Modelling the Fate of Xenobiotic Trace Chemicals via Wastewater Treatment and Agricultural Resource Reuse

As a result of widespread human activities, pharmaceuticals and biocides are ubiquitously present at trace levels in the environment. Large amounts of these substances, also identified as xenobiotic trace chemicals (XTCs), are released daily from: (i) households and healthcare facilities, following human consumption and disposal; (ii) husbandry and other analogous facilities, following veterinary consumption; and (iii) industrial facilities. A significant fraction of these emissions reaches municipal wastewater treatment plants (WWTPs), where XTCs undergo incomplete removal partly due to WWTP design limitations. These chemicals are thus eventually released to the environment, e.g. in freshwater bodies receiving WWTP effluents, representing a threat to living organisms.

WWTPs have been generally identified as a major point source of XTC emissions to the environment. Nevertheless, due to the high number of marketed and consumed chemicals, and to the uncertainties associated to sampling and analytical methodologies, quantifying the elimination of XTCs during wastewater treatment still remains a challenge. Developing robust modelling tools to predict the fate of XTCs in WWTPs can help overcoming this challenge. However, in-depth understanding of mechanisms and processes, determining XTCs removal during wastewater treatment, is still required. This PhD thesis aimed at filling knowledge gaps in the field of XTC fate modelling during and beyond wastewater treatment. We aimed at improving the comprehension of XTC fate, and thus the predictive capabilities of fate models: (i) at process scale, with a focus on sorption and biological transformation of XTCs in biological treatment systems; (ii) in full-scale WWTPs, assessing the impact of retransformation and WWTP operation on XTC elimination; and (iii) in integrated WWTP-agricultural systems. Different modelling tools, suited the specific purposes of our investigations, were developed, extended and/or innovatively applied. Fate models used as reference in this thesis include: the Activated Sludge Modelling framework for Xenobiotics (ASM-X); the generic WWTP model SimpleTreat Activity; and the dynamic soil-plant model for fate prediction in agricultural systems.

Experimental and model-based observations were combined to assess sorption of ionizable XTCs onto activated sludge and XTC biotransformation in moving bed biofilm reactors (MBBRs). Most XTCs are in fact multispecies chemicals, being present in neutral and/or ionized form in wastewater. We demonstrated that pH conditions and, to a lesser extent, iron salt dosing for chemical phosphorus removal can significantly affect solid-liquid partitioning of the zwitterionic antibiotic ciprofloxacin onto activated sludge. Electrostatic interactions and complexation are thus dominating sorption mechanisms. Under a range of pH, redox and iron salt dosing conditions, non-linear sorption (n=0.62–1.33) was observed. Extensions to traditional partitioning models were accordingly proposed for ciprofloxacin and other zwitterionic XTCs, accounting for: (i) high non-linearity of XTC sorption; or (ii) ionization with changing pH and different sorption potential of ionized species. Furthermore, XTCs are typically present in ng L^{-1} to μg L^{-1} concentrations in wastewater, being referred to as non-growth substrates, and their biological degradation can be associated with microbial growth processes. In this PhD thesis, we assessed the influence of primary metabolic processes on XTC biotransformation in MBBR biofilm. Our investigation was performed by comparing biotransformation kinetics in pre-denitrifying MBBRs operated in single-stage and three-stage configurations. The latter configuration produced a prolonged biofilm exposure to organic electron donor (COD) loading and complexity tiered by segregated and integrated biofilm reactors, which significantly influenced kinetics of heterotrophic denitrification and XTC biotransformation. Biotransformation rate constants for a number of non-recalcitrant XTCs were found correlated to the denitrification potential of MBBR biofilm, suggesting that XTC degradation occurred via microbial co-metabolism. In addition, enhanced biotransformation kinetics was shown for a number of XTCs (sulfamethoxazole, erythromycin, atenolol) as compared to previous findings for conventional activated sludge. A number of factors have been described to influence the elimination of XTCs in full-scale WWTPs. Specifically, relevant impact was attributed to (i) solid residence time (SRT), at which biological treatment is operated; and (ii) the formation of XTCs due to, e.g., deconjugation of human metabolites. Many XTCs are in fact excreted by humans in the form of conjugates, which can undergo biotic retransformation to parent chemicals. In this PhD thesis, we specifically assessed the influence of retransformation processes and SRT on the fate of sulfamethoxazole in full-scale WWTPs. A methodology based on the comparison of ASM-X predictions and literature data was used. We demonstrated that the impact of retransformation during secondary wastewater treatment is determined by: (i) the size of WWTP catchments, with major in-sewer retransformation expected in large catchments; (ii) the type of catchment (hospital or urban catchment). This evidence accordingly suggests an integrated approach to XTC fate assessment in wastewater systems (sewer networks and WWTPs). Furthermore, improved elimination of sulfamethoxazole was found and predicted in WWTPs operated at SRT greater than 16 d. Beyond this critical SRT, enhanced biotransformation kinetics may occur due to the enrichment of slow-growing organisms (e.g., specialist degraders) or mixed substrate utilization strategies. This finding supported our experimental evidence of enhanced sulfamethoxazole biotransformation kinetics in denitrifying MBBRs.

As a result of incomplete biodegradation in WWTPs, XTCs persist in effluents and sewage sludge. Reuse of municipal biosolids and treated wastewater or use of freshwater for agricultural purposes eventually leads to XTC uptake into food crops. In this PhD thesis, we developed and tested a generic simulation tool to predict the fate of XTCs from consumption, through wastewater treatment and eventually to the uptake by winter wheat for a number of geographical scenarios in the European Union. The tool combined was specifically addressed for fate prediction of ionizable XTCs (the biocide triclosan, the diuretic furosemide and the antibiotic ciprofloxacin). Furosemide was found rather persistent to wastewater treatment and eventually to the uptake by winter wheat. Uptake of furosemide was predicted compared to soil amendment with biosolids. Due to the scarce availability of experimental data, our model predictions indicate the need of deepening investigations of XTC fate in agricultural systems. Accumulation in food crops may result in additional XTC emission pathways (e.g., manure application, irrigation with reclaimed WWTP effluent) in terms of food.
crop accumulation.

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