Use of suspended and attached growth wastewater treatment systems for the removal of benzotriazoles and benzothiazoles

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A. Introduction

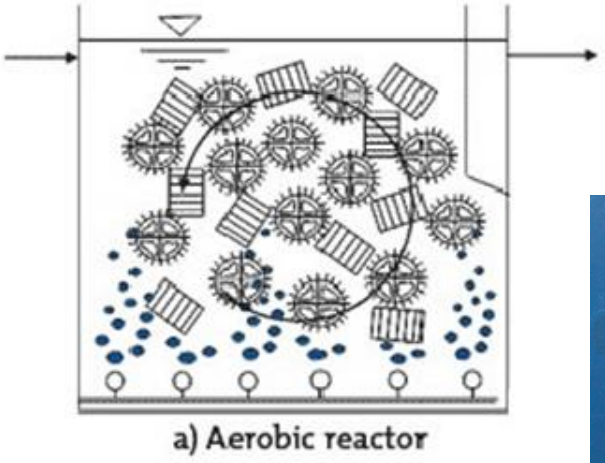
Organic micropollutants in the environment

- ✓ Low concentrations
- ✓ Many compounds – Many sources
- ✓ Partial removal in Waste Water Treatment Plants (WWTPs)

Biological Systems

A. Suspended growth systems
(Activated Sludge)

B. Attached growth systems
(Moving Bed Biofilm Reactors)

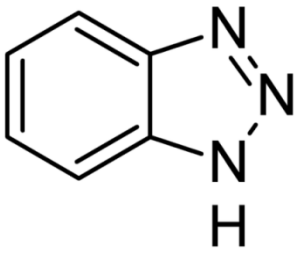


C. Hybrid systems
(Combination of A. and B.)

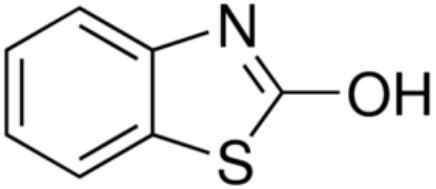
BTRs and BTHs

- **Uses:** Metal finishing industry (corrosion inhibitors), Brake fluids, cooling fluids, de-icing fluids, Dishwashing detergents, Tire and rubber manufacturing industries, Biocides and drugs

- **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

Occurrence and Removal

Based on recent researches:

- BTR's detection frequency in European surface waters, higher than 90 % Loos et al. (2009) Environ Pollution 157, 561-568
- BTR's median detected concentration in European treated wastewater, higher than 2500 ng L^{-1}

  Loos et al. (2013) Water Res 47, 6475-6487
- BTR's removal from WWTP in Australia, lower than 60 %

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

There is lack of information regarding BTRs and BTHs removal in lab-scale biological treatment systems.

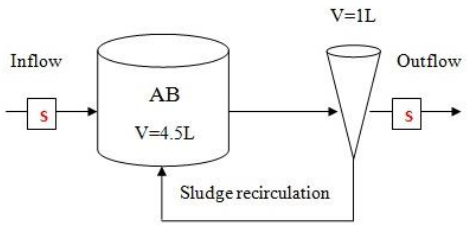
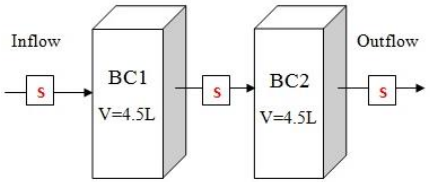
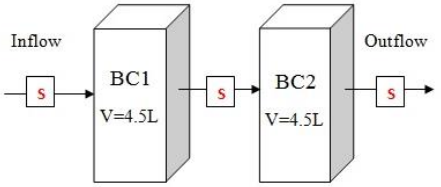
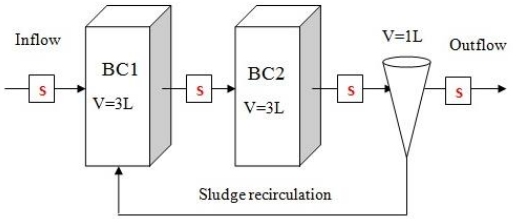
Objectives of the study

✓ To investigate the removal of 5 BTRs (**BTR, XTR, CBTR, 4TTR, 5TTR**) and **OHBTH** during biological treatment

✓To operate 4 different biological lab-scale continuous flow treatment systems for the comparison of target compounds removal

I. **Activated Sludge system (AS)**
II. **Moving Bed Biofilm Reactor system (MBBR-high)**
III. **Moving Bed Biofilm Reactor system (MBBR-low)**
IV. **Hybrid Moving Bed Biofilm Reactor system (HMBBR)**

B. Materials and Methods

	System's Name	HRT	Organic loading	SRT
	Activated Sludge (AS)	26.4h	0.25 kg /m^3 d	18d
	Moving Bed Biofilm Reactor high loaded (MBBR-high)	21.6h	0.77 kg /m^3 d	∞
	Moving Bed Biofilm Reactor low loaded (MBBR-low)	52.8h	0.30 kg /m^3 d	∞
	Hybrid Moving Bed Biofilm Reactor (HMBBR)	25h	0.75 kg /m^3 d	8d

Acclimatization phase: ***30-45 days (approx. $3\theta_c$)***

Raw municipal wastewater was provided. Monitoring of systems.

Experiment with micropollutants: ***10 days***

Target compounds were spiked, 12 dissolved phase samples were collected and analysed with SPE and HPLC.

Removal was calculated according to:

$$Removal\ (\%) = \frac{m_i - m_{out}}{M_{in}} \times 100$$

and:

$$Specific\ Removal\ Rate = \frac{m_i - m_{out}}{X \times V}$$

C. Results

Wastewater quality and micropollutants

pH	6.6 - 7.4
COD_{dis}	~300 mg /L
NH_4 -N	50 – 80 mg /L
NO_3 -N	1 – 9 mg /L
TSS	10 – 120 mg /L

Each Target compound (inflow concentration): 20 µg /L

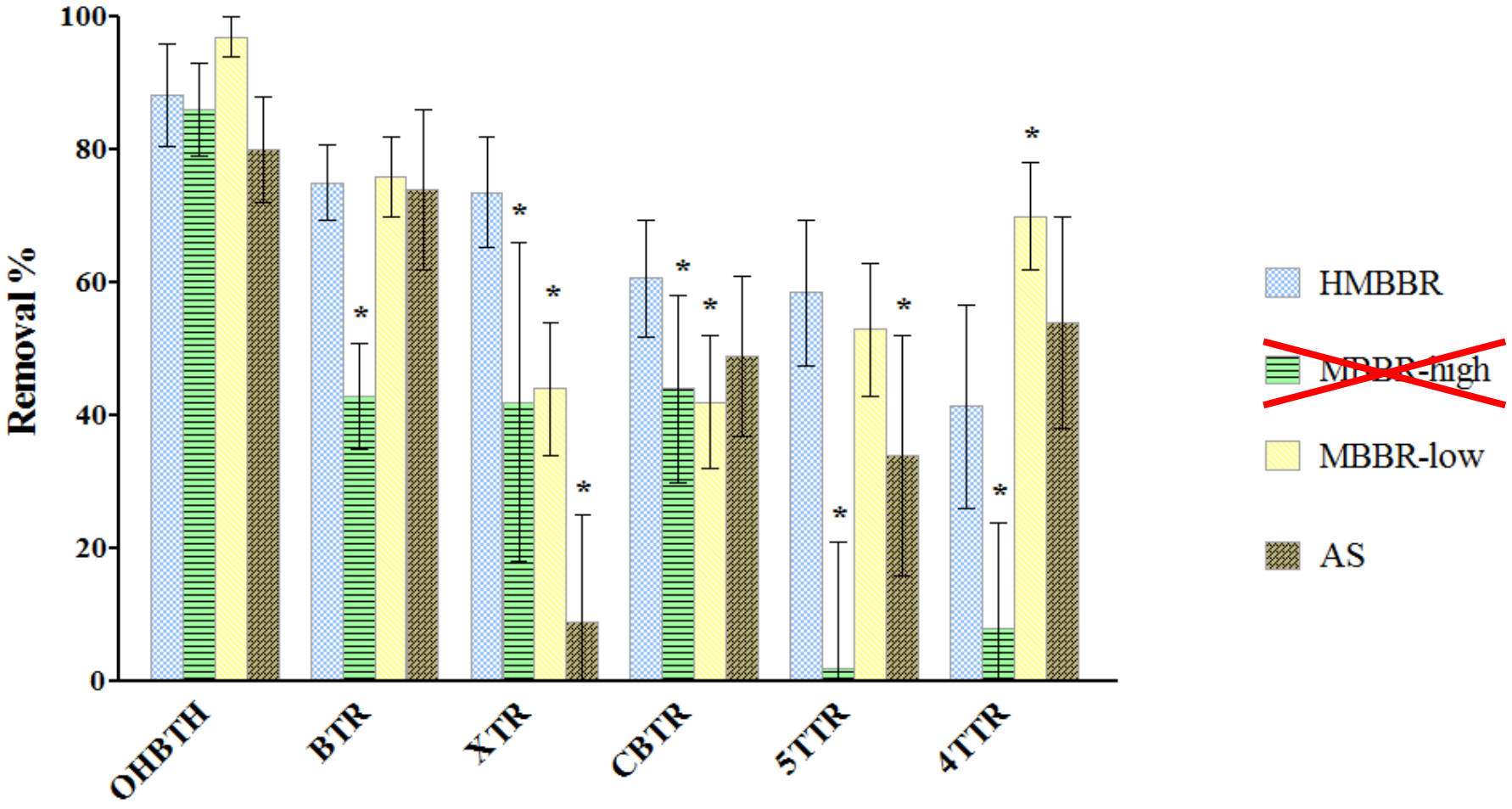
Wastewater Treatment Efficiency

	COD % removal			NH_4-N % removal		
	BC1	BC2	**Total**	BC1	BC2	**Total**
AS	90 (±7)	-	**90 (±7)**	93 (±12)	-	**93 (±12)**
MBBR high	72 (±11)	19 (±9)	**91 (±7)**	73 (±24)	22 (±15)	**95 (±7)**
MBBR low	81 (±13)	5 (±12)	**86 (±11)**	78 (±29)	15 (±21)	**93 (±13)**
HMBBR	80 (±16)	7 (±12)	**87 (±8)**	89 (±11)	9 (±6)	**98 (±2)**

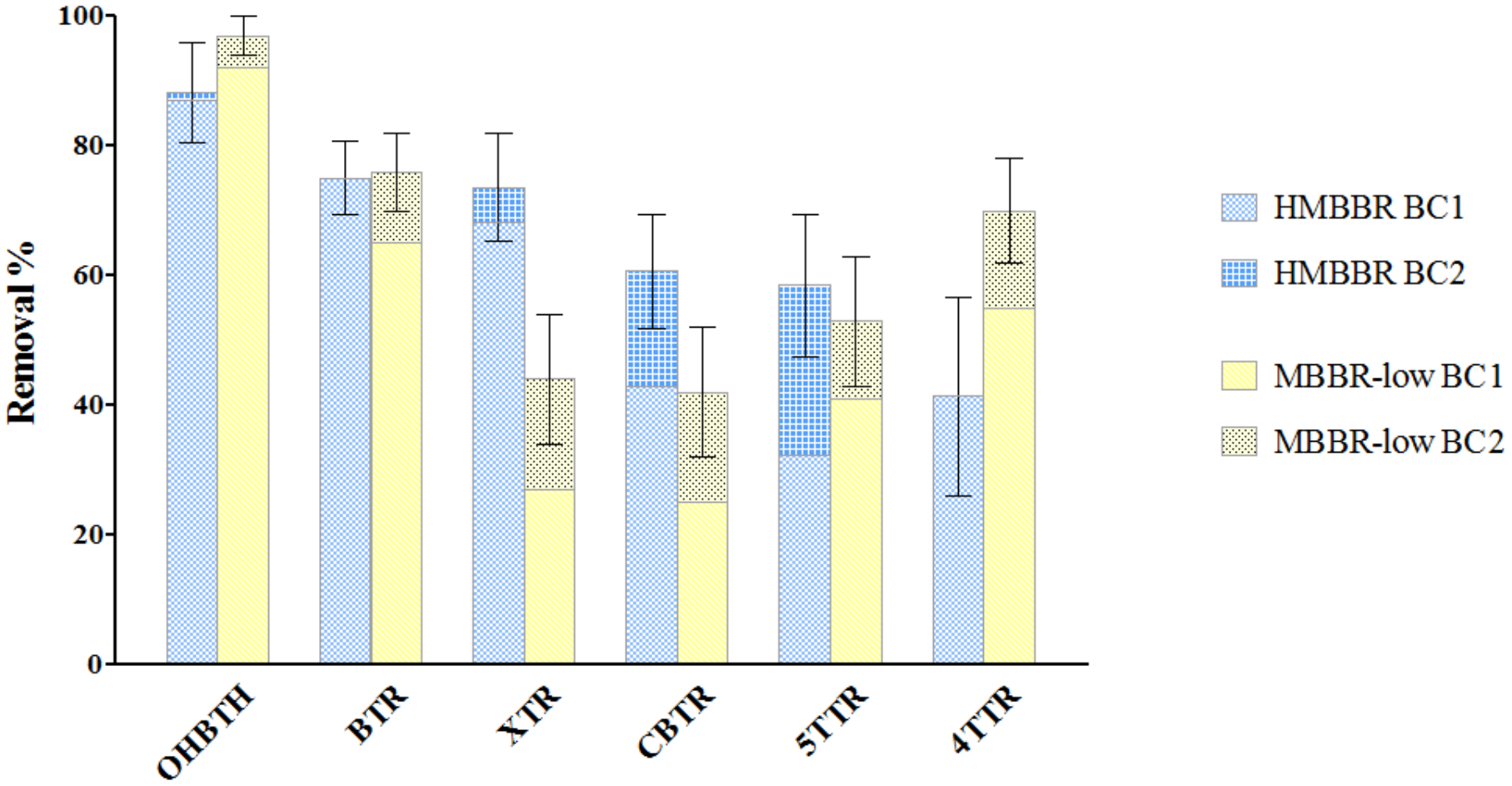
Biomass concentration

	Suspended (mg/L)		Attached (biofilm) (mg/L)		TOTAL (mg/L)	
	BC1	BC2	BC1	BC2	**BC1**	**BC2**
AS	2370 (±590)	-	-	-	**2370**	-
MBBR high	1079 (±715)	312 (±108)	138 (±68)	124 (±68)	**1217**	**436**
MBBR low	726	100	195 (±81)	131 (±89)	**921**	**231**
HMBBR	2914 (±510)	2687 (±524)	1023 (±171)	610 (±203)	**3937**	**3297**

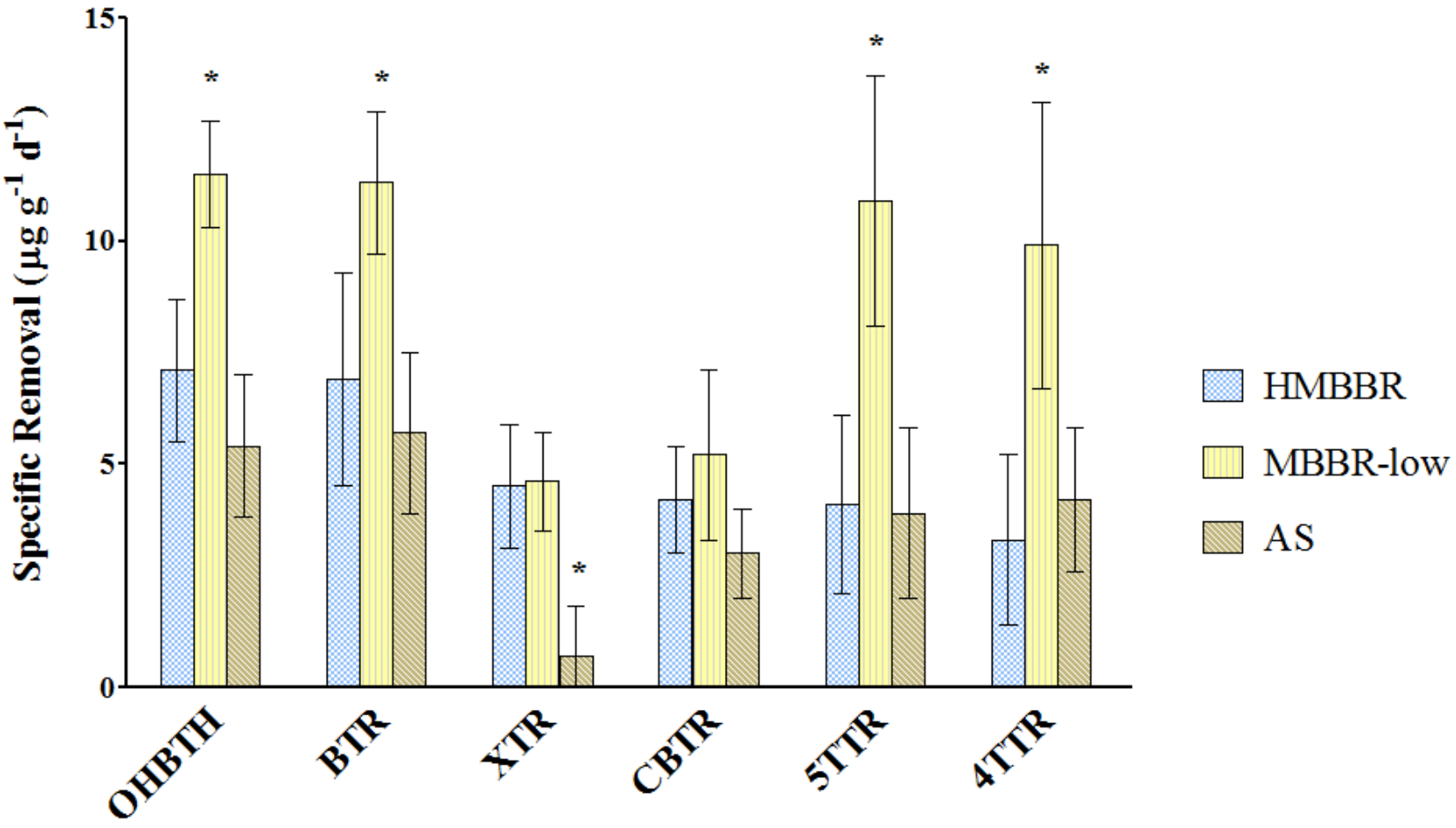
Are the systems able to remove target compounds?



Does a second reactor improves elimination?



Suspended and Attached biomass have the same removal capacity?



Comparison of each system's overall performance

	Target Compounds Removal (>70%)						Operational Parameters	
	OHBTH	BTR	XTR	CBTR	5TTR	4TTR	Organic Loading	HRT
AS	✓	✓	✓	✓	✓	✓	✓	✓
MBBR high	✓	✓	✓	✓	✓	✓	✓	✓
MBBR low	✓	✓	✓	✓	✓	✓	✓	✓
HMBBR	✓	✓	✓	✓	✓	✓	✓	✓

CONCLUSIONS

- All substances examined can be removed to some extent with biological treatment (both suspended and attached growth systems)
- Target compounds were eliminated with the following descending order regarding % removal
OHBTH>BTR>XTR>CBTR>5TTR>4TTR
- The addition of a second reactor in series can enhance the removal of more persistent compounds (CBTR, 5TTR, 4TTR)
- The MBBR systems seems to develop a biomass (biofilm) with high capacity to remove target micropollutants
- The HMBBR system was the more efficient, regarding micropollutants removal and operational parameters (low HRT and high organic loading)

Further information in two recently published articles:

Mazioti, A.A., Stasinakis, A.S., Pantazi Y., Andersen, H.R., 2015, **Biodegradation of benzotriazoles and hydroxy-benzothiazole in wastewater by activated sludge and moving bed biofilm reactor systems**. *Bioresource Technology* 192, 627-635.

Mazioti, A.A., Stasinakis, A.S., Psoma A.K., Thomaidis N.S., Andersen H.R., **Hybrid Moving Bed Biofilm Reactor for the biodegradation of benzotriazoles and hydroxy-benzothiazole in wastewater**, *Journal of Hazardous Materials* (In Press, doi:10.1016/j.jhazmat.2016.06.035).

We Thank AnoxKaldnes for providing the carriers used in the experiments

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Supplementary Material

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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

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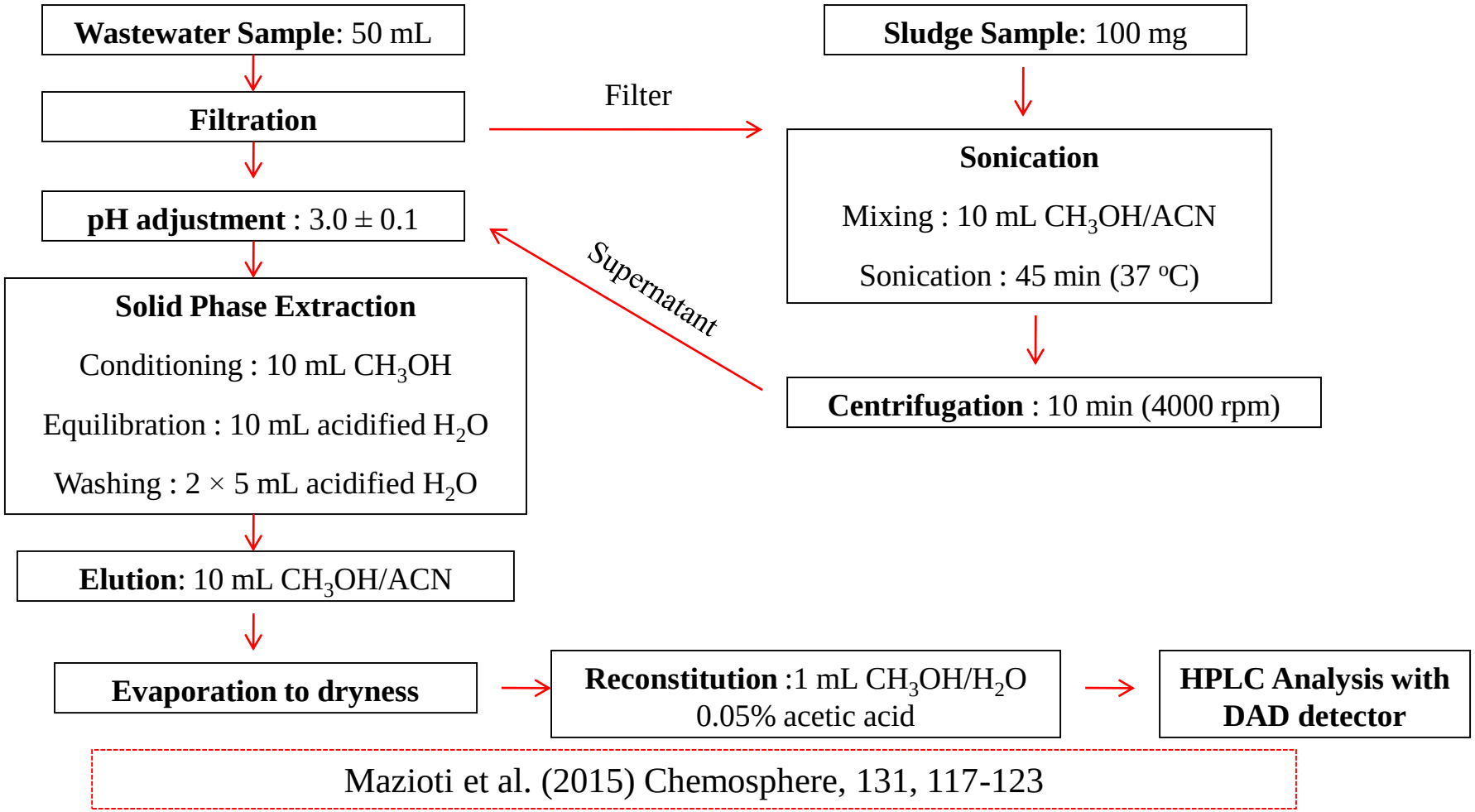
Loos, R., Carvalho, R., António, D.C., Comero, S., Locoro, G., Tavazzi, S., Paracchini, B., Ghiani, M., Lettieri, T., Blaha, L., Jarosova, B., Voorspoels, S., Servaes, K., Haglund, P., Fick, J., Lindberg, R.H., Schwesig, D., Gawlik, B.M. (2013) EU-wide monitoring survey on emerging polar organic contaminants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

Liu Y.-S., Ying G.-G., Shareef A., Kookana R.S. (2012). Occurrence and removal of benzotriazoles and ultraviolet filters in a municipal wastewater treatment plant. Environmental Pollution *165*, 225–232

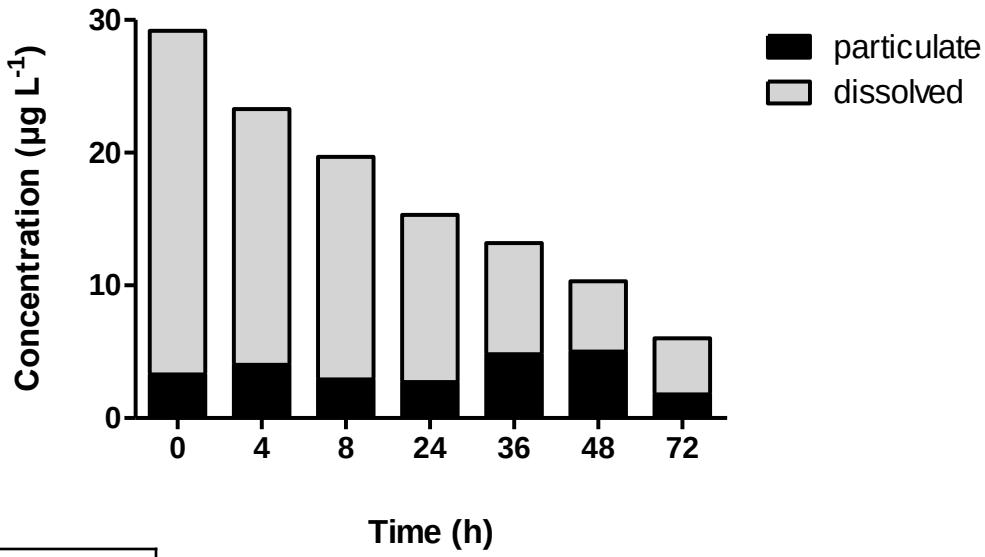
Loos, R., Gawlik, B.M., Locoro, G., Rimaviciute, E., Contini, S., Bidoglio, G. (2009) EU-wide survey of polar organic persistent pollutants in European river waters Environmental Pollution, 157, 561-568.

Analysis of BTRs/OHBTH



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

Distribution in dissolved/particulate phase



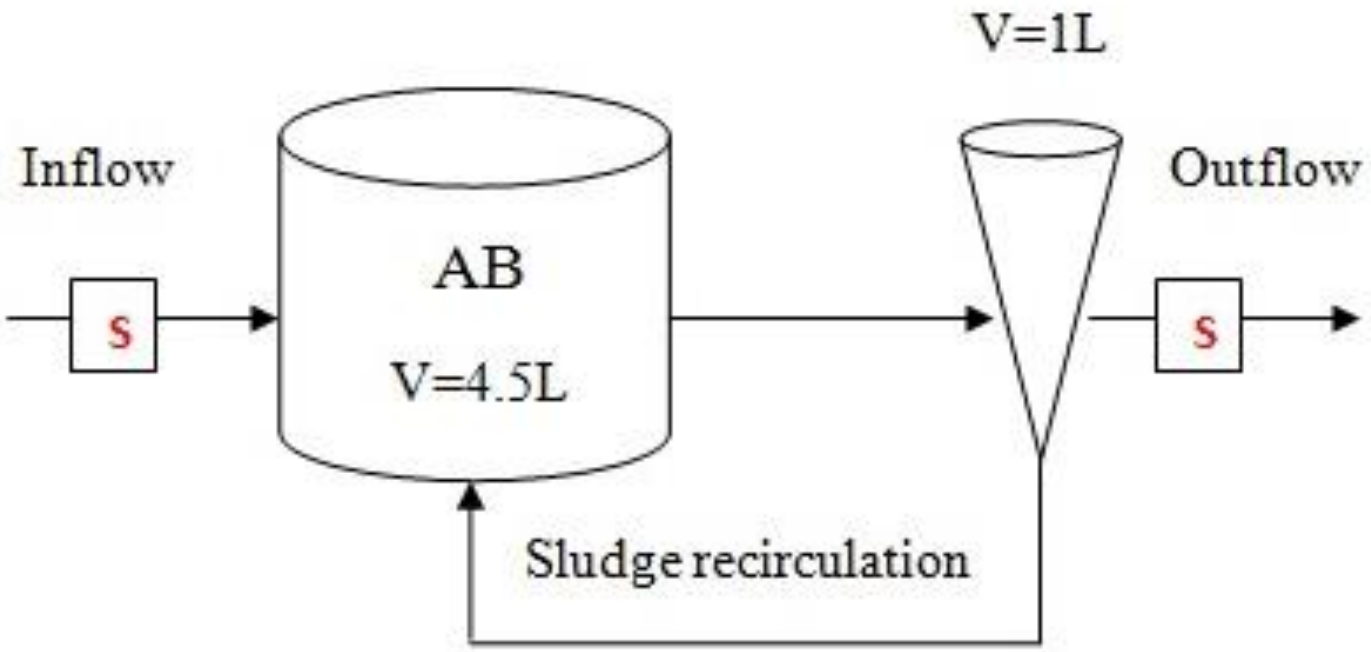
Compound	K_d (L Kg^{-1})	R^2
BTR	220 (± 9)	0.993
4TTR	170 (± 48)	0.870
5TTR	165 (± 14)	0.979
CBTR	242 (± 5)	0.998
XTR	87 (± 17)	0.930
OHBTH	147 (± 29)	0.893

Sorption Coefficients

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

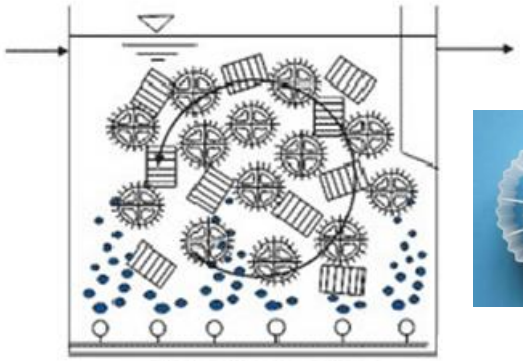
Activated Sludge (AS)

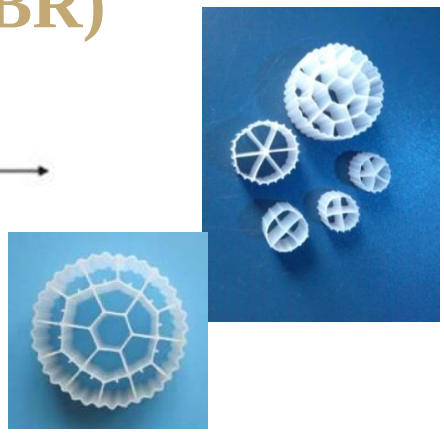
- ✓ Biomass is suspended and circulating in all parts of the bioreactor (due to aeration)

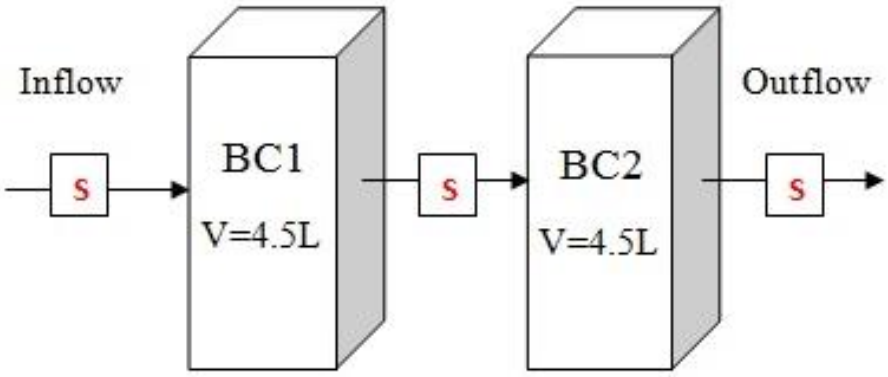


Moving Bed Biofilm Reactor (MBBR)

- ✓ Biomass is attached on carriers and forms a stable biofilm
- ✓ Carriers circulate in all parts of the reactor due to air supply





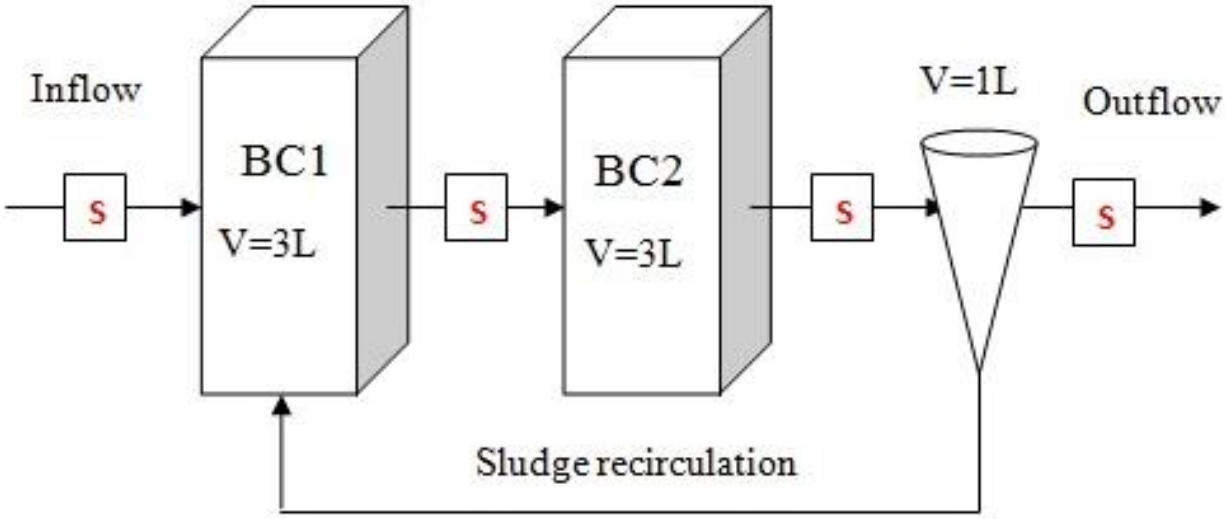


A. High Loading
HRT 10.8 ± 1.2 hours
(in each reactor)

B. Low Loading
HRT 26.4 ± 3.6 hours
(in each reactor)

Hybrid Moving Bed Biofilm Reactor (HMBBR)

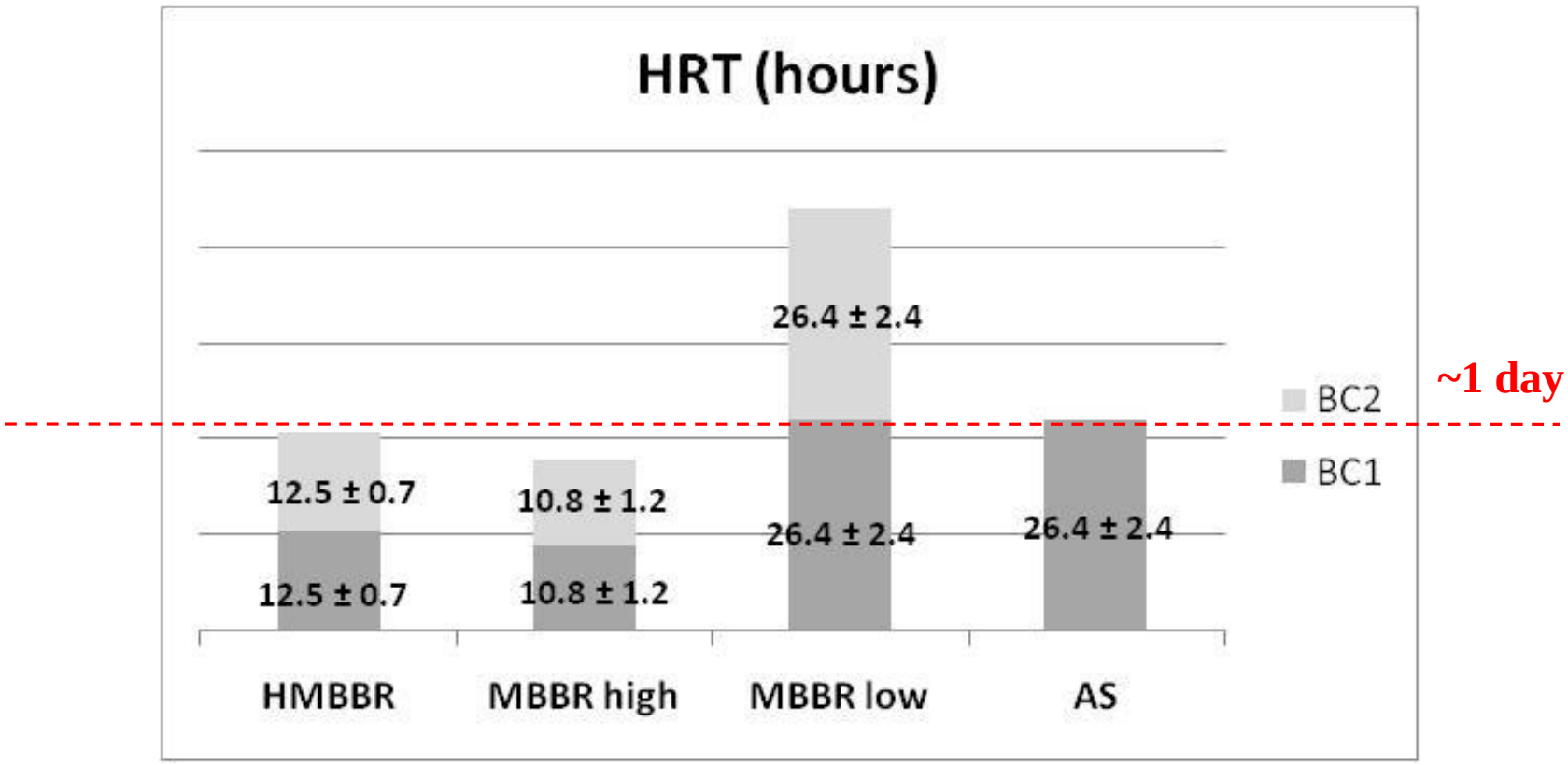
- ✓ Biomass is attached on carriers and forms a stable biofilm
- ✓ Carriers circulate in all parts of the reactor due to air supply
- ✓ Biomass also exists under suspension in high concentration, similar to those observed in AS systems



HRT 12.4 ± 0.6 hours (in each reactor)

SRT 8 days

Comparison of operational parameters



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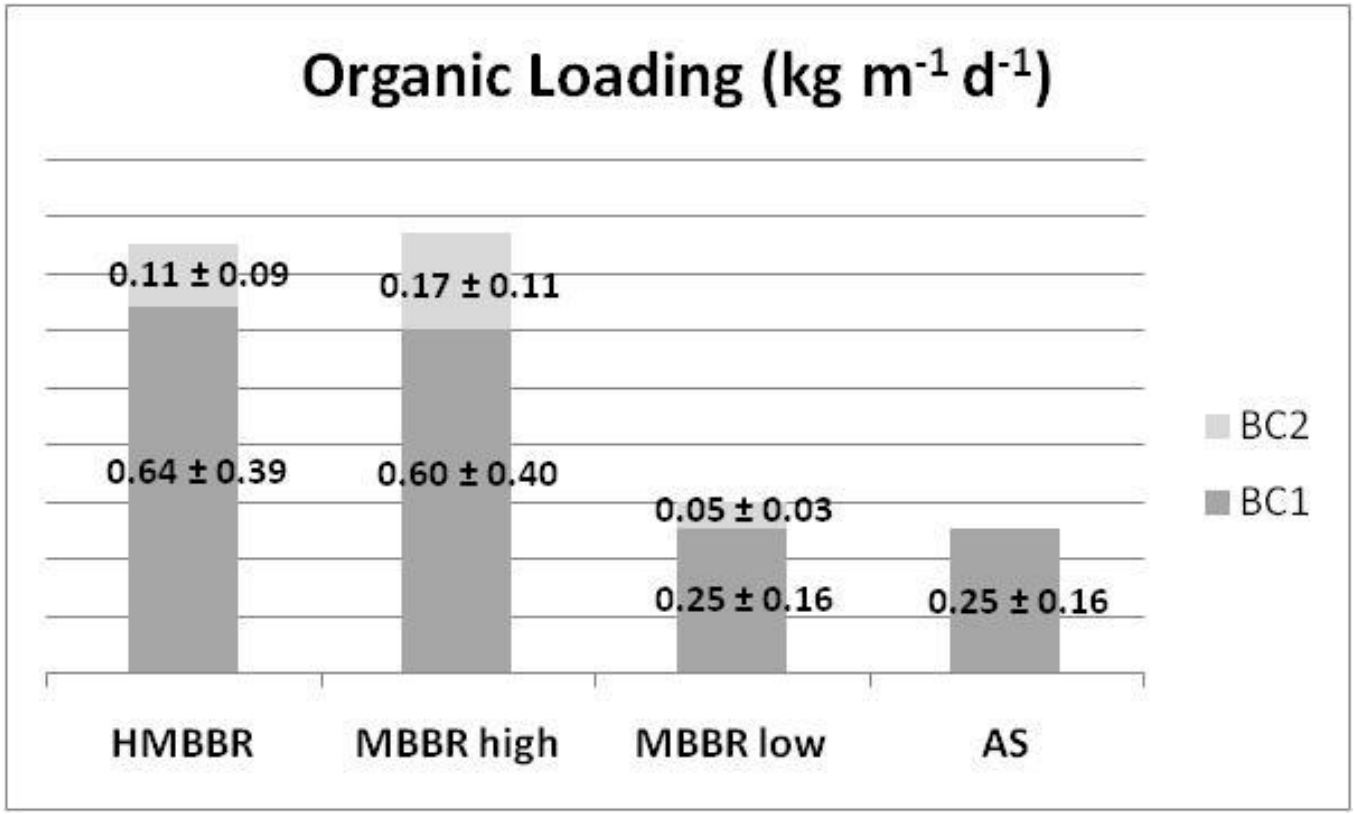

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