Watermatex 2015
9th IWA Symposium on Systems Analysis and Integrated Assessment
14-17 June 2015, Gold Coast, Australia

# Kinetic Analysis of In-Sewer Biotransformation of Selected Pharmaceuticals

**Ludwika Nieradzik*, Jelena Radjenovic*,**, Zhiguo Yuan*, Bing-Jie Ni***
* Advanced Water Management Centre, The University of Queensland, St Lucia QLD 4072, Australia
** Catalan Institute for Water Research (ICRA), Parc Científic i Tecnològic de la Universitat de Girona, 17003 Girona, Spain

**Keywords:** Sewers, Pharmaceuticals, Biotransformation, Kinetics

## Summary of key findings

The biotransformation in sewer pipes is a previously ignored key process for the estimation of pharmaceutical residues in the feed of downstream wastewater treatment plants, and thus determines the fate and behaviour of pharmaceutically active compounds (PhAC) in overall urban wastewater system. In this work, in-sewer biotransformation of several typical PhAC were studied using extensive batch experiments, including enrofloxacin, propanolol, ranitidine, trimethoprim, venlafaxine, atenolol, sulfamethoxazole and diatrizoate. First-order kinetics were applied to estimate their biotransformation rates ($k_{bio}$) in sewers by fitting to the batch experimental data for the first time. The results demonstrated that the studied PhAC were degraded significantly by sewer biofilm, with $k_{bio}$ ranging from $4.84 * 10^{-1}$ (enrofloxacin) to $1.28 * 10^{-2}$ $h^{-1}$ (diatrizoate). The findings of this work are of high interest with regard to the development of comprehensive sewer models for the accurate prediction of in-sewer biotransformation processes.

## Background and relevance

The presence of PhAC in the aquatic environment has been studied by numerous research groups and has been linked with the endocrine disruption in fish and an increasing antibiotic resistance of bacteria, amongst others. Wastewater treatment plants (WWTPs) have been identified as a major emission source and most previous work on the fate and behaviour of PhAC has been focused on wastewater treatment processes [1]. However, a large fraction of their load in WWTP originates from households, where they are consumed, partly metabolised and excreted, reaching the sewer systems. Although sewer pipes are known to be a biological system themselves, little attention has been given to the potential in-sewer biotransformation of PhAC, which may significantly change the occurrence and concentration of PhAC residues in the influent of downstream WWTP. In addition, the biotransformation kinetics are important for the development of reliable sewer models describing in-sewer biotransformation processes, and thus achieving accurate prediction of integrated urban wastewater system. Aiming to study the in-sewer biotransformation kinetics of typical PhAC, the results in this work provide first insights into the biotransformation rates and valuable information for possible extension of the existing SeweX model for accurate predictions of the PhACs removal and estimation of downstream concentrations in the WWTP.

## Results

The 24 h batch experiments using lab-scale rising main reactors showed that biotransformation occurred for all selected compounds (Figure 1), with major changes happening within the first 6 hours after injection. The fastest transformation was observed for EFX, which was removed by 80 % within the first 4 h. Between 8 h and 24 h only minor changes occur with the exception of TMP, which shows another 25 % transformation. On the contrary, for DTR, only 20 % was tranformed after 24 h. SMX and ATN were the most persistent to biodegradation. Similar results have been found for gravity sewer reactors (data not shown). Negligible change of the concentration during the initial phase indicate that adsorption did not have a major impact. These processes are very likely to occur in full-scale sewer pipes, as diurnal fluctuations in flow allow higher retention times outside of peak usage hours.

Table 1 displays the kinetic biotransformation rate constants for the studied compounds in this work. Their $k_{bio}$ are ranked from highest (fastest transformation) to lowest (slowest):

EFX > PRP > RTD > TMP > VLX > ATN > SMX > DTR.

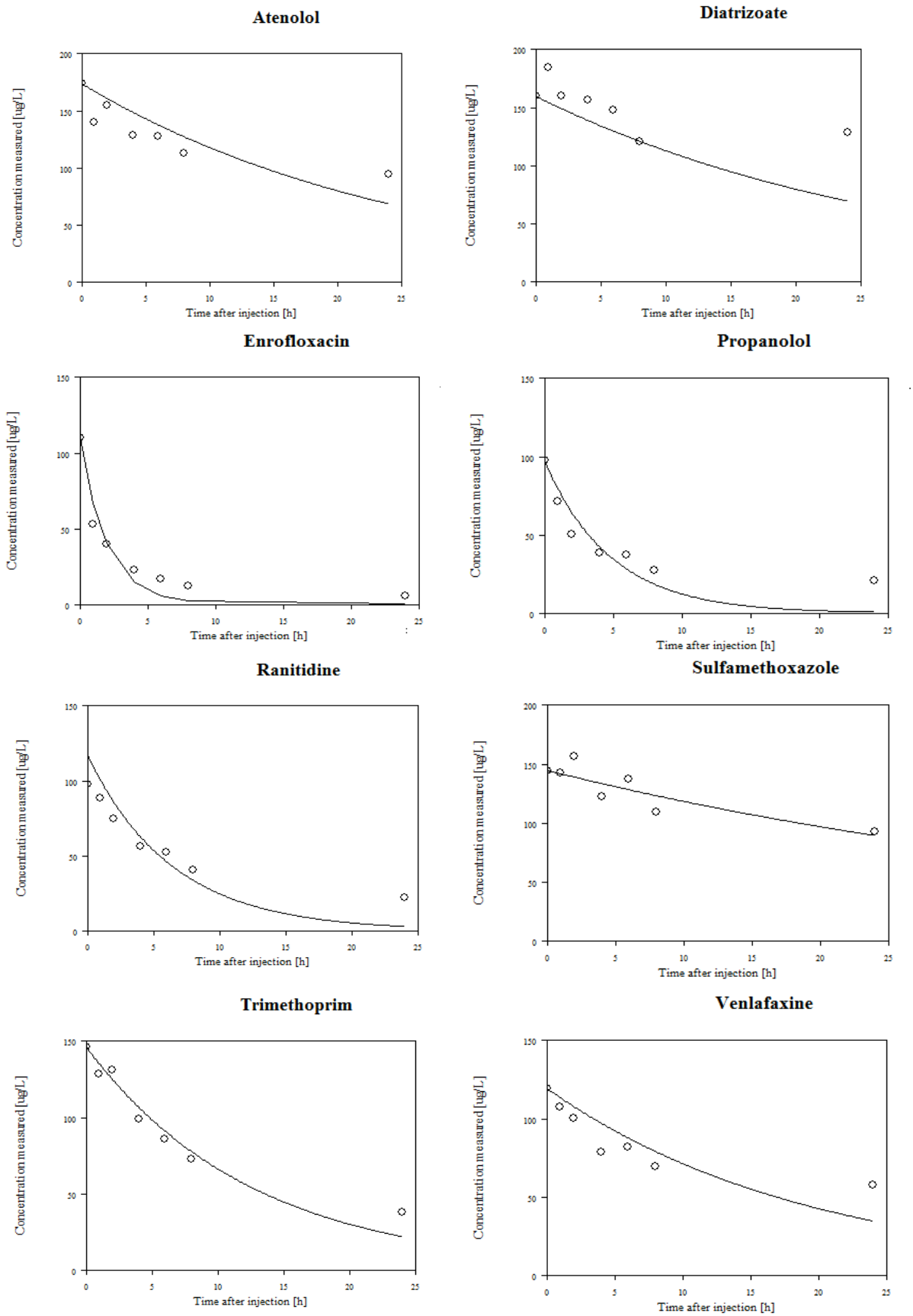


**Figure 1 Biotransformation curves of the chosen pharmaceutical compounds. The circles display measured data the model (solid line) is built upon. The basis for all biotransformation curves is first-order kinetics for experimental data in 24 h.**

**Table 1 Biotransformation rate constants obtained using experimental data. Parameter estimation was done in Aquasim 2.1 using the secant method.**

| | Sampling period: 24 h | | | Sampling period: 8 h | | |
|---|---|---|---|---|---|---|
| **Compound** | **$k_{bio}$ [1/h]** | **Standard error** | **$\chi^2$** | **$k_{bio}$ [1/h]** | **Standard** | **$\chi^2$** |
| **Atenolol (ATN)** | $2.23 * 10^{-2}$ | $4.94* 10^{-3}$ | 2157 | $3.42 * 10^{-2}$ | $5.24* 10^{-3}$ | 702 |
| **Diatrizoate (DTR)** | $7.43 * 10^{-3}$ | $2.99 * 10^{-3}$ | 1432 | $1.28 * 10^{-2}$ | $6.44 * 10^{-3}$ | 1192 |
| **Enrofloxacin (EFX)** | $4.83 * 10^{-1}$ | $7.09 * 10^{-2}$ | 515 | $4.84 * 10^{-1}$ | $7.57 * 10^{-2}$ | 486 |
| **Propanolol (PRP)** | $2.11 * 10^{-1}$ | $3.76 * 10^{-2}$ | 837 | $2.15 * 10^{-1}$ | $3.03 * 10^{-2}$ | 438 |
| **Ranitidine (RTD)** | $1.42 * 10^{-1}$ | $2.40 * 10^{-2}$ | 1155 | $1.47 * 10^{-1}$ | $2.35 * 10^{-2}$ | 788 |
| **Sulfamethoxazole (SMX)** | 1.41 * 10-2 | 3.01 * 10-3 | 715 | 1.66 * 10-2 | 6.03 * 10-3 | 680 |
| **Trimethoprim (TMP)** | $5.52 * 10^{-2}$ | $5.49 * 10^{-3}$ | 454 | $6.15 * 10^{-2}$ | $3.72 * 10^{-3}$ | 121 |
| **Venlafaxine (VLX)** | $3.83 * 10^{-2}$ | $7.99 * 10^{-3}$ | 195 | $5.57 * 10^{-2}$ | $5.13 * 10^{-3}$ | 157 |

## Discussion

While TMP, EFX, SMX, VLX and PRP have $\chi^2$ below 850, with VLX below 200, the final data point at 24 h in all cases has a much higher value than the model predictions (Figure 1), likely due to the decreased activity of biofilm. The other three compounds have sums of squares of up to 2150. A very high $\chi^2$ indicates that the model doesn't fit the experimental data well and the biotransformation process in a period of 24 h may need a more complex structural model rather than the simple first-order kinetics.

Table 1 summarizes the parameters of the first-order biotransformation kinetics of the selected PhACs, which could descibe well the 8-h biotransformation processes (lower $\chi^2$). Given that frequent usage of water and generation of wastewater occurs especially in the hours before and after a normal work day, a period of 8 h is the maximum feasibile retention time in sewer pipes. Hence, the obtained first-order kinetics could be used to evaluate the potential biotransformation processes in sewer pipes and provide basic estimation of their removal, without time-consuming simulations. The results also provide valuable information for possible extension of the existing SeweX model for accurate predictions of the PhACs removal process and the estimation of downstream concentrations in the WWTP.

This study demonstrated that the selected PhACs could be transformed significantly by the biofilms in sewer pipes. The first-order kinetics could well describe the biodegradation processes in simple sewer systems (e.g. single long pipe) with retention times of up to 8 h. All compounds showed a decreasing trend in the aqueous phase and the kinetic rates varied between $1.28 * 10^{-2}$ and $4.84 * 10^{-1}$ $h^{-1}$.

## References

Rizzo, L., Manaia, C. Merlin, C., Schwartz, T., Dagot, C., Ploy, M.C., Michael, I., Fatta-Kassinos, D. (2013) Urban wastewater treatment plants as hotspots for antibiotic resistant bacteria and genes spread into the environment: a review, *Science of the Total Environment*, 447, 345-360

Radjenović, J., Petrović, M., Barceló, D. (2009) Fate and distribution of pharmaceuticals in wastewater and sewage sludge of the conventional activated sludge (CAS) and advanced membrane bioreactor (MBR) treatment, *Water Science and Technology,* 43(3), 831-841

Helbling, D.E., Johnson, D.R., Honti, M., Fenner, K. (2012) Micropollutant biotransformation kinetics associate with WWTP process parameters and microbial community characteristics, *Environmental Science and Technology*, 46(19), 10579-10588