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Removal of pharmaceuticals in biological wastewater treatment systems: model generalisation and implications for environmental risk predictions

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Abstract
An Activated Sludge Modelling framework for Xenobiotics (ASM-X) was recently developed to mechanistically predict the fate of pharmaceuticals in a full-scale treatment plant. In this study, we generalized ASM-X to international literature data. Through the generalization, we assessed the influence on the biological removal efficiency of specific factors, namely influent loading dynamics, SRT and retransformation processes (from e.g., human metabolites back to parent chemicals). With regard to the latter, we show that the estimation of removal efficiency based only on parent chemical (a predominant practice in literature) can lead to an underestimation of the environmental risk.

Keywords
Pharmaceuticals elimination; ASM-X; model validation; retransformation; hospital WWTP

INTRODUCTION

Dynamic fate models can represent a cost-saving option to investigate the elimination of xenobiotic trace chemicals in biological wastewater treatment plants (WWTPs). An Activated Sludge Modelling framework for Xenobiotics (ASM-X) was developed and validated in the fate prediction of pharmaceuticals in a full-scale WWTP (Plósz et al., 2010, 2012). These studies highlighted the potential impact of human conjugated metabolites or other commercial chemicals to retransform back to parent forms, leading to a distinction between the concentration of parent (C_{LI}) and retransformable fractions (C_{CJ}) of pharmaceuticals. In this study, we validated ASM-X by comparing predicted removal efficiencies of three pharmaceuticals (sulfamethoxazole, ciprofloxacin and tetracycline) in Bekkelaget WWTP (Oslo, Norway), with published international data whereby sound sampling techniques were used. The validation with literature data, also referred to as generalization (Plósz et al., 2012), aimed at: (i) assessing the underestimation of removal by considering only the parent fraction; (ii) estimating the significance of this underestimation in terms of risk predictions; and (iii) evaluating factors known to affect pharmaceuticals removal. With regard to (iii), we focused on dynamics of influent load of the substances, WWTP operation (e.g., solid retention time—SRT) and retransformation occurring in upstream sewer systems.

MATERIALS AND METHODS

The full-scale implementation of ASM-X in WEST 2012®, calibrated with the results of batch experiments as presented by Plósz et al. (2010), was used to estimate the elimination of sulfamethoxazole, ciprofloxacin and tetracycline in Bekkelaget WWTP. We distinguished between removal efficiency [-], in the biological treatment, referred to parent fraction (Eq.1) and to both parent and retransformable fraction (Eq. 2)

$$\eta_{LI} = (C_{LI,in} - C_{LI,eff}) / C_{LI,in} \quad [1]$$

$$\eta_{TOT} = (C_{LI,in} + C_{CJ,in} - C_{LI,eff} - C_{CJ,eff}) / (C_{LI,in} + C_{CJ,in}) \quad [2]$$

where C_{in} and C_{eff} [ng L^{-1}] were concentrations in secondary influent and effluent, respectively. Estimated removal efficiencies were plotted as a function of the normalized influent load of the chemicals [mg h^{-1} $1000PE^{-1}$], calculated from the design population equivalent of the WWTP. A literature review was performed for the generalization of ASM-X predictions, with the collection of international data on the full-scale removal of pharmaceuticals. Only data derived from flow-proportional sampling campaigns were included. Additionally, literature studies on the separate treatment of hospital wastewater were selected to characterize a "zero-catchment" scenario, describing the removal of pharmaceuticals in WWTPs with negligible upstream sewer transport.
A preliminary environmental risk assessment of the pharmaceuticals was performed. Predicted environmental concentrations (PECs) were estimated from the effluent concentrations from Bekkelaget WWTP (assuming 10-fold dilution). We distinguished between PECs accounting for only effluent C_{LI}, and for both effluent C_{LI} and C_{CJ}. PECs were then compared to predicted non-effect concentrations (PNECs) reported in literature to assess risk dynamics.

RESULTS AND DISCUSSION (the case of sulfamethoxazole)

Scenario simulations, considering increased influent loads compared to measurements in Bekkelaget WWTP, were used to generalise ASM-X predictions of sulfamethoxazole removal with literature data. In Fig. 1a, we compared model predictions (5-fold increased influent loading) with removal efficiencies of sulfamethoxazole in municipal WWTPs. Predicted η_{LI} and η_{TOT} were consistent with data reported by Göbel et al. (2005, 2007), including a comparable underestimation of the efficiency when the retransformable metabolite (N4-acetyl sulfamethoxazole) was not considered. A similar underestimation error was shown by Yang et al. (2011). Values of η_{LI} reported by Radjenovic et al. (2009) were significantly higher than our estimations and any other literature data at comparable influent loads, suggesting a possible enhancement of biotransformation (due to e.g., operation at high SRT). With regard to the zero-catchment scenario (Fig. 1b), predicted η_{LI} and η_{TOT} at a 25-fold increased load are in close agreement with values reported by Kovalova et al. (2012).

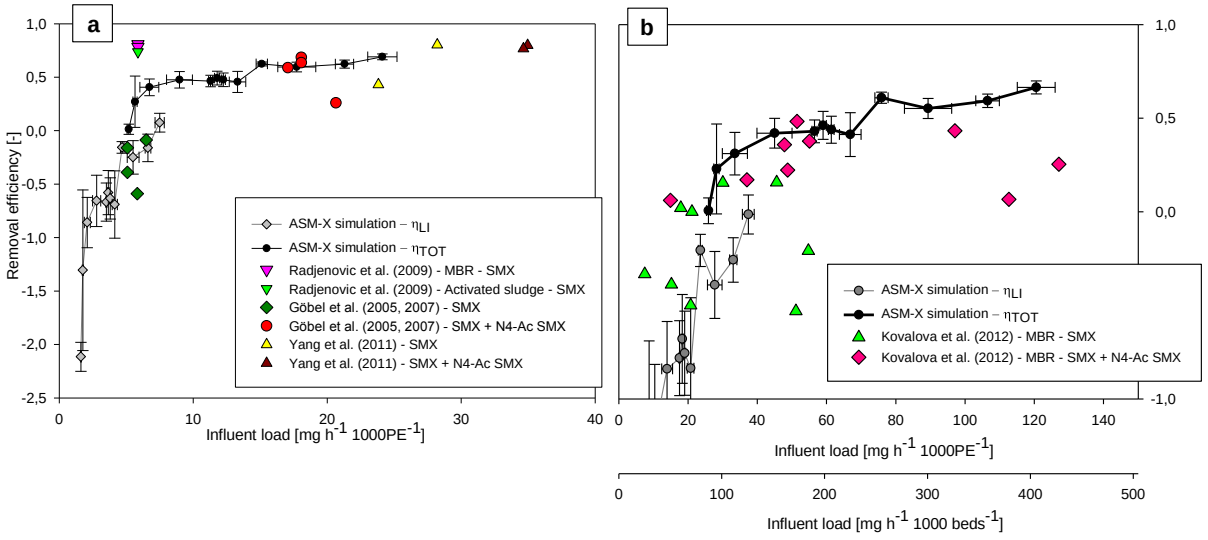

Figure 1. Generalization of ASM-X predicted removal of sulfamethoxazole (SMX) with literature data for municipal WWTPs (a) and for the hospital wastewater treatment—zero-catchment scenario (b). ASM-X predictions of removal efficiency accounted for only parent SMX (grey diamonds) and for parent and retransformable fractions of SMX (black circles). 5-fold and a 25-fold increased influent load, as compared to Plósz et al. (2010), were used for the validation in (a) and (b), respectively. Error bars refer to standard deviations in influent loads and removal efficiencies.

In Fig. 2, values of the PECs in the recipient water body of the Bekkelaget WWTP were shown. Results obtained in this preliminary assessment suggest that tetracycline (Fig. 2a) and—

significantly—ciprofloxacin (Fig. 2b) can represent a considerable chemical risk. The predicted effluent C_{CJ} of tetracycline can pose a substantial additional risk (up to 130% increase as compared to parent-based PEC), whereas the parent-based tetracycline results suggested a marginal violation of the no-effect limit. Estimated as 131–397 times higher than the respective PNEC value, PECs of ciprofloxacin exhibited a marked temporal variability (3-fold increase at the peaks).

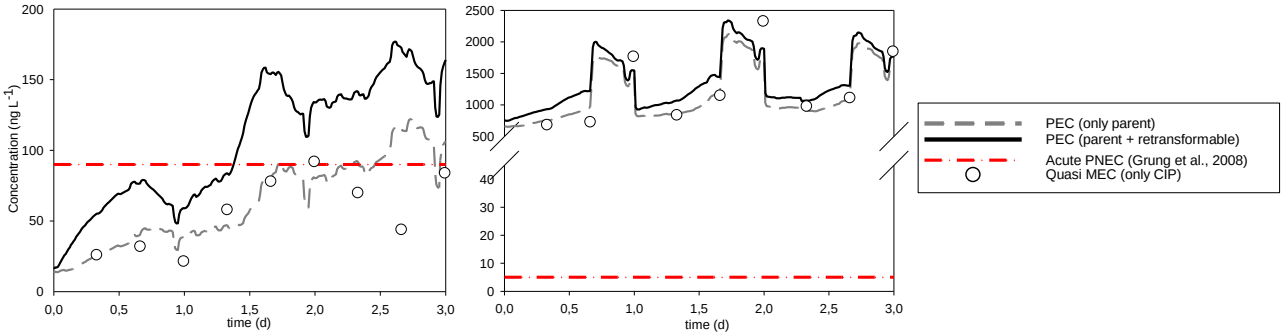

Figure 2. PEC values of tetracycline (a) and ciprofloxacin (b) calculated from ASM-X predictions. For PNEC values used, please refer to Grung et al. (2008). Quasi MECs (measured environmental concentrations) identify effluent measured environmental concentrations divided by a dilution factor.

Overall, these results suggest the importance of using dynamic models for and the necessity of considering retransformable chemical fractions in assessing pharmaceuticals removal in biological WWTPs. Additionally, we show that environmental risk assessments should account for (i) concentrations of retransformable chemicals released in WWTP effluents, potentially representing an additional source of hazard; and (ii) temporal variations in effluent concentrations.

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