993), and TOXCHEM (Melcer *et al.*, 1994). Meanwhile, the development of the state-of-the-art Activated Sludge Models (ASM) (Henze *et al.*, 1987) allowed modellers to create various add-on models or ASM-based models to simulate both the fate of traditional pollutants and specific MPs (e.g. Plósz *et al.*, 2010a). Models published concern volatile organic carbons (VOCs), surfactants, and metals (particularly priority metals Cd, Pb, and Ni) with more than three different models for each (Lee *et al.*, 1998; Byrns, 2001; Dionisi *et al.*, 2008). Moreover, PAHs (regulated in the WFD), bisphenol A (BPA), some pesticides (like DDT, dieldrin, lindane) are referenced in 2 or 3 models (Lee *et al.*, 1998; Byrns, 2001; Urase and Kikuta, 2005). In recent works, a few papers dealt with emerging contaminants as hormones and pharmaceutical substances (Urase and Kikuta, 2005; Plósz *et al.*, 2010b). Only a few papers have defined the conditions for which these models have been set-up, for instance temperature range, mixed liquor suspended solids concentration, etc.

The partitioning of MPs (i.e. the sorption and desorption processes), onto suspended solids, X_{TSS} [g.L^{-1} as TSS] (e.g. activated sludge), can be characterised with an equilibrium state between the concentrations of the dissolved parent compound, S_{XOC} [g.L^{-1}], and that in the solids phase, X_{XOC} [g.L^{-1}] that gives:

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

where the partitioning or sorption coefficient is denoted as K_D [$\text{L.g}X_{TSS}^{-1}$]. The equilibrium partitioning can also be characterised 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 ten times higher than the biodegradation flux (Ternes and Joss, 2006). Consequently, a K_D value is usually measured instead of using an equilibrium constant. The main limit identified in the existing models is the variety of protocols used for the direct determination of the K_D . The common procedure consists in spiking biological sludge by chemical addition, and then measuring the equilibrium concentrations in the liquid and solid phases of sludge. The occurrence of biotransformation during the experiment is limited by using different protocols, like a prior aeration period to reduce the residual substrate (COD and $\text{NH}_4\text{-N}$), washing of the sludge with distilled water, sterilization, inhibition with chemical agents or sparging with argon gas. However, the authors of those studies did not prove that these methods have no influence on sludge properties.

Sorption also occurs on colloids (Holbrook *et al.*, 2004), and the concentration and the nature of these colloids (varying from one sludge to another) influences greatly the sorption/desorption capacity on suspended solids (Vinken *et al.*, 2004) and the commonly measured K_D (Barret *et al.*, 2010). In addition, several MPs, such as most of the pharmaceuticals and personal care products present in municipal sewage, are ionizing substances, i.e. anionic, cationic or zwitterionic, and their partitioning behaviour thus is impacted by pH and ionic interactions. In WWTP models, one way to

account for the impact of pH on partitioning behavior is to use different K_D values estimated under typical pH conditions, prevailing in aerobic and anoxic reactors (Plósz et al., 2010a).

Biotransformation comprises processes, such as the cleavage of chemical moieties (e.g., methyl) or oxidation processes (e.g., carboxylation), catalysed by microbial enzyme activities. This has also been shown by several studies, which implies that biotransformation is a more appropriate term to use instead of complete biodegradation (Kim et al., 2007). The biotransformation of MPs can be modeled in several manners. Lindblom et al. (2009) used a specific biomass which grows on MPs with a maximum specific growth rate, while other models did not involve specific bacteria, but instead, the biotransformation was a first (Byrns, 2001) or pseudo-first order reaction proportional to X_{TSS} (Joss et al., 2006). Different hypotheses exist concerning the compartment in which biotransformation can prevail. Dissolved MP biotransformation is generally considered. In this case, kinetic parameters are determined by measuring the concentration evolution of the dissolved MP. Models by Lee et al. (1998), Byrns (2001), and Peev et al. (2004) include biotransformation for both compartments. However, the experimental evidence related to the biotransformation of sorbed fractions is limited as shown by Delgadillo-Mirquez et al. (2011).

Parameter values are mainly available for aerobic conditions, for PAHs, surfactants, and a few pharmaceutical compounds (Urase and Kikuta, 2005; Joss et al., 2006). But values for numerous other MPs are lacking. A few papers studied the effect of redox conditions on the transformation rates of MPs. Plósz et al. (2010a) and Suarez et al. (2010) have compared aerobic and anoxic conditions for some pharmaceutical compounds, and obtained different biological rates. As for the biotransformation rate, its value can significantly vary under aerobic and anaerobic/anoxic conditions (Plósz et al., 2010a; Vezzaro et al., 2009). This is due to the different MP biotransformation capacity of reactions catalysed by heterotrophic and autotrophic bacteria populations in activated sludge. Numerous papers have also reported that the degradation of MPs is only possible in the presence of another compound used as carbon and energy source (Clara et al., 2005b).

Co-metabolism is a mechanism in which the removal of the MP does not result in any significant biomass growth, i.e. the biomass yield attributed to MP degradation is insignificant. Recently, Delgadillo-Mirquez et al. (2011) used such co-metabolism kinetic in a four-compartment (gas, aqueous, suspended solids and colloidal matter) dynamic model to describe the fate of polycyclic aromatic hydrocarbons (PAHs) in anaerobic digestion. In their model, biotransformation is described using the co-metabolic model of Criddle (1993) and Chang and Alvarez-Cohen (1995). Conversely, readily biodegradable growth substrates can also competitively inhibit MP transformation by limiting the access to the non-specific enzyme sites (Chang and Alvarez-Cohen, 1995; Plósz et al., 2010a).

Volatilization is modeled along with air stripping using a kinetic that is proportional to the $k_{L,a}$ value (Lee et al., 1998). Models also consider that the fraction of MP that is sorbed to the TSS is not available for mass transfer across the water/air interface (Byrns, 2001). Volatilization can also be a relevant process in treatment trains with large surface area (e.g., waste stabilization ponds). In these large ponds, but also in tertiary treatments where irradiation is involved, photolysis becomes another relevant removal mechanism. 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). Therefore, it is mainly affected by UV radiation in stabilization ponds

(from the sun) and in tertiary treatment units (from UV lights), the suspended solids concentration which limits the penetration of light in the tank, and the absorbance characteristics of the MP. A possible modelling approach is described in Vezzaro *et al.* (2009).

Models predicting the fate of MPs through WWTPs are a mean to evaluate the emissions, that is to say how much MPs will be removed with the sludge, volatilized, photolyzed or released in the receiving waters. In addition, recent development and experimental investigations lead to a proposal of more suitable concepts to use. However, our understanding as included in MPs models is still not sufficiently advanced for these models to be used for the design and optimization of treatment processes. The understanding of the mechanisms implied and the influence of local and operating conditions still needs to be improved.

Model uncertainty related to the sampling strategy

To assess the overall performance of a WWTP related to MP removal we need to know at least influent and effluent loads. Significant knowledge about matrix effects is required when analyzing MPs to minimize the uncertainty associated with the data obtained and thus, the resulting model uncertainty. The sampling step also has a significant impact on the quality of the data that will be implemented in the model. Indeed, the sampling strategy has to be designed taking into account the questions that need to be answered and the site-specific setting (e.g., inflow, recirculation, etc.).

For the removal of MPs associated with the solid phase, the design and performance of primary and secondary clarifiers are important. The affinity of a compound to different solid matter must be characterized (maybe sufficiently in laboratory experiments) and in the WWTP the solid matter and its removal must be assessed. Influent loads to primary clarifiers can be highly dynamic (Ort *et al.*, 2010a). This must be considered with an appropriate, typically precautionary high sampling frequency as demonstrated by Ort *et al.* (2010b) - note that the sampling frequency (determined by the substances' fluctuations) is not directly linked to the frequency of the model analysis (that is determined by the research questions). If a primary clarifier exists, most of the high intra-hour fluctuations in the influent to biological treatment steps are attenuated, which implies that the sampling frequency can be reduced to obtain representative average influent concentrations. For the sampling location it is important to know whether internal recirculation can be captured or not (both hydraulically as well as for the impact on average concentrations).

Different temporal resolutions and sampling approaches have been proposed in the past to better understand influent variability and the effect on the performance of treatment systems: three 8-h composite samples (e.g. Göbel *et al.*, 2005 (one day, flow-proportional); Joss *et al.*, 2005 (one day, time-proportional); Plósz *et al.*, 2010a, b (three days, flow-proportional)). Recently, samples were collected even at higher temporal resolution (only influent: e.g. Gerrity *et al.*, 2011 (two 12-h periods, 30-minute composites, continuous time-prop.); Salgado *et al.*, 2011 (four days, grab samples every 2h). This contrasts with suggestions to reliably determine average removal rates by averaging influent loads over longer periods (e.g. Joss *et al.*, 2005 and Wick *et al.*, 2009 (3 weeks, flow-proportional mixed two 2-day composites and one 3-day composite to 7-consecutive-day composites); Majewsky *et al.*, 2011 (4-consecutive-day influent composite and 1-day effluent composite)).

Assessing the sampling error for a particular sampling campaign (e.g. a given individual 24-hour period) is not possible. It can only be assessed on average for a well characterized urban drainage system and compound of interest. Therefore, it should be the primary goal to minimize sampling

uncertainty by using a non-biased sampling mode (i.e. flow-proportional, or at least volume-proportional) with a sampling frequency to capture the relevant dynamics. If the dynamics are unknown, the sampling frequency should be precautionary high e.g. (Ort et al., 2010a). Conventional sampling equipment is required to collect at least 200 individual samples in a 24-hour period.

Experimentally determining/predicting the average removal of a compound in a given treatment system under stable conditions (i.e. wastewater composition and dry weather conditions) may be possible fairly reliably by evaluating a large number of samples (typically 24-h composites), even if sampled loads are subject to random variation. Another approach would be to evaluate longer time periods as suggested by Majewsky et al. (2011). Note, this does not hold true if a bias exists (e.g. caused by time-proportional sampling with pollutant concentrations positively or negatively correlated to wastewater flows). In contrast, gaining more mechanistic insight at higher spatial/temporal resolution is only possible with non-biased, representative samples. It will be decisive if relevant degradation mechanisms and corresponding variables (i.e. operational parameters) can be reliably measured at sufficiently high spatial and temporal resolution to improve mechanistic models.

In conclusion, there is no general answer to deal with the sampling strategy, it depends on the question: research (fundamental) vs. practice (design) vs. regulation (compliance). It also depends on the dynamics of the processes that are observed, the hydraulic residence time, the assigned objective, and probably the MP that is considered. A consequent spatio-temporal resolution for samples to be analyzed is then determined. The sites' characteristics determine how the samples need to be obtained to be representative. It should be noted that shorter period composite samples meant to gain more insight in the dynamics require shorter sampling intervals to avoid sampling errors - e.g. the collection of a 24-hour composite sample with sampling intervals of 30 minutes may be appropriate while the collection of a representative 1-hour composite sample at the same site may require significantly shorter sampling intervals (Ort et al, 2006).

HOW SHOULD WE MODEL MP FATE IN FUTURE?

As detailed elsewhere in this paper, researchers have made significant progress in developing mathematical structures for deterministic models that predict the fate of MPs through various processes in WWTPs, particularly in the biological treatment process. The question to be answered now is: What information is not helpful in our quest for better predictive models of MP fate, and what data are needed to inform the development of better models? There are several challenges faced by modellers, and suggestions for how models might be modified to incorporate our evolving knowledge about MPs to improve model utility into the future need to be formulated.

The different needs risen by regulators, engineers and modellers on MPs should be integrated in an overall approach. Therefore, of equal importance to predicting the fate of MPs through WWTPs is translating the model outputs into an ecotoxicological framework responding to regulation based on biological effects of MPs.

Model structure

Our knowledge about factors that are causal in the fate of MPs and the mathematical structure that those factors require when being modelled is evolving. For example, many of the early

experimental papers that reported on MP fate did not provide enough information about the process engineering parameters that differed between the various sites that were sampled. Eventually, 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, however, SRT proved to be an insufficient predictor of MP fate (Strenn *et al.*, 2004). More recently, research on the relative 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.*, 2011; Love *et al.*, 2012). Therefore, a lack of correlation by SRT may be due more to our lack of knowledge about the physiological condition of various ecological groups that are present in biological processes. Current model structures do not consider this evolving knowledge, but if it did our ability to more consistently model the fate of MPs would improve. It is helpful to consider that we have a long and relatively successful history of modelling processes that combine these ecological groups.

Model calibration and validation

The quality of data that is used to both develop the mathematical structure for MP models and to adequately calibrate the models is insufficient. Methods between research groups are inconsistent, and very often insufficient information is provided by experimentalists about factors that may be causal and should be included in models. Furthermore, it is important to perform well controlled laboratory studies in order to better understand causal mechanisms of MP fate. However, many of these studies are analytically constrained so that MP concentrations that are higher than what is typically encountered in full-scale systems are used (e.g. Lindblom *et al.*, 2009). Doing so allows experimentalists to test hypotheses about fate and causal factors, but it is questionable whether model structures that evolve from those experiments are relevant to full-scale systems. Therefore, modellers have to carefully scrutinize which experimental results to use in structuring and parameterizing their models, and experimentalists need to conduct experiments at environmentally relevant conditions. A unified agreement on protocols that are to be used when conducting experiments on MP fate would be helpful toward this end.

In addition, the frequency of data collected during experiments is often inadequate for model calibration and validation. This occurs because MP analysis is time consuming and expensive. It requires expensive analytical equipment, detailed protocols that require costly consumable supplies, and analysts with significant knowledge about matrix effects when analyzing MPs. Furthermore, we have very limited to no knowledge about how the ecology of biological processes evolves or adapts to the presence of MPs. Therefore, we need both frequent data collection over short (<1 day) time periods appropriate for model calibration, but then repeated sampling events over long time periods (e.g., a sampling event once a month for a few years) to see how parameters change with time and season. To reduce costs when executing such a plan, some are proposing the use of surrogate MPs that serve to represent classes of MPs, and to use the fate of those surrogates to predict the fate of a broader range of compounds (Drewes *et al.*, 2009). This reduces the scale of the analytical problem and should be considered by the modelling community, in cooperation with experimentalists, when planning future experimental campaigns.

Adaptation to future wastewater treatment technologies

Thinking beyond current-day WWTP technology, there are dramatic changes underway in the WWT industry that are motivated by a desire to develop more sustainable (Triple Bottom Line: less environmental impact, more cost effective, acceptable by society) strategies for wastewater

management. The WWT sustainability movement considers treatment technology options (e.g., mainstream anaerobic treatment, source separation with physical chemical treatment of yellow water where many MPs reside) that will dramatically change the pathways through which MPs are stabilized, and in some cases a WWT design that is touted as being more sustainable may have poorer overall removal of MPs and be more of an ecotoxicological threat. Therefore, the structured models we are developing today to predict MP fate should be vetted against these new generation WWT strategies to consider if modified model structures are needed.

Limit of fate models

There is a lack of information on important by-products and their physico-chemical, biotransformation, and ecotoxicological characteristics. Identifying by-products involves complicated analytical techniques that often can't be rendered on full-scale systems. This is because use of radiolabeled forms of MPs and tracing the fate of the radiolabeled carbon is one of the best methods for detecting and identifying by-products, using a range of analytical instruments. There is also value in identifying by-products because not doing so renders the biological reactor to being a black box. An example of the importance of by-product identification was reported by Khunjar et al. (2011). In that study, the authors showed that 17α -ethinylestradiol (EE2) was converted into the conjugated form, sulfo-EE2, that can ultimately be deconjugated to the highly estrogenic EE2, rendering the impact of the effluent more estrogenic than would have been predicted based on the composition of the effluent as it left the treatment plant. This is very important, because almost no analytical campaigns on MP fate in full-scale WWTPs monitors for sulfo-EE2.

We have inadequate knowledge of the degree to which by-products that have ecotoxicological relevance are created during WWT, and therefore models do not (or rarely) consider these effects. No current MP models consider the role that the WWTP biota plays in transforming MPs into ecotoxicologically-relevant by-products, and how WWTP design and operation can be modified to reduce the ecological risk imposed by the effluent. As stated previously in this paper, regulation is more oriented toward the overall biological effect of MPs rather than concentrations of every suspected MPs. Indeed, ecological risk assessment (ERA) is widely used by decision-makers to predict potential adverse effects of anthropogenic activities on various ecosystems (Newman and Unger, 2003). ERA is evolving from experimental measurements to ecological models that predict the effect of contaminants on the aquatic organisms. Therefore, the combination of fate models with ecological models would allow accurate prediction of WWTP's impact on the receiving waters. Integrated urban wastewater systems (IUWS) already consider the system from the sewers to the receiving waters by combining hydrological, geomorphological and fate models (De Keyser et al., 2010). Why not add ecological models to complete this integrated system?

Adaptation to regulatory targets:

Benchmarking is commonly applied in treatment modeling to objectively compare different wastewater treatment technologies, designs and operating strategies. Model simulations provide the benchmark criteria for energy use, effluent quality and greenhouse gas emissions (Flores-Alsina et al., 2011). What about a simulation benchmark criterion for the ecological impact?

A typical aquatic ecosystem model is currently developed to calculate a benchmarking criterion for WWTPs (De Laender et al., 2008; Clouzot et al., accepted). The model inputs are the concentrations of selected MP indicators or overall estrogenicity predicted or measured in WWTP effluents. The model outputs are the biological effects of WWTP effluents on the receiving waters

considering direct effects of MPs on aquatic organisms (e.g., endocrine disruption, acute toxicity, etc.) as well as the consequences on the whole ecosystem through ecological interactions i.e. feeding and competition relationships. Therefore, the ecosystem model can be used to benchmark various WWT technologies within an ecotoxicological context.

In future, MP regulation will probably require ecological models as a means to support decision-making regarding modifications to wastewater treatment and thus, researchers should start now considering the integration of such models in WWTP benchmarking.

CONCLUSION

Upcoming regulations towards MPs are one of the driving forces that could increase the use of modeling by engineers and decision-makers. Also research work must still be carried out to improve our mechanistic knowledge and to structure it into mathematical models. Experimental data with associated uncertainty, sample analysis at higher temporal resolution, new concepts (e.g. co-metabolism), new inputs (organic matter characterization) are the key-issues for improving the knowledge included of fate model. The relative role of heterotrophic bacteria versus ammonia oxidizing autotrophic bacteria towards the fate of MPs should be addressed, and the elaboration of a unified agreement on experimental protocols would be also necessary to progress on model calibration. In future, MP regulation will probably require ecological models as a means to support decision-making regarding modifications to wastewater treatment and thus, researchers should start now considering the integration of such models in WWTP benchmarking. The degree to which by-products that have ecotoxicological relevance are created during treatment is also a key issue that needs to be considered in future models.

ACKNOWLEDGEMENT

Maxime Pomiès is a PhD student at Irstea, financed by Onema (French National Agency for Water and Aquatic Ecosystems), and directed by Dr. Marina Coquery (Irstea, UR MALY) and Professor Christelle Wisniewski (UMR Qualisud, UFR des Sciences Pharmaceutiques et Biologiques, université Montpellier 1). Peter Vanrolleghem holds the Canada Research Chair on Water Quality Modelling and receives funding from the Canadian Water Network for the EC-2 project.

REFERENCES

- Anon (2004). *A Guide to Understanding the Canadian Environmental Protection Act of 1999*. Environment Canada, Government of Canada (www.ec.gc.ca/ceparegistry), Ottawa, Canada, December 2004.
- Barret, M., Patureau, D., Latrille, E., and Carrère, H. (2010). A three-compartment model for micropollutants sorption in sludge: Methodological approach and insights. *Water Research*, **44**(2), 616-624.
- Byrns, G. (2001). The fate of xenobiotic organic compounds in wastewater treatment plants. *Water Research*, **35**(10), 2523-2533.
- Chang, H.L. and Alvarez-Cohen, L. (1995). Model for the cometabolic biodegradation of chlorinated organics. *Environmental Science and Technology*, **29**(9), 2357-2367.
- Criddle, C. S. (1993). The kinetics of cometabolism. *Biotechnology and Bioengineering*, **41**, 1048-1056.
- Choubert J.M., Martin Ruel S., Esperanza M., Budzinski H., Miège C., Lagarrigue C. and Coquery M. (2011). Limiting the emissions of micropollutants: what efficiency can we expect from wastewater treatment plants? *Water Science and Technology*, **63**(1), 57-65.
- Clara, M., Strenn, B., Gans, O., Martinez, E., Kreuzinger, N. and Kroiss, H. (2005a). Removal of selected pharmaceuticals, fragrances and endocrine disrupting compounds in a membrane bioreactor and conventional wastewater treatment plants. *Water Research*, **39**(19), 4797-4807.

- Clara, M., Kreuzinger, N., Strenn, B., Gans, O. and Kroiss, H. (2005b). The solids retention time-A suitable design parameter to evaluate the capacity of wastewater treatment plants to remove micropollutants. *Water Research*, **39**(1), 97–106.
- Cloutier F., Clouzot L. and Vanrolleghem P.A. (accepted). Predicting the fate of emerging contaminants in wastewater treatment plants. In: *85th Annual WEF Technical Exhibition and Conference (WEFTEC2012)*. New Orleans, USA, September 29 - October 3 2012.
- Clouzot L., Dupuis A., Paterson M., Kidd K. and Vanrolleghem P.A. (accepted). An ecosystem model to predict endocrine disruptions in the aquatic environment. In: *SETAC Europe 32nd Annual Meeting*. Berlin, Germany, May 20-24 2012.
- Cowan, C.E., Larson, R.J., Feijtel, T.C.J. and Rapaport, R.A. (1993). An improved model for predicting the fate of consumer product chemicals in wastewater treatment plants. *Water Research*, **27**, 561-573.
- De Keyser, W., Gevaert, V., Verdonck, F., Nopens, I., De Baets, B., Vanrolleghem, P.A., Mikkelsen, P.S. and Benedetti L. (2010). Combining multimedia models with integrated urban water system models for micropollutants. *Water Science and Technology*, **62**(7), 1614-1622.
- De Laender F, De Schamphelaere KAC, Vanrolleghem PA and Janssen CR. (2008). Validation of an ecosystem modelling approach as a tool for ecological effect assessment. *Chemosphere*, **71**,529-545.
- Delgadillo-Mirquez, L., Lardon, L., Steyer, J.-P. and Patureau, D. (2011). A new dynamic model for bioavailability and cometabolism of micropollutants during anaerobic digestion. *Water Research*, **45**(15), 4511-4521.
- Dionisi, D., Bornoroni, L., Mainelli, S., Majone, M., Pagnanelli, F. and Papini, M.P. (2008). Theoretical and experimental analysis of the role of sludge age on the removal of adsorbed micropollutants in activated sludge processes. *Industrial & Engineering Chemistry Research*, **47**(17), 6775-6782.
- Drewes, J. E., Sedlak, D., Lim, M. H., Dickenson, E., Luna, J., Snyder, S., Vanderford, B. and Trenholm, B. (2009). *Development of Indicators and Surrogates for Chemical Contaminant Removal during Wastewater Treatment and Reclamation*. WERF Report No. 04-HHE-1CO.
- European Community (2008). Directive 2008/105/EC of the European Parliament and of the Council on Environmental Quality Standards in the Field of Water Policy. *Official Journal of the European Union*, L 348/84-97, 24 December, 2008.
- European Community (2000). Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy.
- Flores-Alsina, X., Corominas, L., Snip, L. and Vanrolleghem, P.A. (2011). Including greenhouse gas emissions during benchmarking of wastewater treatment plant control strategies. *Water Research*, **45**, 4700-4710.
- Gernaey, K.V., van Loosdrecht, M.C.M., Henze, M., Lind, M. and Jorgensen, S.B. (2004). Activated sludge wastewater treatment plant modelling and simulation: state of the art. *Environmental Modelling and Software*, **19**(9), 763-783.
- Göbel, A., Thomsen, A., Mcardell, C.S., Joss, A. and Giger, A. (2005). Occurrence and sorption behaviour of sulfonamides, macrolides, and trimethoprim in activated sludge treatment. *Environmental Science and Technology*, **39**, 3981-3989.
- Gerrity, D., Trenholm, R.A. and Snyder, S.A. (2011). Temporal variability of pharmaceuticals and illicit drugs in wastewater and the effects of a major sporting event. *Water Research*, **45**(17), 5399-5411.
- Henze, M., Leslie Grady, C.P., Gujer, W., Marais, G.v.R., and Matsuo, T. (1987). A general model for single-sludge wastewater treatment systems. *Water Research*, **21**(5), 505–515.
- Holbrook, R. D., Love, N. G. and 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.
- International Joint Commission (IJC) (2009). *The Challenge of Emerging Substances of Concern in the Great Lakes Basin: A Review of Chemicals Policies and Programs in Canada and the United States*. Report prepared for the IJC Multi-Board Work Group on Chemicals of Emerging Concern in the Great Lakes Basin by Canadian Environmental Law Association and Lowell Center for Sustainable Production, January 2009.
- Joss, A., Keller, E., Alder, A.C., Göbel, A., McArdell, C.S., Ternes, T. and Siegrist, H. (2005). Removal of pharmaceuticals and fragrances in biological wastewater treatment. *Water Research*, **39**(14), 3139-3152.
- Joss, A., Zabczynski, S., Gobel, A., Hoffmann, B., Löffler, D., McArdell, C.S., Ternes, T.A., Thomsen, A. and Siegrist, H. (2006). Biological degradation of pharmaceuticals in municipal wastewater treatment: Proposing a classification scheme. *Water Research*, **40**(8), 1686-1696.
- Khunjar, W.O., Mackintosh, S.A., Skotnicka-Pitak, J., Baik, S., Aga, D.S. and Love, N.G. (2011). Elucidating the relative roles of ammonia oxidizing and heterotrophic bacteria during the biotransformation of 17 α -ethinylestradiol and trimethoprim. *Environmental Science and Technology*, **45**(8), 3605-3612.

- Kim, J.Y., Ryu, K., Kim, E.J., Choe, W.S., Cha, G.C., and Yoo, I.K. (2007). Degradation of bisphenol A and nonylphenol by nitrifying activated sludge. *Process Biochemistry*, **42**(10), 1470-1474.
- Lee, K.C., Rittmann, B.E., Shi, J.C. and McAvoy, D. (1998). Advanced steady-state model for the fate of hydrophobic and volatile compounds in activated sludge. *Water Environment Research*, **70**(6), 1118-1131.
- Lindblom, E., Press-Kristensen, K., Vanrolleghem, P.A., Mikkelsen, P.S., and 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.
- Love, N.G., Moline, C., Ernstoff, A. and Stadler, L. (2012). *Understanding Microaerobic Metabolism in a Sustainable World, Status Report*, WERF Report No. U1R09.
- Majewsky, M., Gallé, T., Bayerle, M., Goel, R., Fischer, K. and Vanrolleghem, P.A. (2011). Xenobiotic removal efficiencies in wastewater treatment plants: Residence time distributions as a guiding principle for sampling strategies. *Water Research*, **45**(18), 6152-6162.
- Mackay, D. (1979). Finding fugacity feasible. *Environmental Science and Technology*, **13**, 1218-1223.
- Martin Ruel, S., Choubert, J.M., Esperanza, M., Miège, C., Navalón Madrigal, P., Budzinski, H., le Ménach, K., Lazarova, V. and Coquery, M. (2011). On-site evaluation of the removal of 100 micro-pollutants through advanced and conventional treatments for re-use applications. *Water Science and Technology*, **63**(11), 2486-2497.
- Melcer, H. Bell, J., Thompson, D.J., Yendt, C.M., Kemp, J. and Steel, P. (1994). Modeling Volatile Organic contaminants' fate in wastewater treatment plants. *Journal of Environmental Engineering*, **120**, 588-609.
- Miège, C., Choubert, J.-M. Ribeiro, L., Eusebe, M. and Coquery M. (2009). Removal efficiency of pharmaceuticals and personal care products with varying wastewater treatment processes and operating conditions: conception of a database and first results. *Environmental Pollution*, **157**, 1721-1726.
- Newman, M.C. and Unger, M.A. (2003). *Fundamentals of ecotoxicology* (second edition). Lewis Publisher, Boca Raton.
- North, K. (2006). *Report on the San Francisco Bay Area's Safe Medicine Disposal Days*, Bay Area Pollution Prevention Group, Oakland, California, August 2006.
- Ort, C., Lawrence, M.G., Reungoat, J. and 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. and 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.
- Ort, C. and Gujer, W. (2006). Sampling for representative micropollutant loads in sewer systems. *Water Science and Technology*, **54**(6-7), 169-176.
- Peev, M., Schonerlee, M. and De Wever, H. (2004). Modelling the degradation of low concentration pollutants in membrane bioreactors. *Water Science and Technology*, **50**(5), 209-218.
- Pileggi, V., Feisthauer, N., Chen, X., Parker, W., Parrott, J., Van Der Kraak, G., Tabe, S., Kleywegt, S., Schroeder, J., Yang, P. and Seto, P. (2011). Impact of wastewater treatment process configuration on effluent chemistry and biological responses. In: *Proceedings 84th Annual WEF Technical Exhibition and Conference (WEFTEC2011)*. Los Angeles, USA, October 15-19 2011.
- Plósz, B.G., Leknes, H. and Thomas, K.V. (2010a). Impacts of Competitive Inhibition, Parent Compound Formation and Partitioning Behavior on the Removal of Antibiotics in Municipal Wastewater Treatment. *Environmental Science & Technology*, **44**(2), 734-742.
- Plósz, B.G., Leknes, H., Liltved, H. and Thomas, K.V. (2010b). 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**, 1915-1924.
- Rogers, R. (1996). Sources, behaviour and fate of organic contaminants during sewage treatment and in sewage sludges. *Science of the Total Environment*, **185**(1-3), 3-26.
- Salgado, R., Marques, R., Noronha, J.P., Mexia, J.T., Carvalho, G., Oehmen, A. and Reis, M.A.M. (2011). Assessing the diurnal variability of pharmaceutical and personal care products in a full-scale activated sludge plant. *Environmental Pollution*, **159**(10), 2359-2367.
- Schnoor, J.L. (1996). *Environmental Modelling. Fate and Transport of Pollutants in Water, Air, and Soil*. John Wiley & Sons, New York, USA.

- Strenn, B., Clara, M., Gans, O. and Kreuzinger, N. (2004). Carbamazepine, diclofenac, ibuprofen and bezafibrate - investigations on the behaviour of selected pharmaceuticals during wastewater treatment. *Water Science and Technology*, **50**(5), 269-276.
- Struijs, J., Stoltenkamp, J. and 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. and Omil, F. (2010). Removal of Pharmaceutical and Personal Care Products (PPCPs) under nitrifying and denitrifying conditions. *Water Research*, **44**(10), 3214-3224.
- Ternes, T. and Joss, A. (2006). Human Pharmaceuticals, Hormones and Fragrances: The challenge of micropollutants in urban water management. *IWA Publishing*, ISBN10: 1843390930.
- Urase, T. and Kikuta, T. (2005). Separate estimation of adsorption and degradation of pharmaceutical substances and estrogens in the activated sludge process. *Water Research*, **39**(7), 1289-1300.
- Vezzaro, L., Gevaert, V., Benedetti, L., De Keyser, W., Verdonck, F., Vanrollegem, P.A., Boisson, P. and Mikkelsen, P.S. (2009). *Unit Process Models for Fate of Priority Pollutants*. Deliverable 7.2 – ScorePP project. European Union.
- Vinken, R., Hollrigl-Rosta, A., Schmidt, B., Schaffer, A. and Corvini, P.F.X. (2004). Bioavailability of a nonylphenol in dependence on the association to dissolved humic substances. *Water Science and Technology*, **50**, 277-283.
- Water Environment Federation (WEF) (2007). *Current Regulatory Framework for Microconstituents in Water*. Technical Practice Update Report, WEF, Alexandria VA, November 2007.
- Wick, A., Fink, G., Joss, A., Siegrist, H. and Ternes, T.A. (2009). Fate of beta blockers and psycho-active drugs in conventional wastewater treatment. *Water Research*, **43**(4), 1060-1074.