

Modelling the fate of drugs of abuse in a WWTP using in-process measurements

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Overview

- Problem statement
- Objective
- Methodology
- Modelling
- Results
- Conclusion

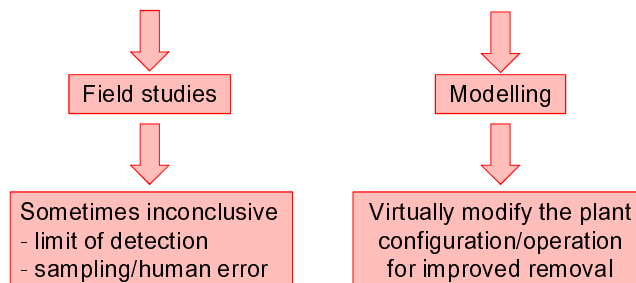
Problem statement

- Drugs of abuse are found in:
 - Sewage
 - Wastewater treatment plant effluents
 - Surface waters = Incomplete removal!
- Undesirable effects similar to therapeutic drugs
 - Genetic mutations of zebra fish (cocaine)
 - Reduced intracellular activity on mussels (morphine)

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Problem statement

- How can we improve the situation?
 - Get a better understanding of the processes



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Objective

- Model the removal pathways of selected drugs of abuse in an activated sludge treatment plant using in-process measurements

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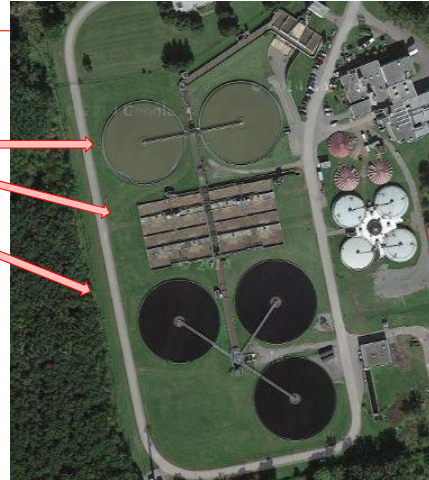
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Methodology

- Gatineau WWTP
 - Nitrifying activated sludge
 - 2 primary clarifiers
 - 4 series of 2 aeration tanks
 - 3 secondary settlers
 - 127 500 m³/d
 - 235 000 inhabitants



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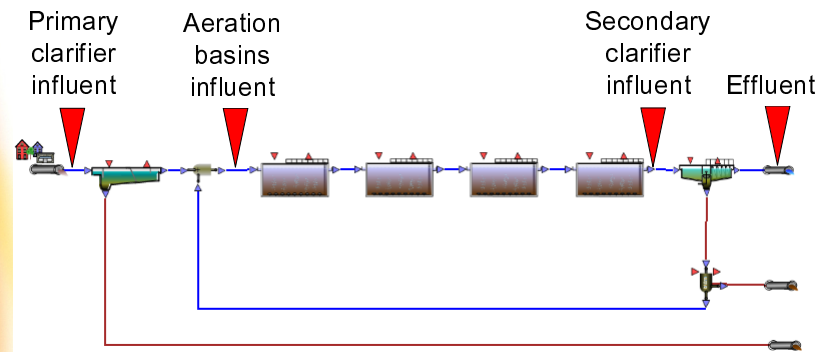
Methodology

- Sampling campaign
 - Hydraulic calibration to take into account residence time distribution (RTD) for proper sampling of non-ideal process configurations (Yargeau et al., paper 520, 4pm)
 - 24h time-proportional composite samples for 3 consecutive days

Methodology

▼ = Sampling locations

- Simplified configuration of the Gatineau WWTP



Methodology

- 19 drugs of abuse and metabolites studied

Stimulants

- amphetamine
- methamphetamine
- methylenedioxy-amphetamine
- methylenedioxy-methamphetamine
- ephedrine
- cocaine
- benzoylecgonine

Opioids

- codeine
- acetylcodeine
- dihydrocodeine
- morphine
- acetylmorphine
- methadone
- heroin
- tramadol
- ketamine
- oxycodone
- EDDP*
- fentanyl

*Ethylidene-1,5-dimethyl-3,3-diphenylpyrrolidine

Methodology

- Processes affecting each contaminant

Process →	Volatilization	Sorption	Degradation
Property →	Henry's law constant	Partition coefficient	Aerobic half-life
Cocaine	-	+	+++

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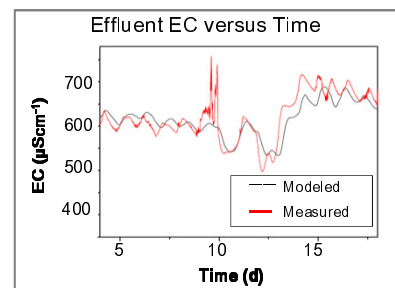
Modelling

- Model based on ASM2d
(Activated Sludge Model No 2d – Henze et al., 1997):
 - Organic matter removal
 - Nitrification / denitrification
 - Biological phosphorus removal
- Extensions for micropollutant fate
 - Volatilization
 - Biodegradation
 - Sorption / desorption
 - Advanced oxidation processes (e.g. ozone)
 - Photolysis

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Modelling

- Hydraulic calibration results
 - 1 primary clarifier
 - 4 series of 4 aeration tanks
 - 3 secondary clarifiers



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Results

- Following results were obtained:
 - Using aerobic half-life, partition coefficient, and Henry's constant (no calibration, literature default)
 - After getting a model that is adequately describing traditional pollutant removal (fit to routine data):

- $r = -k_r \cdot S_{MP} \cdot X_{OHO}$

r: degradation rate

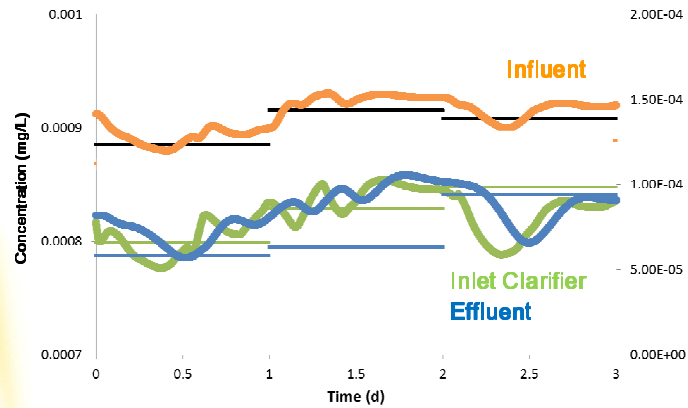
k_r : rate constant

S_{MP} : micropollutant concentration

X_{OHO} : ordinary heterotrophic organism concentration

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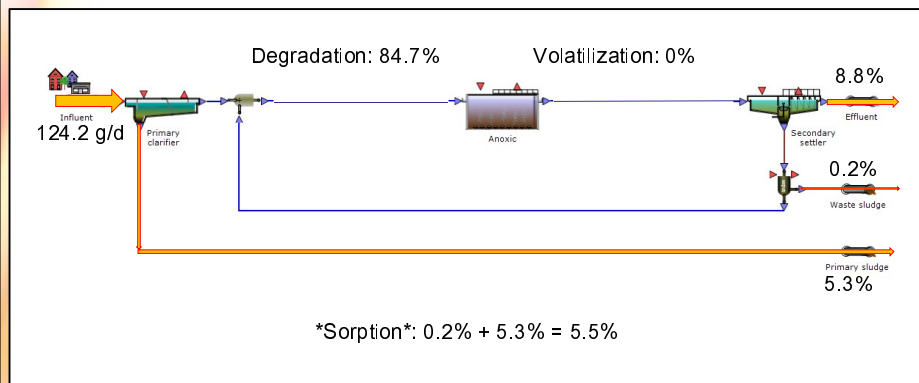
Results – Cocaine



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Results – Cocaine

- Substance flux analysis of cocaine



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Results – Cocaine

- Removal: expected vs modelled

	Measured removal %	Modelled removal %
Aeration basins	73	88
Secondary settlers	17	3
Total	90	91

- Total removal OK, but not in-process measurements!



Results

- Looking back at the plant configuration...

Total aeration basins volume	23 850 m ³
Total secondary clarifier volume	36 500 m ³

- ... and the sludge mass distribution

Total aeration basins sludge mass	38 000 kg
Total secondary clarifier sludge mass	27 000 kg

- Biodegradation in the settlers?

Results

Compounds	Aeration/clarifier removal meas.	Compounds	Aeration/clarifier removal meas.
Cocaine	4.3	Dihydrocodeine	-
Benzoyllecgonine	3.9	Morphine	3.1
Amphetamine	2.7	Acetylmorphine	3
Methamphetamine	3.2	Methadone	2.5
methylenedioxy-amphetamine	-	Heroin	-
methylenedioxy-methamphetamine	5.6	Tramadol	3.7
Ephedrine	0.4	Ketamine	3.8
Codeine	0.8	Oxycodone	0.5
Acetylcodeine	4.4	Fentanyl	-
EDDP	0.9		



Results

Compounds	Aeration/clarifier removal meas.	Compounds	Aeration/clarifier removal meas.
Cocaine	4.3	Compounds with > 50% removal. Ratio of removal in bioreactors vs removal in clarifiers ~ 4 LET'S MAKE THE SECONDARY CLARIFIER REACTIVE!	
Benzoyllecgonine	3.9		
Amphetamine	2.7		
Methamphetamine	3.2		
methylenedioxy-amphetamine	-		
methylenedioxy-methamphetamine	5.6	Tramadol	3.7
Ephedrine	0.4	Ketamine	3.8
Codeine	0.8	Oxycodone	0.5
Acetylcodeine	4.4	Fentanyl	-
EDDP	0.9		



Results

- Model experiment:
 - Volume and mass in clarifier bottom layer
 - 3650 m³, 23 000 kg (out of the 27 000 kg)
 - Mixed liquor coming from the bioreactors passes through this bottom layer
 - Addition of a biodegradation model to this layer, same kinetics, same kinetic parameters

Results – Cocaine

- Removal: expected vs modelled

	Measured removal %	Modelled removal %
Aeration basins	73	88
Secondary settlers	17	3
Total	90	91

- Removal with « reactive » clarifier

	Modelled removal %
Aeration basins	73
Aeration basin + secondary settlers	16
Total	89



Conclusion

- Water quality models allow:
 - Predicting the fate of traditional pollutants
- Micropollutant sub-models allow:
 - Predicting the fate of drugs of abuse (cocaine)
- In-process measurements allow:
 - Better understanding of the mechanisms
 - Realizing need to model biodegradation in clarifiers

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Acknowledgements

- 3Cs group (Viviane Yargeau)
- NSERC Strategic Projects



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