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Modelling Illicit Drug Fate in Sewers for Wastewater-Based Epidemiology

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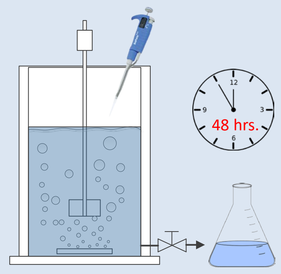
The sewer as a bioreactor

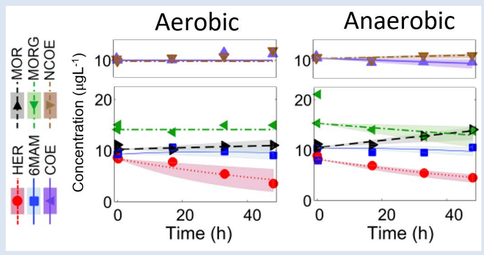
Sewer pipelines, although primarily designed for sewage transport, is in fact a bioreactor where the primary substrates (e.g. natural organic fractions) and trace organic substrates (e.g. excreted drug biomarkers) can undergo significant transformation. Hence, the occurrence of illicit drug biomarkers can be potentially influenced by physico-chemical and biological processes (fate processes) in the sewer

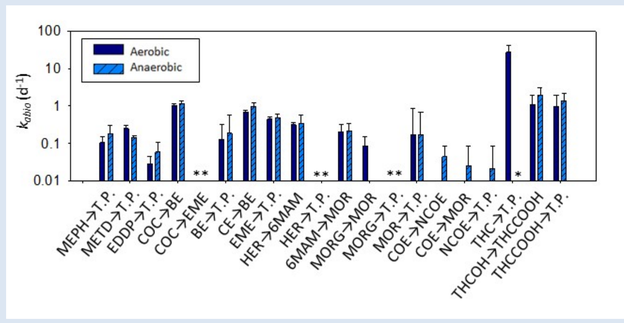
Aims

- Providing new evidences on drug transformation and sorption in the sewer
- Predicting the fate processes using mathematical models and statistical analysis
- Primarily focusing on batch experiments representing the sewer as well as preliminary analysis in catchments

Abiotic transformation





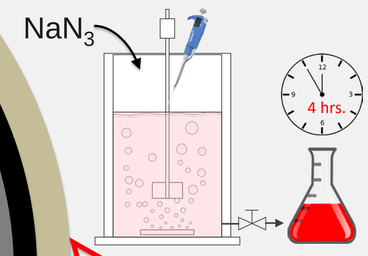


- Experiments were performed with mineral water
- First order equation was used for predictions
- Abiotic transformation is significant (>1 d^{-1}) for many of the compounds specially for COC, CE, THC, THCOH and THCOOH
- No major difference was found between aerobic and anaerobic abiotic transformation except for COE and NCOE [1]

$$\frac{dC_{LI}(t)}{dt} = \underbrace{-k_{abio}C_{LI}(t)}_{\text{Abiotic transformation}} \underbrace{- k_{des,w}k_{d,w}C_{LI}(t)\frac{A_T(t)}{V_T(t)}}_{\text{Sorption to reactor wall}} \underbrace{+ k_{des,w}C_{Sw}(t)}_{\text{Desorption from reactor wall}}$$

C_{LI}	Dissolved trace organic chemical	mg L^{-1}
C_{Sw}	Trace organic chemical onto tank wall	mg L^{-1}
$k_{des,w}$	Desorption from reactor wall	d^{-1}
K_{dw}	Reactor wall–liquid partition coefficient	L dm^{-2}
k_{abio}	Abiotic transformation rate constant	d^{-1}
A_T	Area of liquid in external tank	dm^{-2}
V_T	Volume of liquid in external tank	L

Sorption (biofilm)



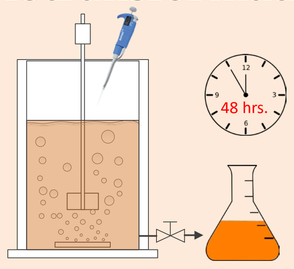
$$K_{df} = \frac{C_{SL,eq} - C_{loss}}{(C_{LI,eq} + C_{loss})X_{SS}}$$

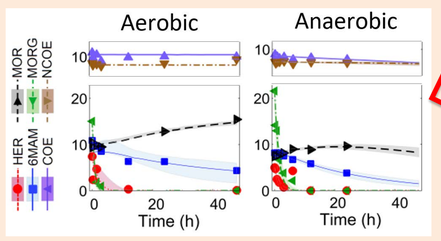
$$C_{loss} = C_{LI,t=0} - C_{LI,t=end}$$

Compound	K_{df} (L g^{-1}) aerobic	K_{df} (L g^{-1}) anaerobic
MEPH	0.2	0
METD	0.32	0.55
EDDP	0	0.15
BE	0.9	0.62
EME	0	1.59
THCOH	2.81	1.68
THCCOOH	0	1.06

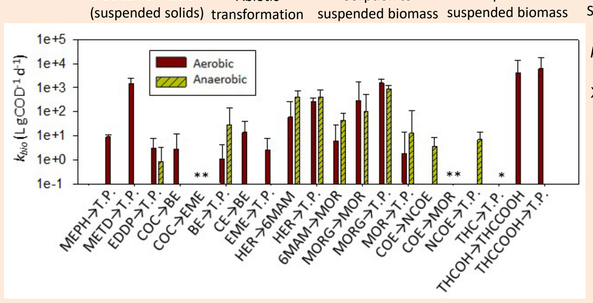
- Sorption tests were performed with suspended biofilm [4]
- Sorption to biofilm was observed for few compounds

Biotransformation (suspended solids)



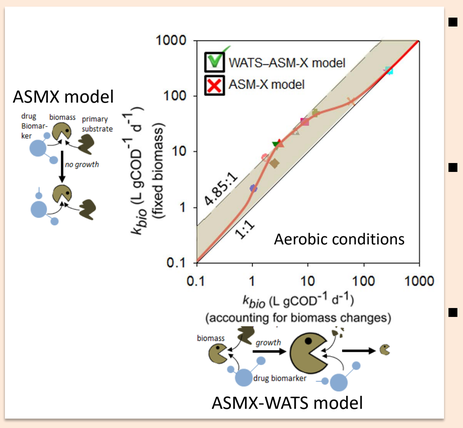


$$\frac{dC_{LI}(t)}{dt} = \underbrace{-k_{bio}C_{LI}(t)X}_{\text{Biotrasnformation (suspended solids)}} \underbrace{- k_{abio}C_{LI}(t)}_{\text{Abiotic transformation}} \underbrace{- k_{des}k_dC_{LI}(t)X_{SS}}_{\text{Sorption to suspended biomass}} \underbrace{+ k_{des}C_{LI}(t)}_{\text{Desorption from suspended biomass}} \underbrace{- k_{des,w}k_{d,w}C_{LI}(t)\frac{A_T(t)}{V_T(t)}}_{\text{Sorption to reactor wall}} \underbrace{+ k_{des,w}C_{Sw}(t)}_{\text{Desorption from reactor wall}}$$



k_{bio}	Biotransformation rate constant	L $gCOD^{-1}$ d^{-1}
X	Total particulate solids/biomass	dm^{-2}

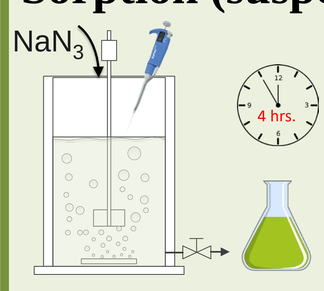
Suspended solids/biomass play and important role in biotransformation of most of the selected compounds [1]



- Redox condition has significant impact on biotransformation rates for nearly all selected drugs
- Accounting for biomass growth to estimate biotransformation rate under aerobic conditions is crucial
- Biomass growth do not play a major role in estimation of anaerobic biotransformation rate

Fate of the drug biomarkers was assessed using two modelling approaches
I- Describing the biokinetics only for secondary metabolic substances (drug biomarkers) assuming that biomass is constant (based on ASM-X [2])
II- Modelling the primary metabolic processes (related to COD fractions) (based on WATS [3]) combined with secondary metabolic processes (WATS—ASM-X model [1])

Sorption (suspended solids)



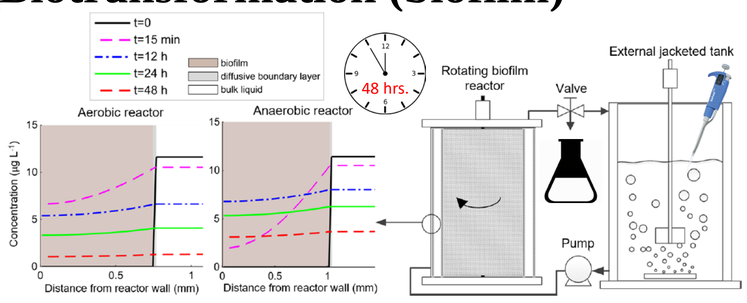
$$K_d = \frac{C_{SL,eq} - C_{loss}}{(C_{LI,eq} + C_{loss})X_{SS}}$$

$$C_{loss} = C_{LI,t=0} - C_{LI,t=end}$$

Compound	K_d (L g^{-1})
MEPH	0.25
EDDP	0.03
6MAM	0.31
NCOE	0.01
THCOH	0.75
THCCOOH	0.8

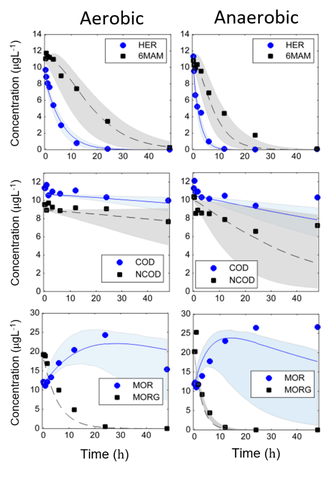
- Sorption tests were performed with washed-off diluted primary sludge [1]
- Sorption to reactor wall and hydrolysis (loss) were accounted for in calculation of k_d using blank experiments
- Sorption to suspended solids was found to be relevant for a few compounds
- THC was found to completely sorped to reactor wall

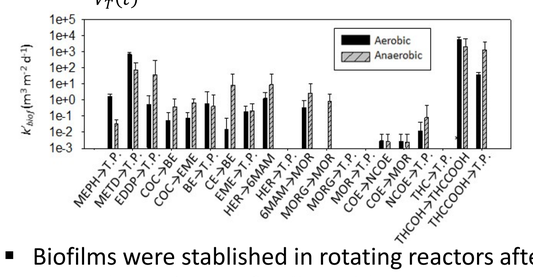
Biotransformation (biofilm)



1. Abiotic transformation: $-k_{abio}C_{LI}(t)$
2. Biotransformation and sorption (suspended solids): $-\frac{k_{bio}X_{SS}}{1 + K_dX_{SS}}C_{LI}(t)$
3. Biotransformation and sorption (biofilm): $-\frac{k_{biof}X_{Sf}}{1 + K_{df}X_{Sf}}C_{LI}(t)$
4. Sorption-desorption to wall: $-k_{des,w}k_{d,w}C_{LI}(t)\frac{A_T(t)}{V_T(t)} + k_{des,w}C_{LI}(t)$

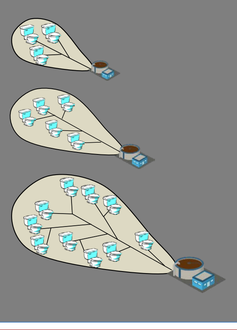
- In external tank: 1+2+4
- In reactor bulk: 1+2
- In Biofilm: 1+3





- Biofilms were stablished in rotating reactors after 7 month continuous feeding with wastewater
- A 1-D multi-compartment model was built to describe spatial and temporal variations inside the biofilm
- Mass transfer limitation from bulk phase to biofilm was considered
- Diffusive boundary layer and number of discretization were carefully assigned [4]

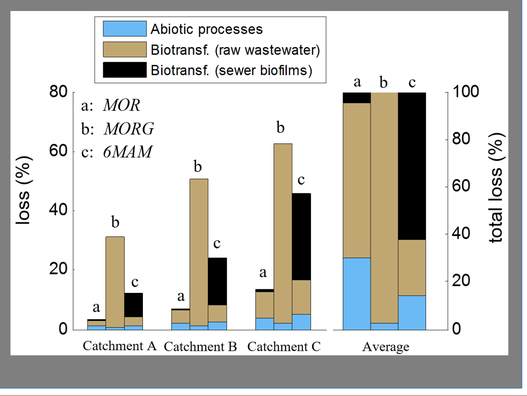
Drug biomarkers loss in three hypothetical catchments (simulation study) [5]



A: 10000 PE, HRT=1.4 h

B: 50000 PE, HRT=2.8 h

C: 200000 PE, HRT=5.5 h



Final remarks

- Through different experimental assessments, it was found that drug biomarkers can potentially undergo significant sorption and transformation in the sewers
- Sorption and transformation rates are the key indicators of *drug stability* in the sewer which can be estimated using mathematical models and statistical analysis
- In the sewer, different drug biomarkers can transform to each other, hence pathway identification is crucial when modelling transformations [6]
- Ignoring in-sewer fate processes for drug biomarkers can be a significant source of bias for wastewater-based epidemiology

[1] Ramin, P., Brock, A.L., Polesel, F., Causanilles, A., Emke, E., de Voogt, P., Plósz, B.G., 2016. Transformation and sorption of illicit drug biomarkers in sewer systems : understanding the role of suspended solids in raw wastewater. Environ. Sci. Technol. 50, 13397–13408.
[2] Plósz, B. G.; Reid, M. J.; Borup, M.; Langford, K. H.; Thomas, K. V. Biotransformation kinetics and sorption of cocaine and its metabolites and the factors influencing their estimation in wastewater. *Water Res.* **2013**, *47*, 2129–2140.
[3] Hvitved-Jacobsen, T.; Vollertsen, J.; Nielsen, A. H. Sewer Processes: Microbial and Chemical Process Engineering of Sewer Networks, Second Edition; CRC Press, 2013
[4] Ramin, P., Brock, A.L., Causanilles, A., Valverde Pérez, B., Emke, E., de Voogt, P., Polesel, F., Plosz, B.G., 2017. Transformation and sorption of illicit drug biomarkers in sewer biofilms. Environ. Sci. Technol. 51, 10572–10584.
[5] Ramin, P., Vezzaro, L., Mikkelsen, P.S., Plósz, B.G. Back-calculating illicit drug abuse rates in urban areas – Quantifying uncertainties associated with in-sewer transformation and sampling. Submitted
[6] Ramin, P., Valverde Pérez, B, Polesel, F., Locatelli, L., Plósz, B.G., 2017b. A systematic model identification method for chemical and biochemical transformation pathways combined with reaction kinetics – the case of heroin biomarkers. Sci. Rep. 7, 9390.

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