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Extensions for the activated sludge modelling framework for xenobiotic organic micro-pollutants (ASM-X) - sorption, sequestration and co-metabolism of diclofenac and carbamazepine

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Conventional models, describing the xenobiotic organic micro-pollutant fate in sewage treatment can be limited in describing full-scale systems. This can, in part, be explained by the fact that these models have been identified and calibrated using data obtained in batch experiments spiked with reference substances. Xenobiotic parent compounds, however, can be formed from other sewage fractions, occurring in municipal sewage, i.e. from human conjugates, other commercial chemicals and from fractions sorbed onto hydrolysable particulate, dissolved and colloidal matter (DCM) – some of which are very difficult or impossible to detect (Plósz et al., 2010a). Additionally, besides neutral chemicals, contaminants, in particular pharmaceuticals can be acidic, basic, amphoteric or zwitterionic. Under different pH conditions, typical to WWTPs, their partitioning behaviour thus cannot be accounted for by a single sorption coefficient, K_D (Plósz et al., 2010b). Furthermore, growth substrates can impact the cometabolic substrate oxidation process – a compound specific impact that should be accounted for in process models (Plósz et al., 2010b). The available terminal electron acceptors (e.g., oxygen, nitrate) and the metal salt (iron, aluminium) dosed for phosphorus removal can additionally influence contaminant removal (Plósz et al., 2010b). Thus a new framework of activated sludge modelling for xenobiotics (ASM-X) has been recently proposed (Plósz et al., 2010a,b).

Here we present extensions for the ASM-X, and the process model developed predicts the removal of diclofenac and carbamazepine in an activated sludge system. In this outline paper, we only demonstrate our research work using concentration data obtained for diclofenac in the liquid phase (C_L) and in the solid phase (C_{SL}) in the full-scale samples (Fig. 1). Batch experimental results, obtained using the micro-pollutant content of pre-clarified municipal sewage, were used to identify the process model and to solve the inverse problem of estimating the biotransformation rate and half-saturation coefficient values, under anoxic and aerobic conditions (Fig. 1a). This method has originally been proposed by Plósz et al. (2010a). For model evaluation and confirmation, forward dynamic simulations were carried out using measured data obtained in a full-scale wastewater treatment plant, WWTP (Fig. 1b and Fig. 1c). For the forward simulations, eight-hour flow proportional samples, collected in 3 days under dry-weather conditions in the WWTP, were used (Plósz et al., 2010c).

What is notable for the biotransformation of pollutants is that the combination of the measurement and simulation results suggest relatively high rate of contaminant biodegradation when the microbial growth is not limited by readily biodegradable substrates, S_S , contained in the pre-clarified sewage – initial concentration in the batch experiments: 130 mg L^{-1} as COD (Fig. 1a). Approximation of the batch and full-scale experimental results can effectively predict the contaminant removal using the model that accounts for the cometabolism of diclofenac and carbamazepine under different redox conditions. Experimental results obtained by Tran et al. (2009) using

acetate as S_S , confirms our findings, i.e. the diclofenac and carbamazepine biodegradation efficiencies, exhibited by heterotrophic bacteria, can be enhanced by increasing the initial growth substrate concentration. The separate biotransformation potential of heterotrophic organisms was assessed by Tran et al. (2009) via inhibiting the growth of nitrifiers in a reference experimental setup.

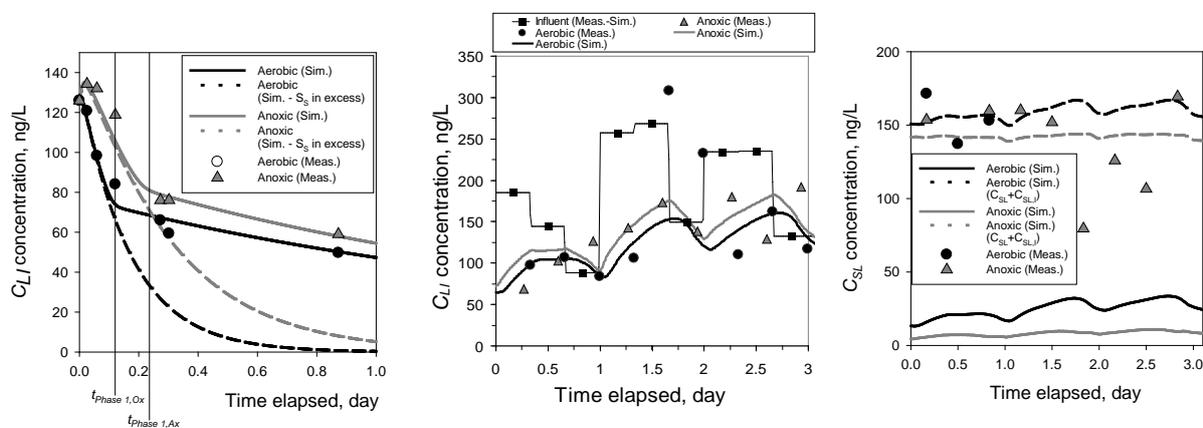


Figure 1 Values of diclofenac concentration measured (symbols) and simulated (solid and dashed line) in the aerobic and anoxic batch tests in the liquid phase, C_{LI} (A-left); and diclofenac concentration measured (symbol) and simulated (solid and dashed line) in the pre-anoxic and aerobic effluent streams of the full-scale WWTP in the liquid phase (B-middle) and in the solid phase, C_{SL} (C-right). The measured WWTP influent C_{LI} concentration is shown with a square symbol (B-middle), and the concentration values used in the dynamic input time-series are shown with a thin black line.

Model approximation of contaminant concentration, detected in the solid phase (Fig. 1c), suggest that only approximately 16% of the total solid diclofenac concentrations is due to sorption (1% for carbamazepine) – the remainder being non-bioavailable and sequestered ($S_{SL,i}$). Values of the solid-liquid partitioning coefficient (K_D) used in this study are that shown by (Ternes and Joss, 2006). In the WWTP model, for the ionizing diclofenac, we estimated a separate K_D value to account for the impact of pH, prevailing in the aerobic reactors. Our measured solid concentration data is in close agreement with the measured data presented by Radjenović et al. (2009). Taken together, we propose extending the ASM-X (Plósz et al., 2010) to account for (i) the impact of terminal electron donors and acceptors on biodegradation, (ii) the impact of pH, prevailing in anoxic and aerobic basins, on sorption and (iii) physical/chemical contaminant sequestration in solids. This research has particular relevance to model-based regional risk assessment and to decision support systems used in WWTP design and operation.

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