Removal of organic micropollutants by innovative processes: The SIAM system

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Organic micropollutants (OMPs)

- **Heterogeneous** group
- Largely consumed in modern societies
- Concentration in wastewater: **ppb-ppt**
- **Bioactive compounds**
- Effects: **bioaccumulation, toxic, estrogenic and mutagenic**

Pharmaceuticals | Endocrine-Disrupting Compounds | Personal Care Products | Pesticides | Flame retardants | Disinfectants, antiseptics | Linear Alkylbenzene Sulfonates

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Concern about OMPs

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EU legislation

Directives	Priority substances under the Water Framework Directive
Water Framework Directive (2000/60/EC) WFD	▪ Define "Strategies against pollution of water"
Directive on Environmental Quality Standards (2008/105/EC) EQSD	▪ Limits on concentrations of the 33 **priority substances** ▪ **Diclofenac, estradiol and ethinylestradiol** should be included in the first watch list of substances for which Union-wide monitoring data should be gathered.
Directive 2013/39/EU	▪ 12 substances added to the WFD List of Priority Substances. ▪ The first watch list shall contain maximum of 10 substances
Commission implementing decision (EU) 2015/495	▪ The watch list of substances include **4 pharmaceuticals** (**DCF** and **macrolides ERY, AZI, CLA**) and **3 hormones** (**E1, E2, EE2**)

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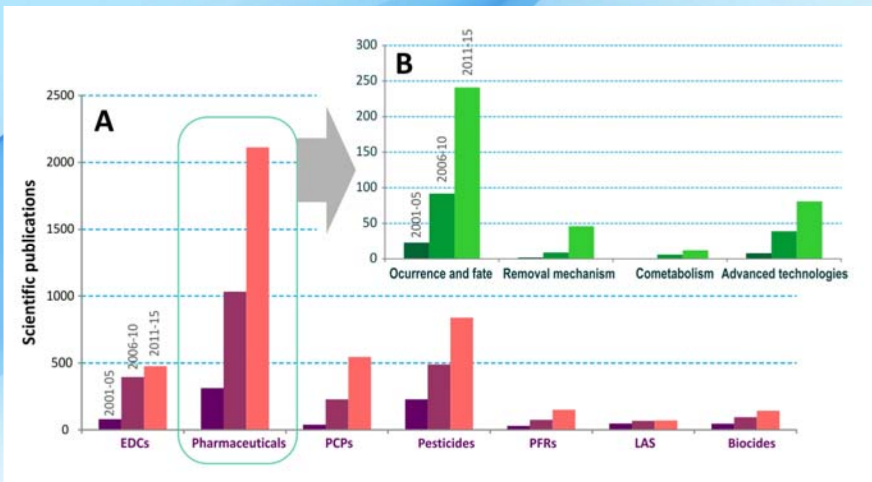
State of the art of OMPs (bibliometrics)



Publication trends in OMPS in WWTPs (reporting period: 2000-2015)

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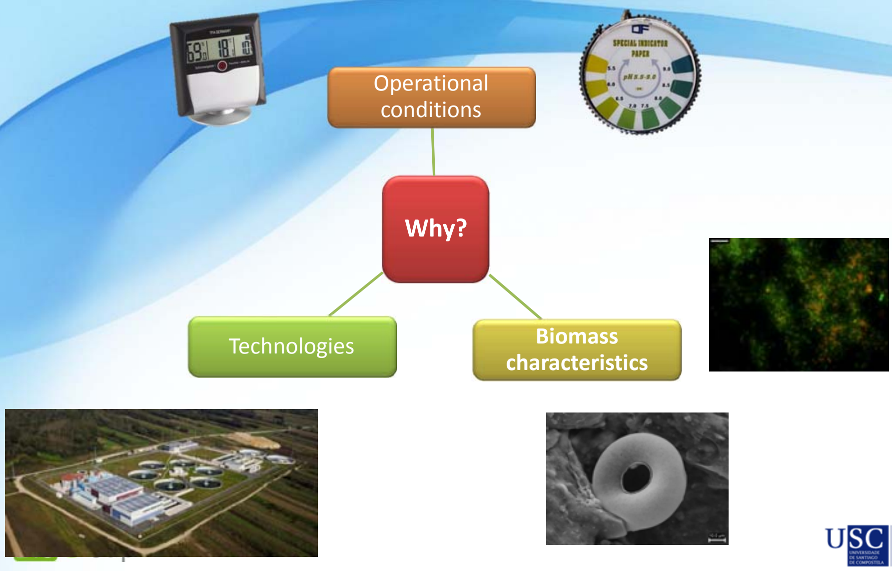
Significant variability for OMPs removal in WWTPs



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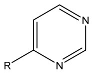
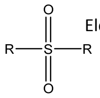
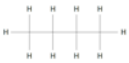
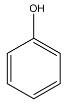
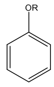
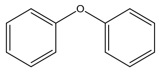
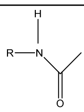
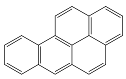
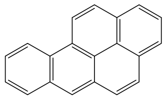
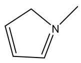
Different OMP chemical structure

	Anaerobic conditions	Aerobic conditions
Biodegradable	 Substituted pirimidine;  Electro-drawing groups;  Straight-chain hydrocarbons;  Hydroxyl group	 Straight-chain hydrocarbons;  Aromatic ether;  Aryl ether
Recalcitrant	 Amide group; R—NH$_2$ Amine group; R—Cl Chlorine groups;  Fused aromatic rings	R—Cl Chlorine groups;  Fused aromatic rings;  Heterocyclic N aromatic rings

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Fernandez-Fontaina et al., 2016; Musson et al., 2010; Field, 2002; Knackmuss, 1996; Adrian et al., 1994; Boethling et al., 1994

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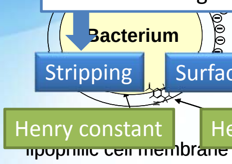
OMPs removal mechanisms

Sorption
transfer to the solid phase

- Adsorption (electrostatic interactions) — Acid dissociation constant
- Absorption (hydrophilic interactions) — Octanol water coefficient

Volatilization
transfer to the gaseous phase



- Stripping — Henry constant
- Surface volatilization — Henry constant

Biotransformation
Chemical reactions with bacteria

- Metabolism
- Cometabolism

$\Delta C/\Delta t$ ($\mu g\ g_{TSS}\ d$ … H; q ($L_{air}\ L_{inf}^{-1}$); C_{eff} (mg L^{-1})

$$F_{biod} = k_{biol} \cdot VSS \cdot C_{eff} \cdot V$$

k_{biol} (L g_{VSS}^{-1} d^{-1}); VSS (g_{VSS} L^{-1}); V (L); C_{eff} (mg L^{-1})

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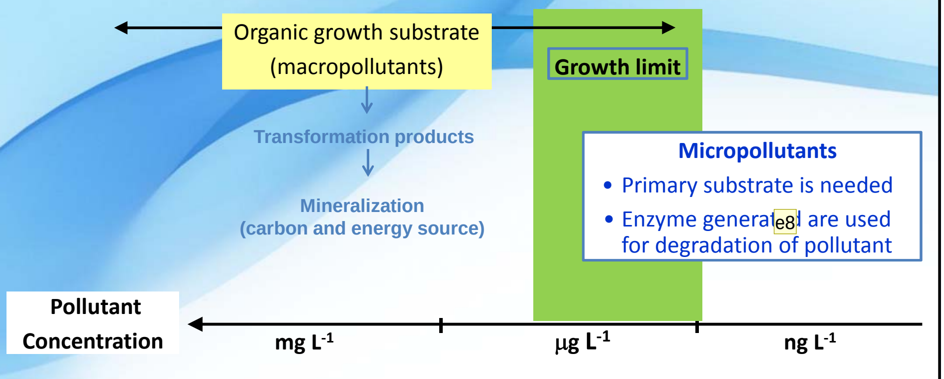
Metabolism-cometabolism



- **Metabolism:** the primary carbon or nutrients source for growth and/or energy source
- **Cometabolism :** the presence of a primary substrate is necessary for inducing the enzymes for micropollutant removal

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The role of redox potential: anaerobic and aerobic. Application to the treatment of urban wastewaters

1) The AnHMBR system

Alvarino, T., Suarez, S., Lema, J.M., Omil, F., 2014. Understanding the removal mechanisms of PPCPs and the influence of main technological parameters in anaerobic UASB and aerobic CAS reactors. *Journal of Hazardous Materials* 278, 506-513.

Alvarino, T., Suarez, S., Garrido, M., Lema, J.M., Omil, F., 2016. A UASB reactor coupled to a hybrid aerobic MBR as innovative plant configuration to enhance the removal of organic micropollutants. *Chemosphere* 144, 452-458.

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AnHMBR process

Anaerobic treatment + Aerobic treatment + Membrane filtration

Anaerobic treatment
- ✓ Biogas production
- ✓ Energy savings
- ✓ Low sludge production

Aerobic treatment
- ✓ High effluent quality
- ✓ High membrane fluxes

Membrane filtration
- ✓ Total retention of microorganisms
- ✓ Elevated quality of effluent (reuse)

Reuse: Agriculture, Silviculture, Gardening

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Reactors at lab-scale

Anaerobic reactor

- UASB reactor
- Volume 4.5 L
- Inoculum 40 g_{VSS} L^{-1}
- Influent Conc.: 1200 mg COD L^{-1}
- COD load: 1200-2400 mg L^{-1} d^{-1}

Aerobic reactor

- Conventional activated sludge
- Volume 2 L
- Inoculum 2 g_{VSS} L^{-1}
- Influent Conc.: 130 mg COD L^{-1}, 40 mg $N\text{-}NH_4^+$ L^{-1}
- COD load: 130-260 mg L^{-1} d^{-1}

Reactor	1º period		2º period		3º period		4º period	
	HRT	v_{up}	*HRT*	v_{up}	*HRT*	v_{up}	*HRT*	v_{up}
UASB	1 d	0.1 m h^{-1}	0.5 d	0.1 m h^{-1}	1 d	0.5 m h^{-1}	0.5 d	0.5 m h^{-1}
CAS	1 d	-	1 d	-	0.75 d	-	0.5 d	-

v_{up}: upward velocity

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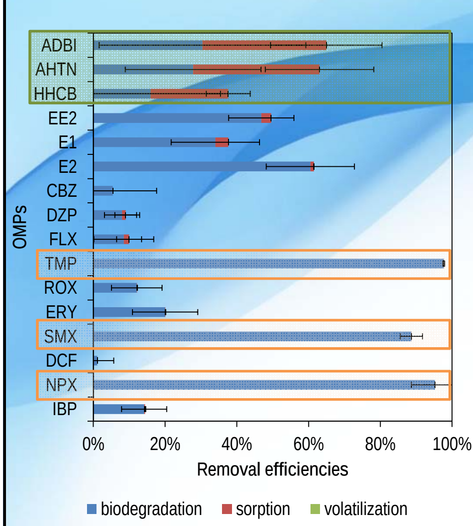
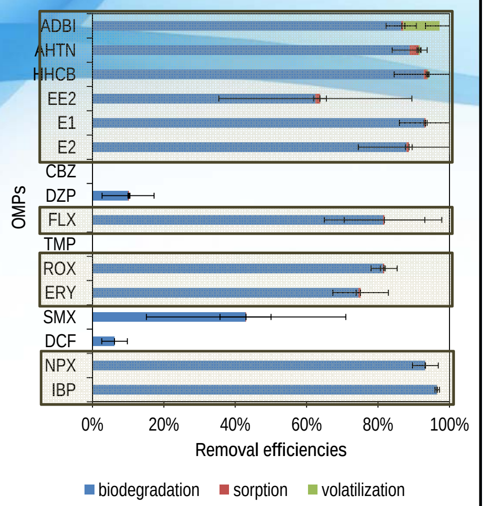
Removal mechanism in UASB and CAS units



UASB reactor



CAS unit

HRT= 1 day

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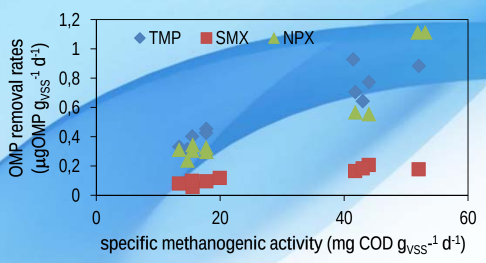
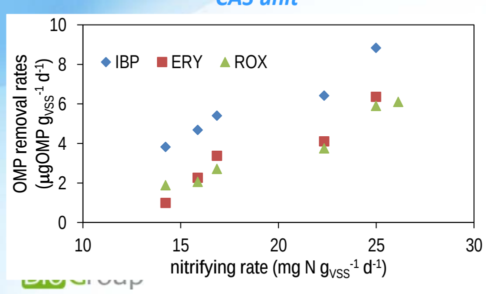
Biotransformation

UASB reactor

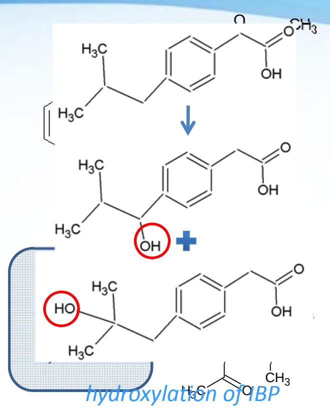


CAS unit



Cometabolic (AOB bacteria)

Anaerobic conditions



Trimethoprim (TMP)

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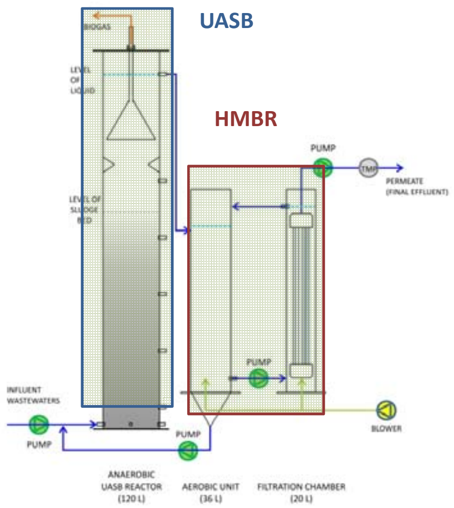
Anaerobic hybrid membrane bioreactor



patent ES 2 385 002 B2

- 3 stage reactor:
  - Upflow anaerobic sludge blanket 120 L
  - Hybrid aerobic chamber 36 L
  - Membrane chamber 20 L
- Influent COD concentration: 1200 mg L^{-1}
- Influent organic load: 1700 mg COD L^{-1} d^{-1}
- HRT: 13 h (UASB). 4 h (HMBR)
- VSS: 40 g L^{-1} (UASB); 1-5 g L^{-1} (HMBR)
- Membrane surface area: 0.9 m^2
- Membrane pore size: 0.04 mm

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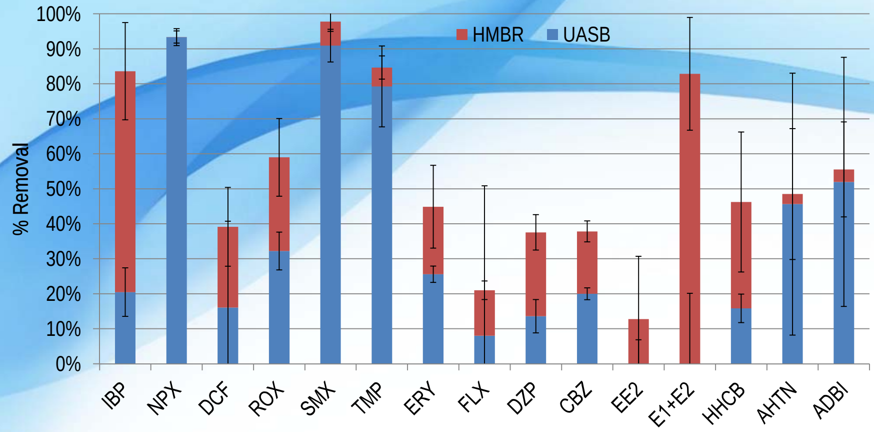
Anaerobic hybrid membrane bioreactor



Lower removals under aerobic conditions → Low COD concentration inlet / **cometabolism** / Lower nitrification

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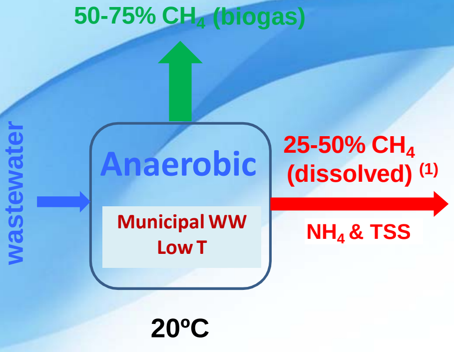
The role of redox potential: anaerobic and aerobic. Application to the treatment of urban wastewaters

2) The SIAM system

Introduction: UASB drawbacks

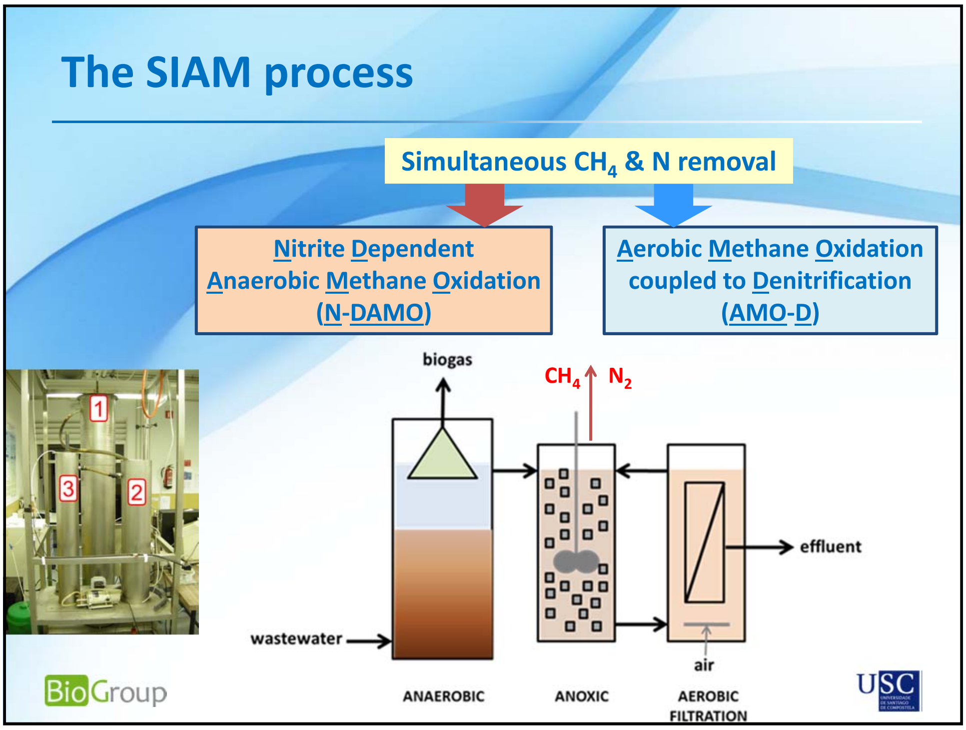


CH_4 GWP: 28 times higher than CO_2

METHANE: STRONG GREENHOUSE GAS

Eutrophication problems

(1) Noyola, A. Morgan, J.M., Lopez, J.E. (2006). Reviews in Environmental Science and Bio-Technology 5, 93-114. Souza, C., Chernicharo, C., Aquino, S. (2011). Water Sci. Technol 64, 2259-2264.


The SIAM process
Simultaneous CH_4 & N removal
Nitrite Dependent Anaerobic Methane Oxidation (N-DAMO)
Aerobic Methane Oxidation coupled to Denitrification (AMO-D)
biogas
CH_4 N_2
effluent
wastewater
air
ANAEROBIC
ANOXIC
AEROBIC FILTRATION
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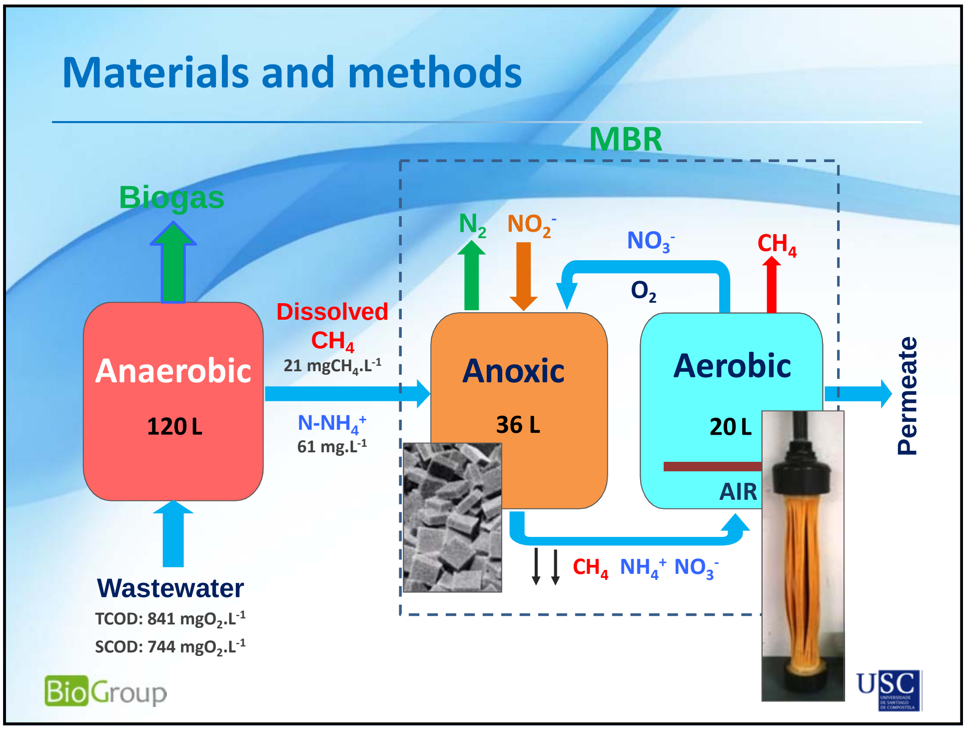
Materials and methods
MBR
Biogas
N_2 NO_2^-
NO_3^-
O_2
CH_4
Dissolved CH_4
21 $mgCH_4.L^{-1}$
Anaerobic
120 L
N-NH_4^+
61 $mg.L^{-1}$
Anoxic
36 L
Aerobic
20 L
AIR
Permeate
CH_4 NH_4^+ NO_3^-
Wastewater
TCOD: 841 $mgO_2.L^{-1}$
SCOD: 744 $mgO_2.L^{-1}$
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Biological methane oxidation coupled to denitrification

- **Aerobic pathway (methanotrophs/heterotrophs)**

  $5CH_4 + 5O_2 + 4NO_3^- + 4H^+ \rightarrow 2N_2 + 12H_2O + 5CO_2$

  1.3 g CH_4/g N (5.7 g-COD/g-N)

  At low [O_2] reverse methanogenesis and HAc production

- **Anaerobic pathway (N-DAMO bacteria)**

  $3CH_4 + 8NO_2^- + 8H^+ \rightarrow 3CO_2 + 4N_2 + 14H_2O$

  0.43 g CH_4/g N (1.71 g-COD/g-N)

- **Anaerobic pathway (N-DAMO arquea & bacteria)**

  $2CH_4 + 8NO_3^- \rightarrow 2CO_2 + 8NO_2^- + 4H_2O$ (**Arquea**)

  $3CH_4 + 8NO_2^- + 8H^+ \rightarrow 3CO_2 + 4N_2 + 14H_2O$ (**Bacteria**)

  0.71 g CH_4/g N (2.86 g-COD/g-N)

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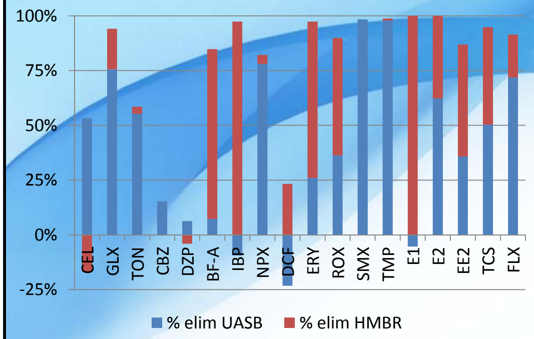
OMPs removal (SIAM)



SIAM

Nitrification: **99%**

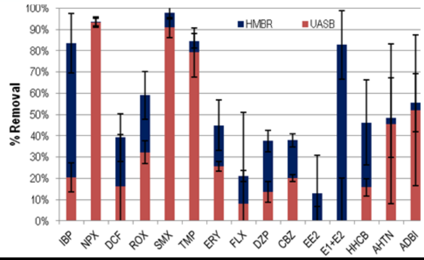
OMPs removal:

- **Anaerobic**: NPX, SMX, TMP
- **HMBR**: BF-A, IBP, E1
- **Both units**: GLX, E2, EE2, ERY, ROX, TCS, FLX

Increased removal due to nitrification: IBP, ERY, ROX, hormones

High improvement of results

AnHMBR Nitrification: **60%**



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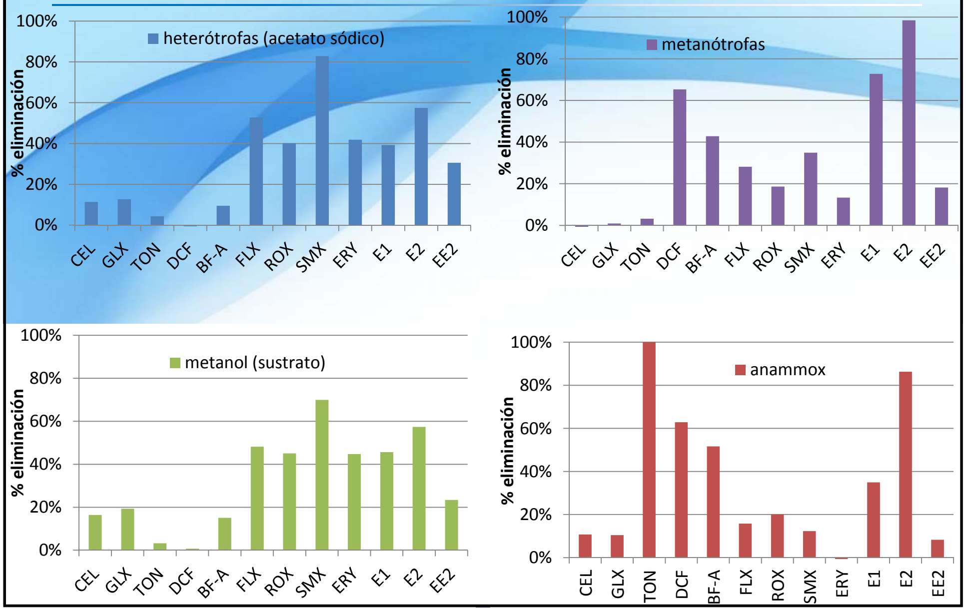
Influence of primary substrate

- **Kinetic assays** to determine biological kinetic coefficients of OMPs removal
- Influence of the type of primary substrate in OMPs removal
- Influence of the concentration of primary substrate in OMPs removal

Primary substrates:

- Nitrite + Methane (*methanotrophs*)
- Nitrite + Sodium Acetate (*heterotrophs*)
- Nitrite + Amonia (*anammox*)
- Nitrite + Methanol (*methanotrophs + anammox*)

Cometabolism: effect of primary substrate



2014-2018

Life SIAMEC project strategy (LIFE+ programme)

- Integrated anaerobic systems for wastewater reclamation at ambient temperature in European climates
  - To Change of mainstream wastewater treatment concept from resource consuming processes into more sustainable treatment schemes
  - Anaerobic treatment of municipal and industrial wastewater
  - Reduce Energy consumption and Sludge production in WWTP
  - To produce reclaimed wastewater to be reused

Validation at pilot scale (Murcia, Spain)

http://www.life-siamec.eu/

Conclusions

- ✓ OMPs biotransformation was dependent on the **nitrifying activity,** the **methanogenic activity** and the **heterotrophic activity**
- ✓ Most OMPs were more **easily biotransformed under aerobic conditions**. However, the **anaerobic stage** is crucial for OMPs biotransformation prone to be removed by reducing conditions
- ✓ Sorption was only significant in the anaerobic reactors for the removal of **lipophilic OMPs.** The increase of **upward velocity** and **HRT** improved sorption.
- ✓ **Biological processes need to be optimized** not only in terms of macropollutants, but also **considering specifically the fate of OMPs**, since the removal of these trace compounds are strongly affected by the main metabolic activities.

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European Commission

European Union
LIFE14 ENV/ES/000849

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Thank you for your attention!

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