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Study on the fate of BTRs and OHBTH in activated sludge and MBBR systems: Biodegradation kinetics and removal efficiencies

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Water Micropol

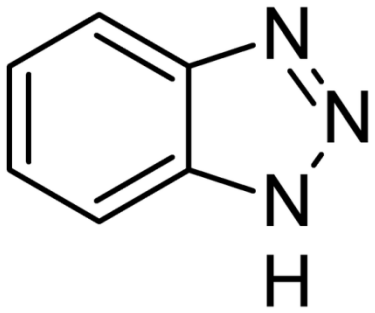
Uses of BTRs and BTHs

- Metal finishing industry (corrosion inhibitors)
- Brake fluids, cooling fluids, de-icing fluids
- Dishwashing detergents

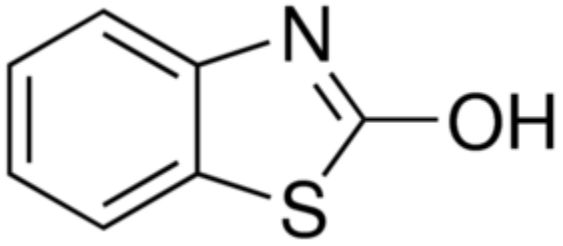
- Tire and rubber manufacturing industries (vulcanization accelerators)
- Biocides and drugs
- Stabilizers in photo industry

Chemical properties

- Highly soluble in water
- Slightly basic (pKa 7.7-8.9)
- High polarity - Weak tendency to sorb onto organic matter

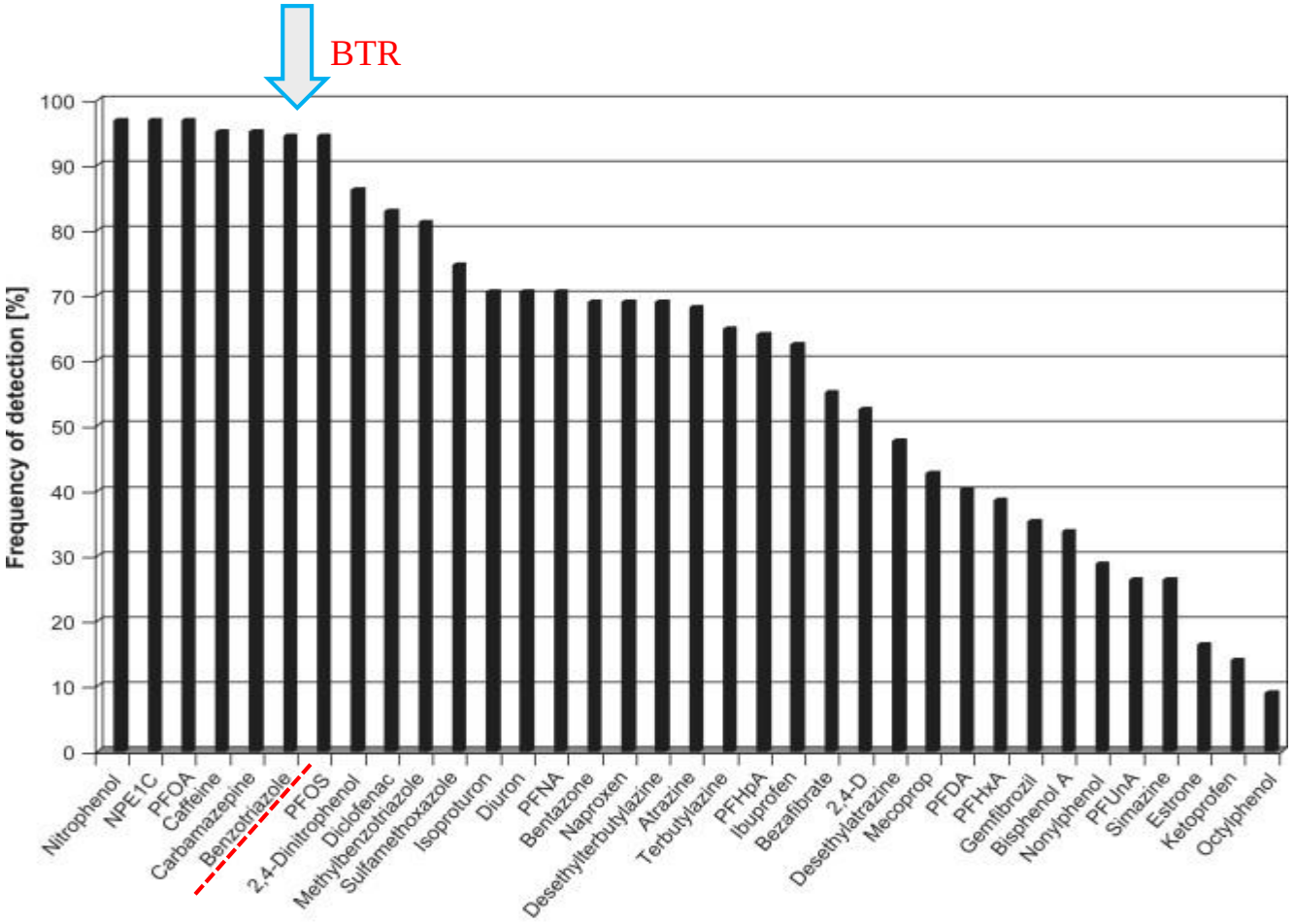


1H-Benzotriazole



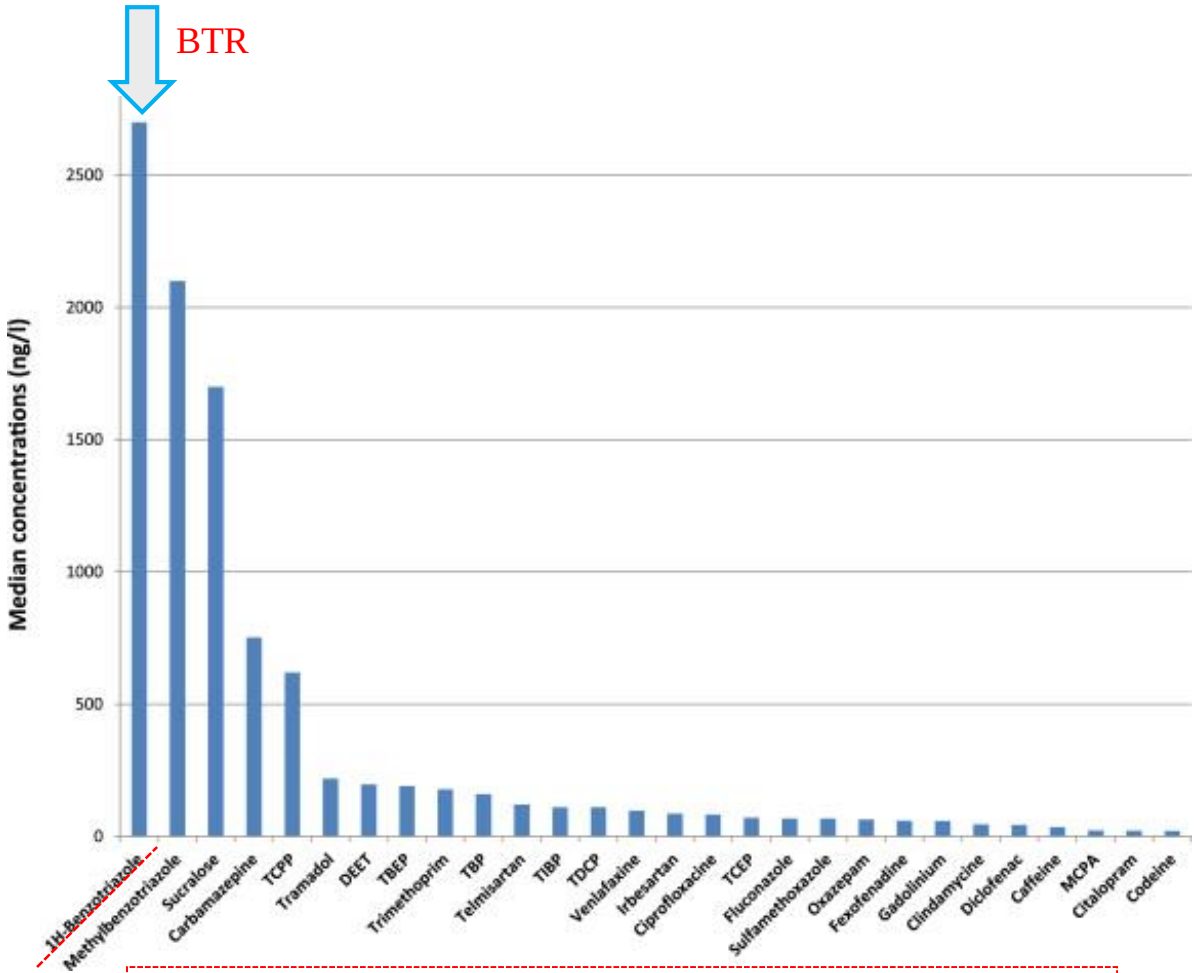
2-Hydroxybenzothiazole

Detection in surface water- EU



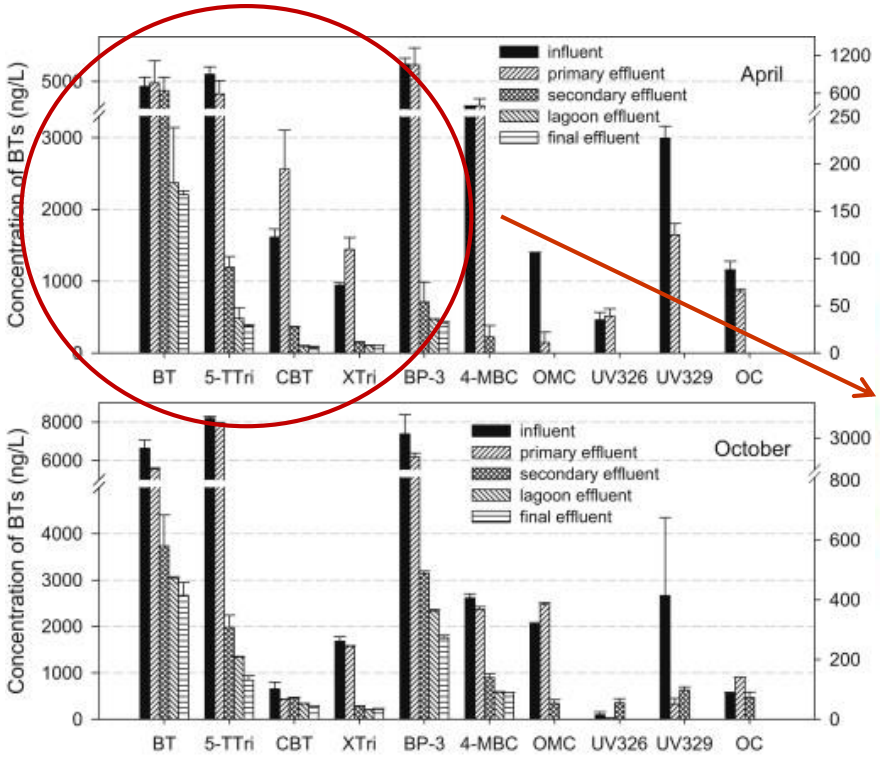
Loos et al. (2009) Environ Pollution 157, 561-568

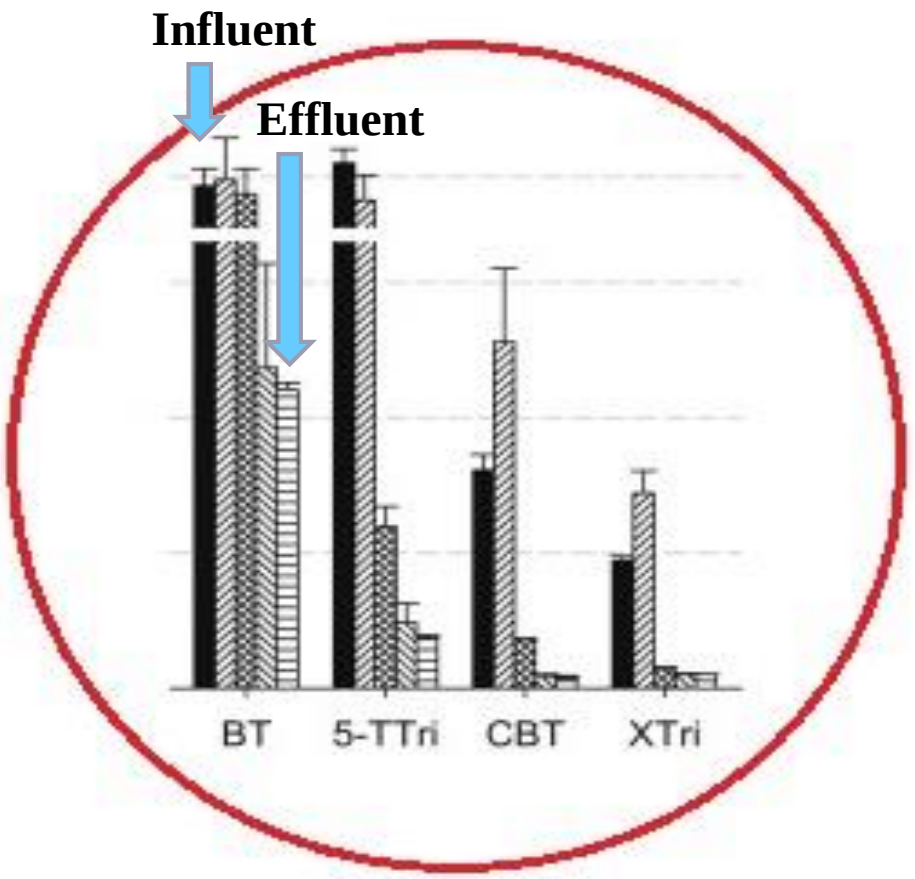
Detection in treated wastewater- EU



Loos et al. (2013) Water Res 47, 6475-6487

Removal in WWTP-Australia





Liu et al. (2012) Environ Pollution 165, 225-232

Objectives of the study

A. To determine **biodegradation kinetics** of selected BTRs and OHBTH with batch experiments

B. To investigate the role of organic substrate on kinetics

C. To compare removal efficiency during **biological treatment** in lab scale systems with

   I. **suspended biomass (AS)**

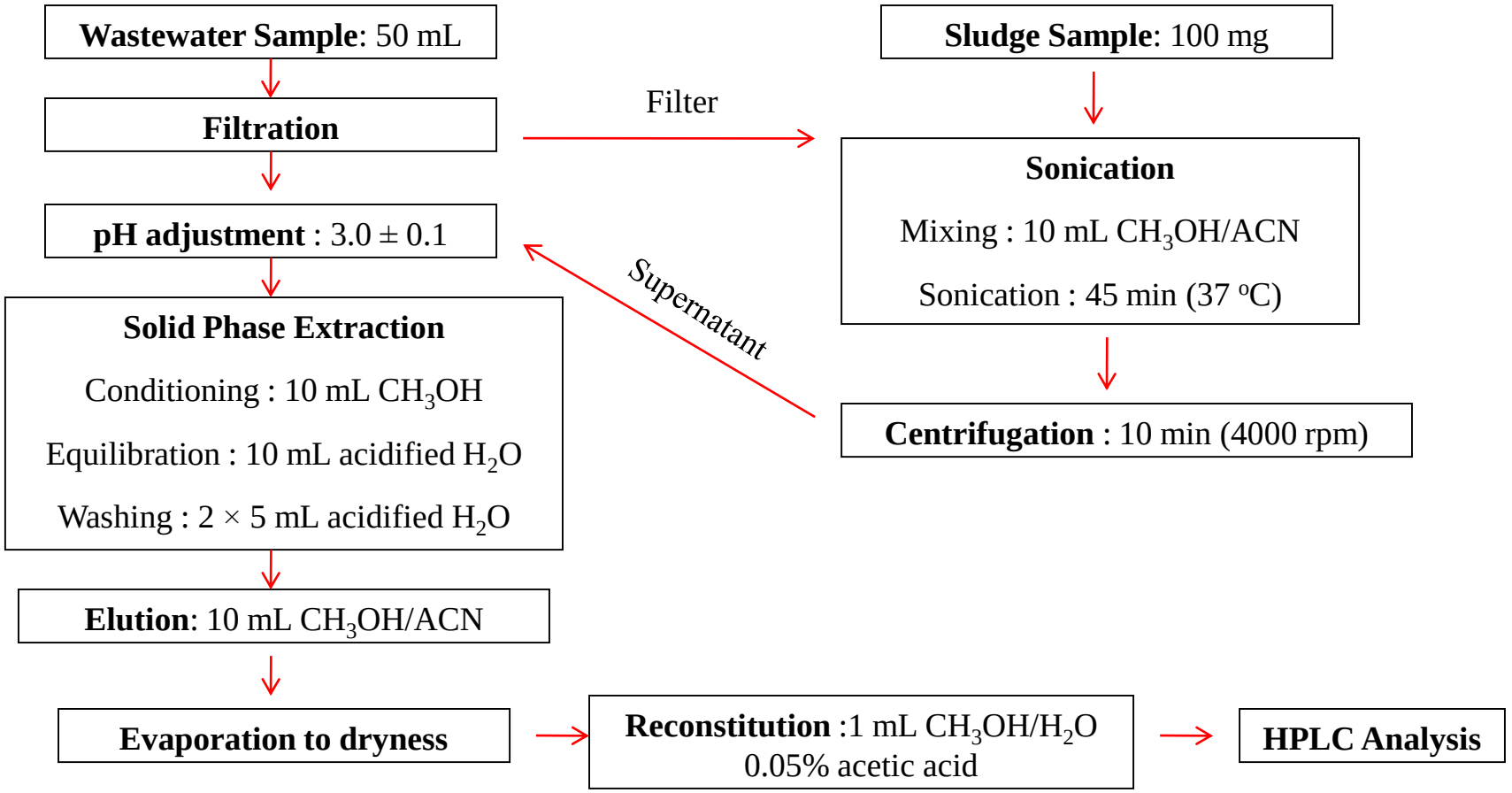
   II. **attached biomass (MBBR)**

D. To investigate the biodegradation potential of each biomass

Target compounds

- Benzotriazole, BTR
- Xylytriazole, XTR
- 5-chlorobenzotriazole, CBTR
- 2-hydroxy-benzothiazole, OHBTH

Analysis of BTRs/OHBTH



Mazioti et al. (2015) Chemosphere, 131, 117-123

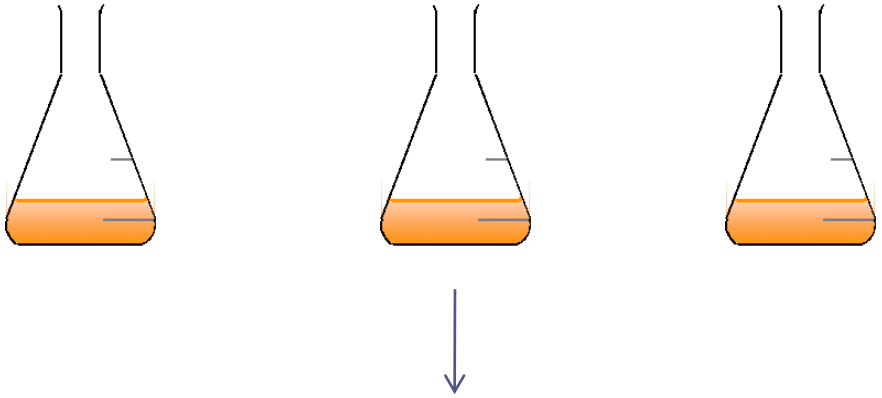
A. Batch experiments

Activated sludge batch experiments

Aerobic

Aerobic + Substrate

Abiotic



COD : 200 mg L^{-1}

Conditions

Volume : 1 L

Target compounds: 30 µg L^{-1}

MLSS: 3000 ± 150 mg L^{-1}

pH: 7.35 ± 0.32

T (°C): 21.2 ± 1.8 °C

Duration: 72 hours

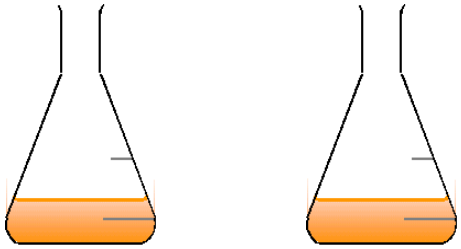
Samples: 0, 4, 8, 24, 36, 48, 72 h

Triplicates

Attached biomass batch experiments

Aerobic

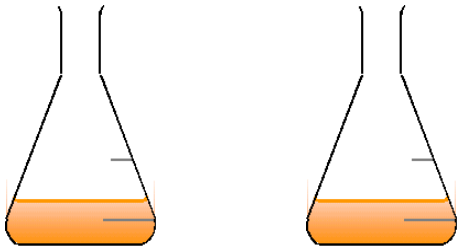
Aerobic + Substrate → COD : 270 mg L^{-1}



Bioreactor 1 (BC1)

Aerobic

Aerobic + Substrate → COD : 270 mg L^{-1}



Bioreactor 2 (BC2)

Conditions

Volume : 4.5 L

Target compounds: 30 µg L^{-1}

MLSS BC1: 1520 ± 980 mg L^{-1}

MLSS BC2: 400 ± 120 mg L^{-1}

Duration: 24 hours

Samples: 0, 1, 2.5, 5, 12, 24 h

One replicate

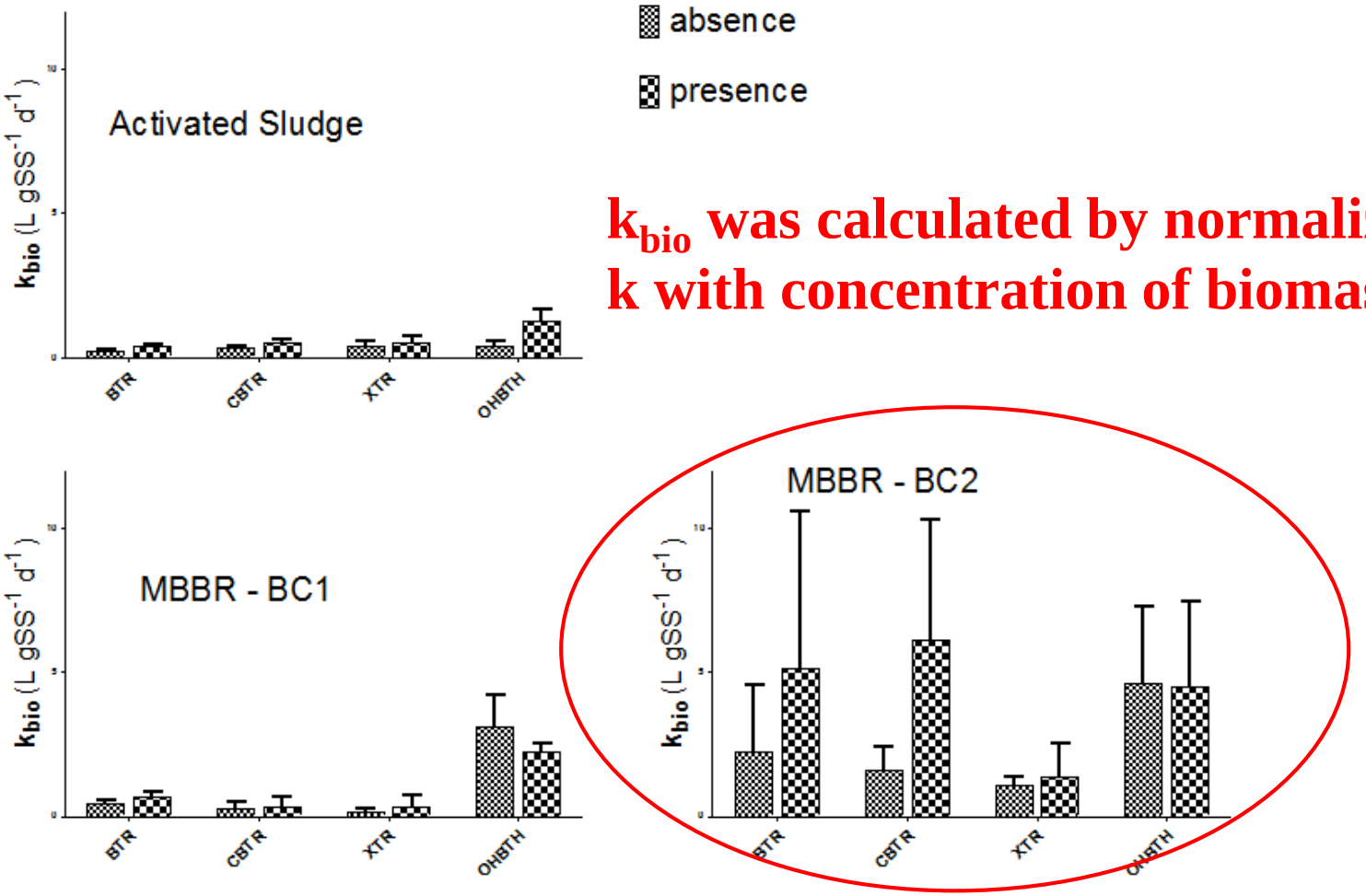
RESULTS: Biodegradation kinetics k (d^{-1})

The presence of easily degradable substance generally increased the k values

Ranged from 0.22 d^{-1} (XTR) to 2.58 d^{-1} (OHBTH)

Compound	Easily degradable organic substances	k (d^{-1})		
		AS	BC1	BC2
BTR	absence	0.38±0.13	0.66±0.20	0.89±0.90
	presence	0.73±0.12	0.98±0.33	2.03±2.15
CBTR	absence	0.54±0.06	0.41±0.37	0.64±0.30
	presence	0.83±0.24	0.48±0.56	2.43±1.64
XTR	absence	0.86±0.35	0.22±0.14	0.43±0.12
	presence	1.19± 0.54	0.49±0.61	0.53±0.46
OHBTH	absence	0.77±0.34	4.74±1.62	1.82±1.06
	presence	2.58±0.72	3.43±0.44	1.78±1.17

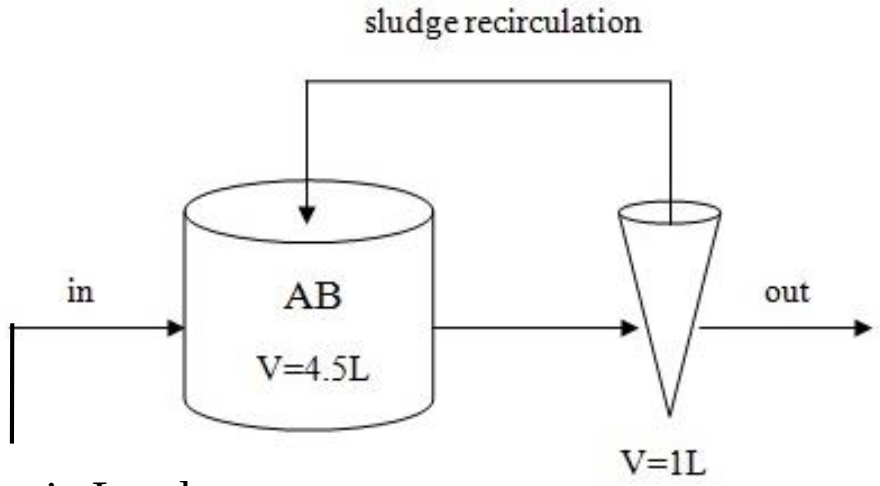
RESULTS: Biodegradation kinetics k_{bio}



k_{bio} was calculated by normalizing k with concentration of biomass

B. Continuous flow experiments

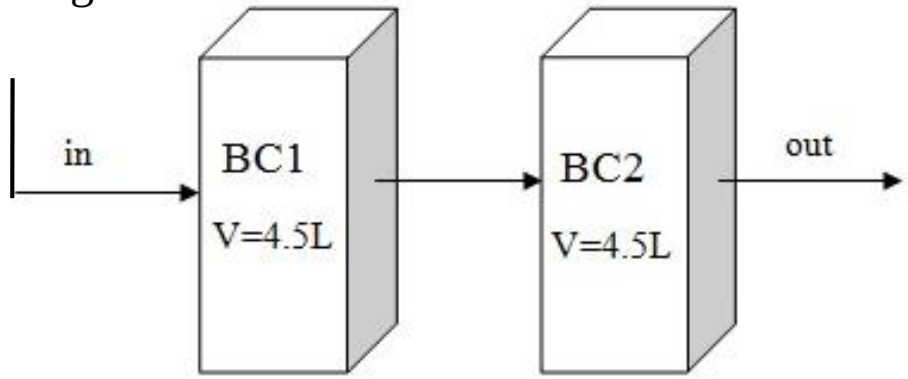
Systems description



HRT: 26.4±2.4 h
SRT: 18 d
pH: 7.2±0.4
MLSS: 2370±590 (mg L^{-1})

Organic Load
0.247 kg m^{-3} d^{-1}

Spike of micropollutants : 20µg L^{-1}

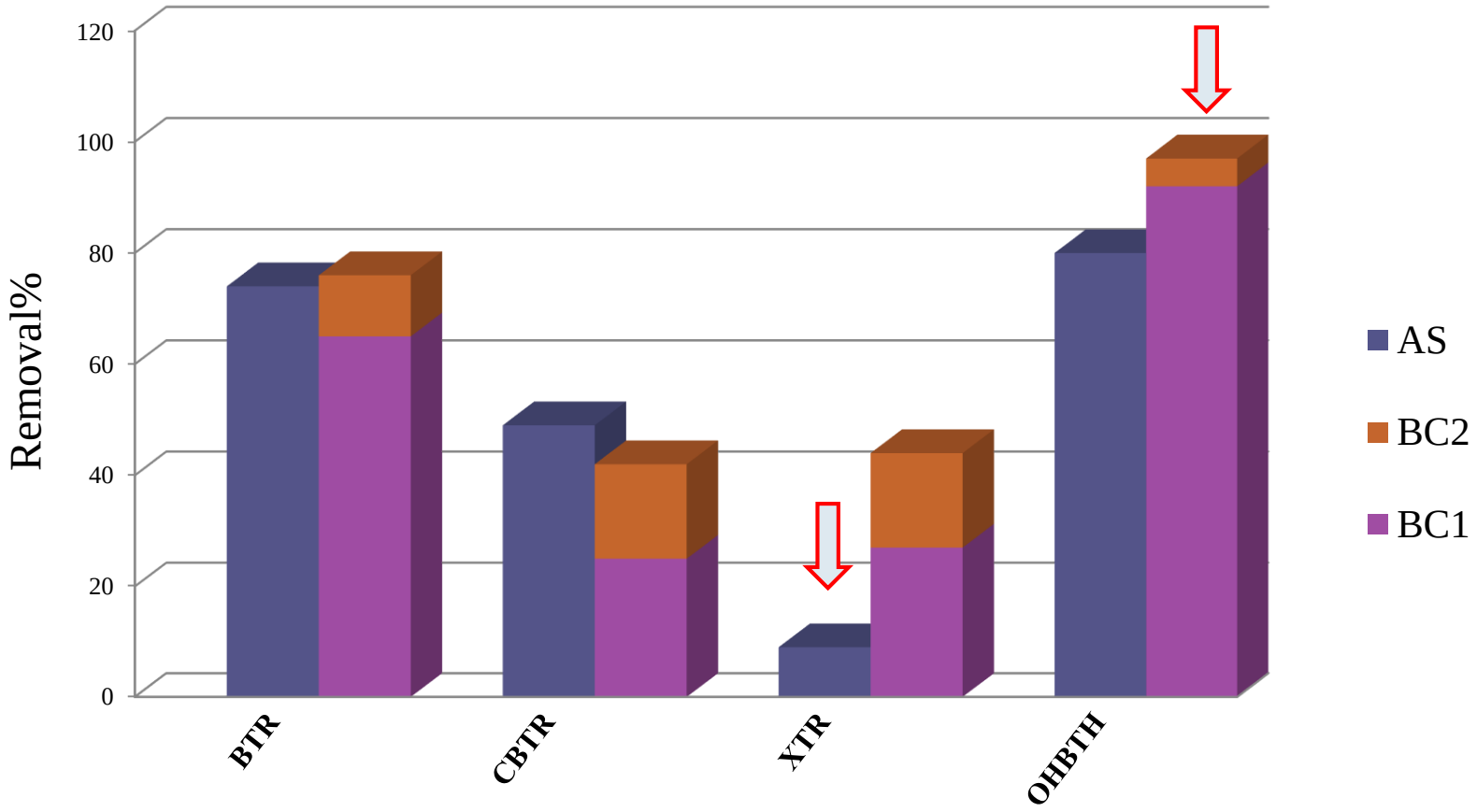


HRT: 26.4±2.4
(in each reactor)

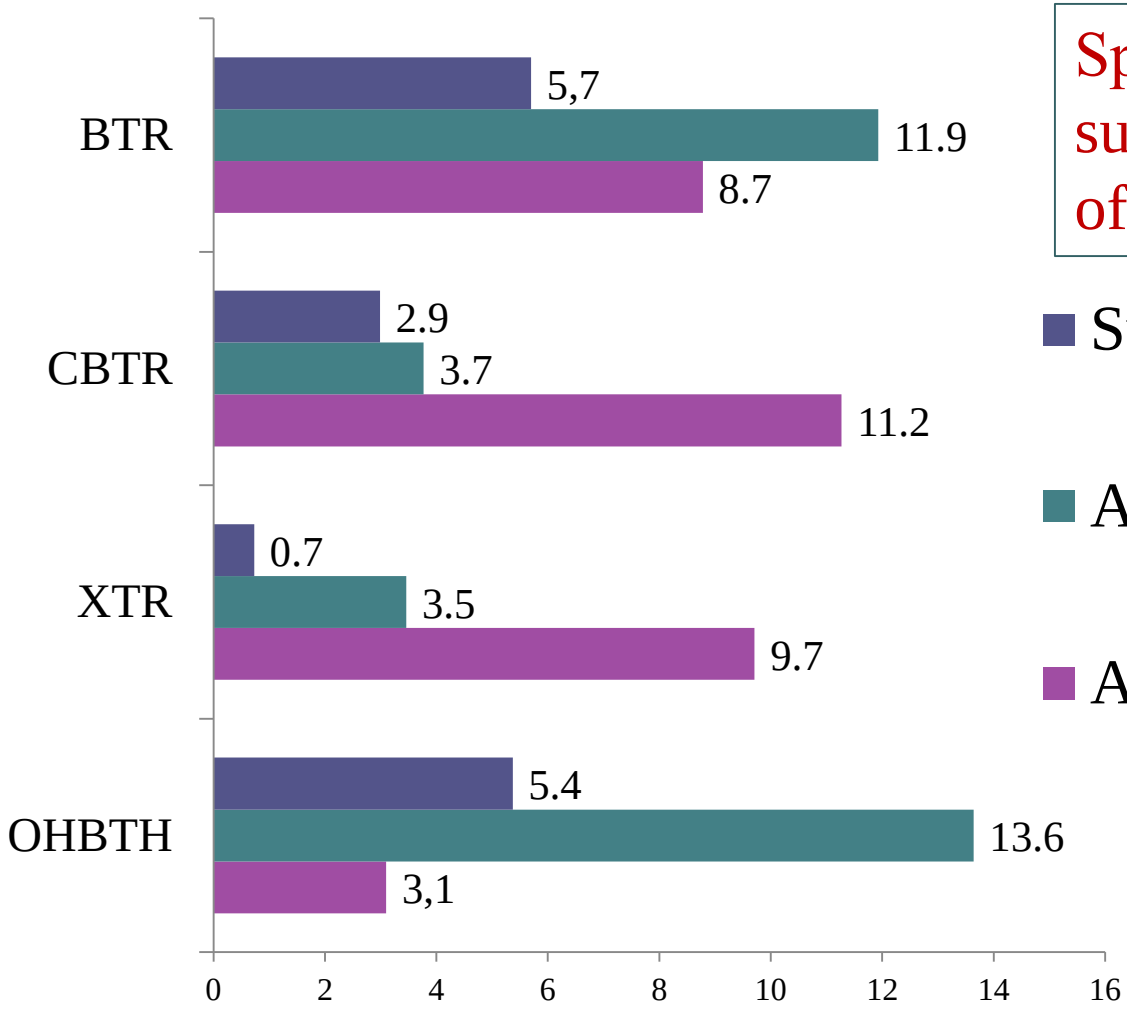
pH (BC1): 7.0±0.5
pH (BC2): 6.8±0.9

TSS (BC1): 921±81 (mg L^{-1})
TSS (BC2): 231±89 (mg L^{-1})

RESULTS: Removal during treatment



RESULTS: Potency of each biomass in removal



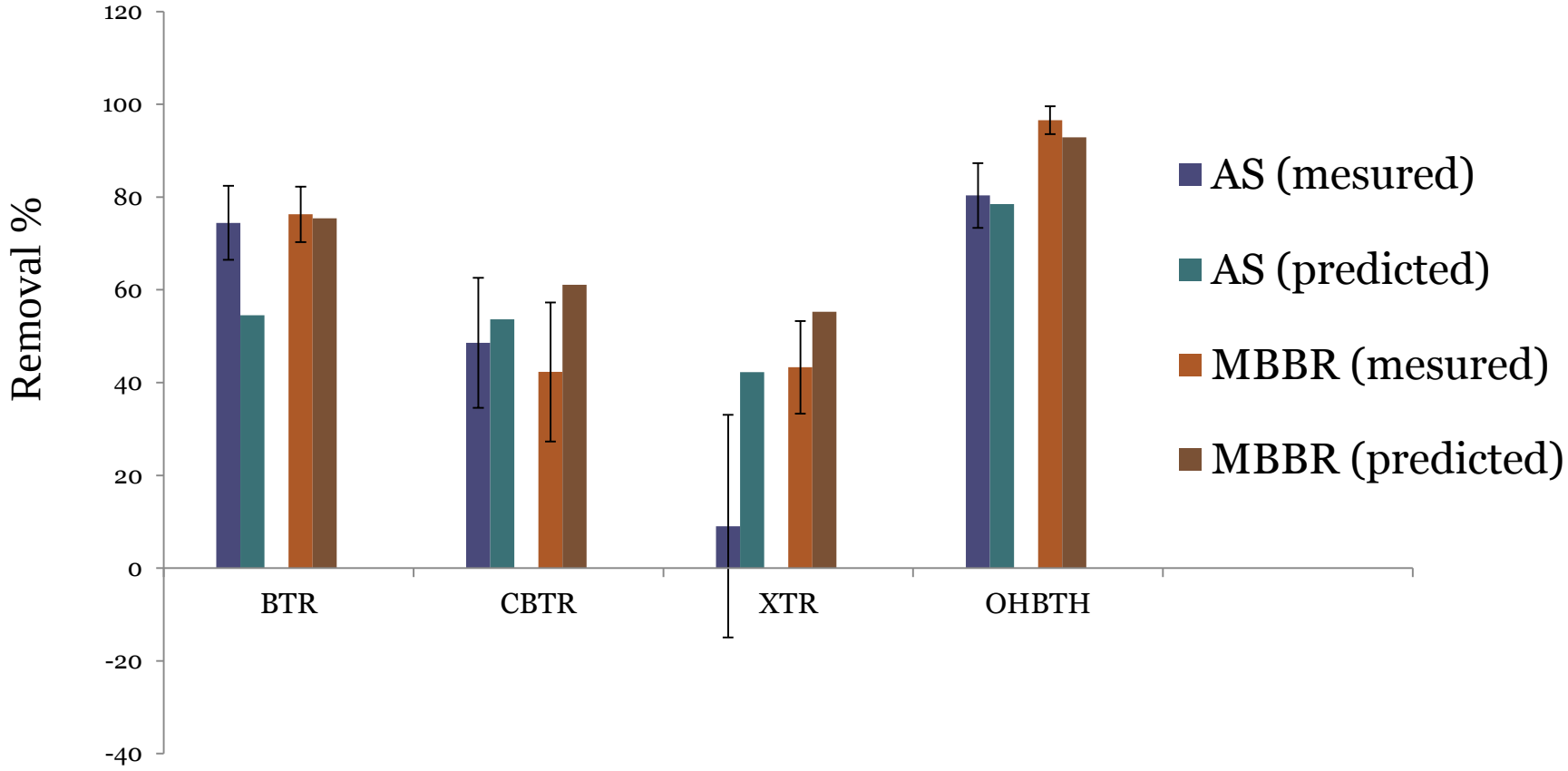
Specific Removal: µg of substance removed per gr of biomass per day

- Suspended Biomass
- Attached Biomass (BC1)
- Attached Biomass (BC2)

RESULTS: Evaluation of calculated kinetics

Kinetics calculated were used in order to predict removal in both systems

- Similar results were obtained with measured removal



CONCLUSIONS (batch experiments)

- All substances are degradated by both suspended and attached biomass
- Biodegradation constants (k_{bio}) were higher for the attached biomass in BC2
- The presence of easily degradable organic substances is clearly favoring the removal of target compounds (co-metabolism)

CONCLUSIONS (continuous flow experiments)

- All substances examined can be removed with biological treatment
- Percent removal of XTR and OHBTH was higher in the MBBR system
- Attached biomass has greater potency to remove target compounds compared to suspended biomass

FUNDING

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WATERMICROPOL
(www.aegean.gr/environment/watermicropol)

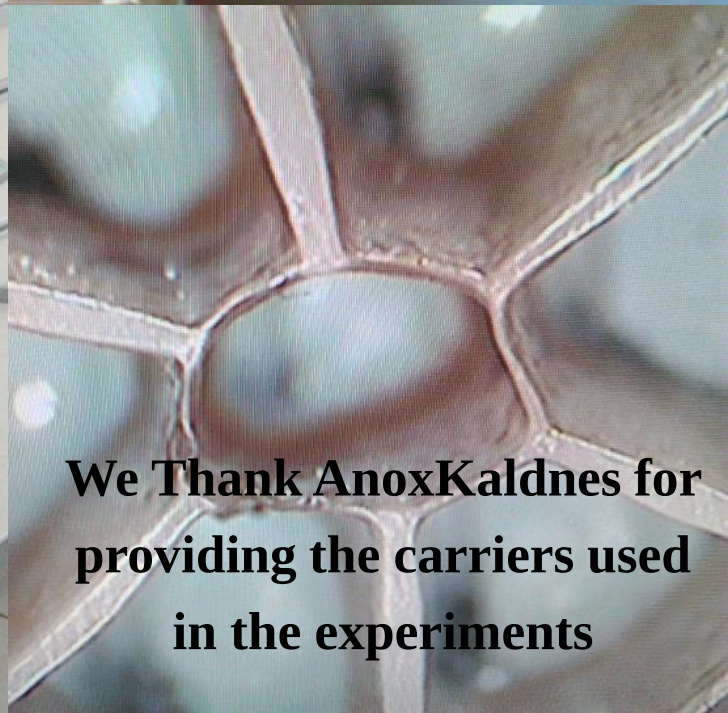
European Union
European Social Fund

OPERATIONAL PROGRAMME
EDUCATION AND LIFELONG LEARNING
investing in knowledge society
MINISTRY OF EDUCATION & RELIGIOUS AFFAIRS
MANAGING AUTHORITY

NSRF 2007-2013
programme for development
EUROPEAN SOCIAL FUND

Co- financed by Greece and the European Union

Thank you for your attention !!!



We Thank AnoxKaldnes for providing the carriers used in the experiments

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Water Micropol

Supplementary Material

REFERENCES

Mazioti A.A, Stasinakis A.S.,Gatidou G., Thomaidis N. S., Andersen H. R. Sorption and biodegradation of selected benzotriazoles and hydroxybenzothiazole in activated sludge and estimation of their fate during wastewater treatment (2015) Chemosphere,131, 117-123

Loos, R., Carvalho, R., António, D.C., Comero, S., Locoro, G., Tavazzi, S., Paracchini, B., Ghiani, M., Lettieri, T., Blaha, L., Jarosova, B., Voorspoels, S., Servaes, K., Haglund, P., Fick, J., Lindberg, R.H., Schwesig, D., Gawlik, B.M. (2013) EU-wide monitoring survey on emerging polar organic contaminants in wastewater treatment plant effluents .Water Research, 47, 6475-6487

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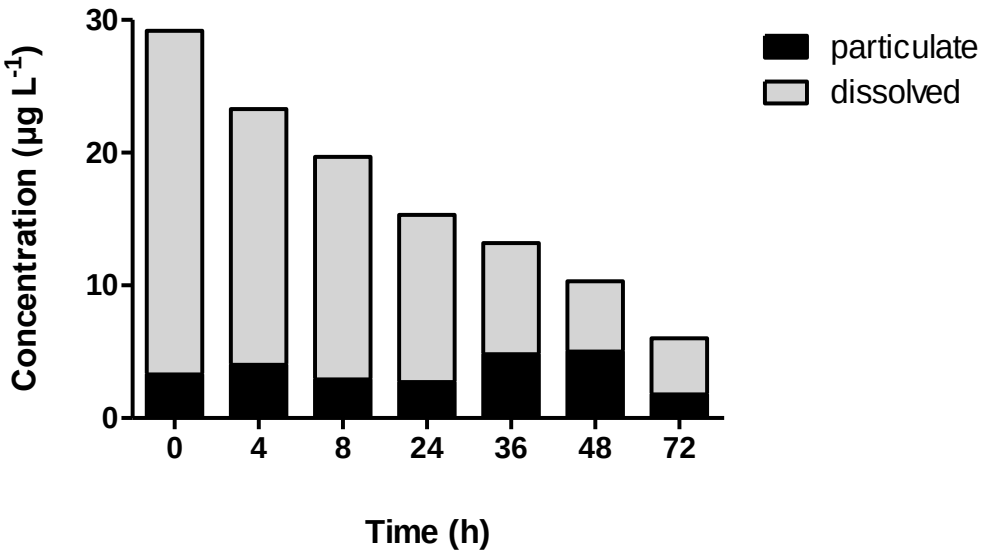
Biodegradation kinetics k_{bio} (L g_{ss}^{-1} d^{-1})

Compound	Easily degradable organic substances	k_{bio} (L g_{ss}^{-1} d^{-1})		
		AS	BC1	BC2
BTR	absence	0.22±0.08	0.44±0.13	2.25±2.28
	presence	0.41± 0.07	0.65±0.22	5.13±5.44
CBTR	absence	0.33±0.04	0.27±0.24	1.62±0.76
	presence	0.49±0.14	0.32±0.37	6.14±4.15
XTR	absence	0.39±0.16	0.15±0.09	1.09±0.30
	presence	0.52±0.24	0.32±0.40	1.34±1.16
OHBTH	absence	0.40±0.17	3.13±1.07	4.60±2.68
	presence	1.29±0.36	2.26±0.29	4.50±2.96

Distribution in dissolved/particulate phase



Compound	K_d (L Kg^{-1})	R^2
BTR	220 (± 9)	0.993
4TTR	170 (± 48)	0.870
5TTR	165 (± 14)	0.979
CBTR	242 (± 5)	0.998
XTR	87 (± 17)	0.930
OHBTH	147 (± 29)	0.893

Sorption Coefficients