Biological technologies for the removal of VOCs, odours and greenhouse gases

Prof. Francisco Omil

University of Santiago de Compostela

Spain

EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

Water_2020 - *Conceiving Wastewater Treatment in 2020 - Action ES1202*

BioGroup

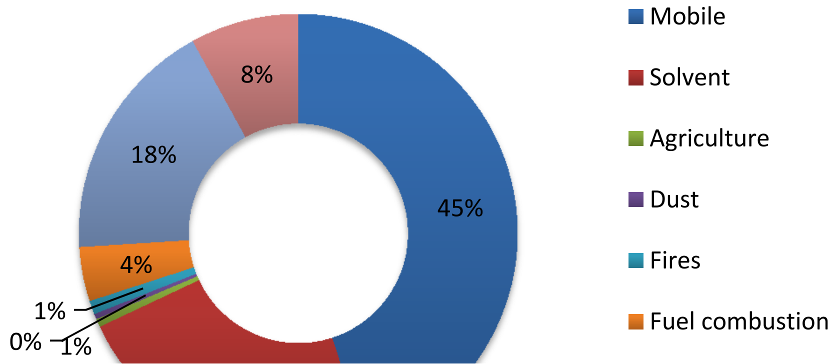
ain current challenges for air pollution

- Particulate matter
- Carbon monoxide and CO_2
- Volatile Inorganic Compounds (VICs)
  - Sulphur: SO_2, SO_3, H_2SO_4, H_2S, R-SH
  - Nitrogen: NO_x, NH_3, R-NH_2
- Volatile Organic compounds: VOCs
  - Ketones, aldehydes, acids, etc.
- Odours
  - H2S, mercaptanes, VFAs, etc.
- Non CO_2 – Greenhouse Gases (GHGs)

...atile Organic Compounds (VOCs)

- Wide range of organic chemicals
  - Non methane-hydrocarbons (NMHC), oxygenated NMHC, BTX
- Types of emissions
  - Natural (largest, diffuse)
  - Anthropogenic (concentrated, impact)
- Anthropogenic emissions 2011
  - US: 12.5 million tons
  - EU-27: 7.1 million tons
- Gothenburg protocol (1999)
  - 50% Reduction by 2020

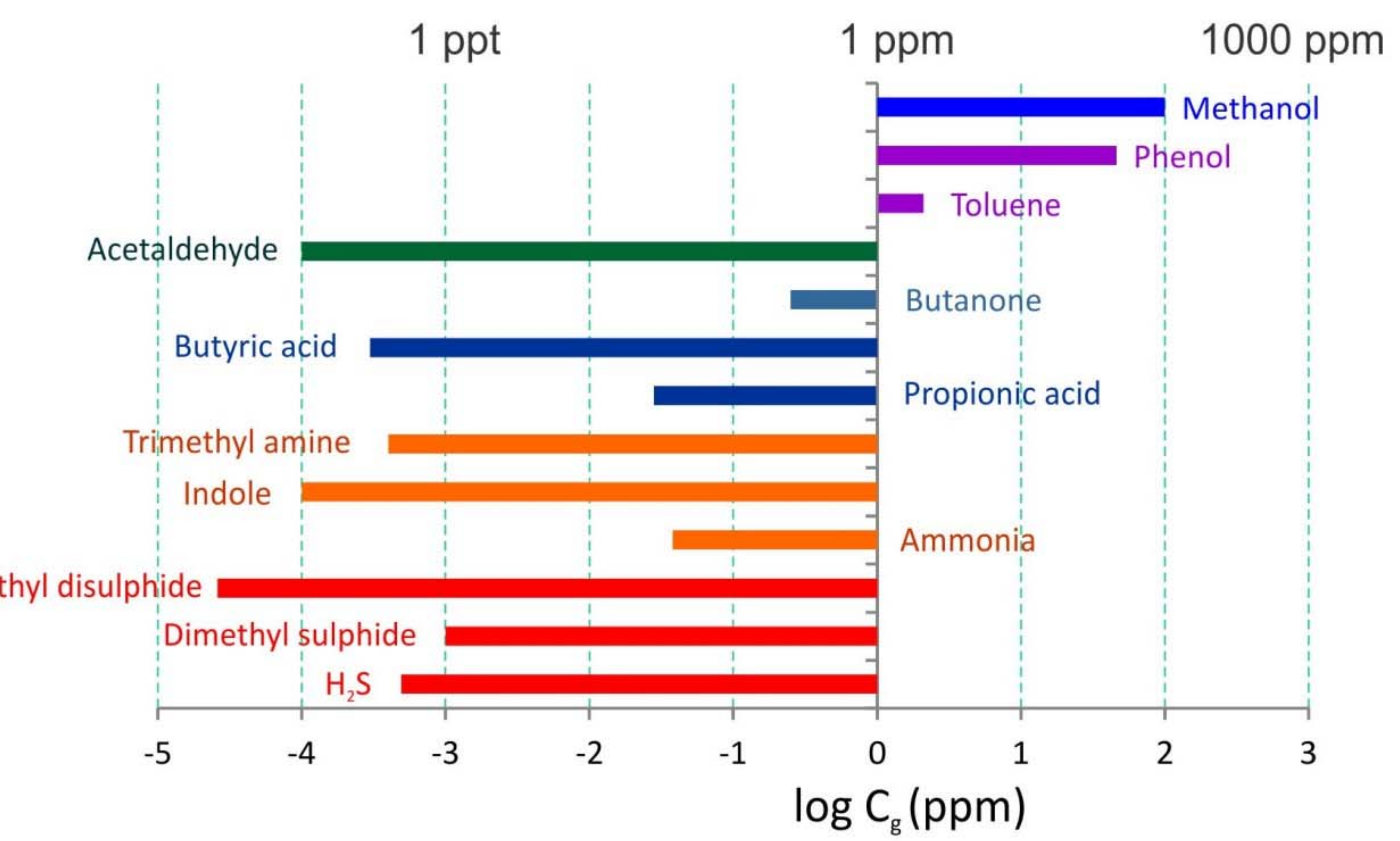
US total VOC emissions 2008 (EPA)



ours

- Odorants
  - Chemicals that stimulate the olfactory sense
- Characterisation
  - Threshold, intensity, character, and hedonic tone.
  - Threshold: minimum concentration of odorant stimulus necessary for perception
- Types of odorants
  - Wide range of VOCs and VICs
  - Complex mixtures at trace level conc. (ppm, ppb)
- Sources
  - Industry, agriculture, food production, waste management, etc.
- Complaints and Policies
  - 13-20% people affected in EU
  - New regulations are being implemented in many countries

Threshold values



compounds emitted by environmental plants

o et al., 2013)	WWTPs	Landfills	Composting	SW Incinerators
lphur ompounds	H_2S Mercaptans	H_2S Mercaptans	H_2S Mercaptans	H_2S Mercaptans
trogen ompounds	NH_3 Amines Indole	NH_3 Amines	NH_3 Amines Cadaverine Putrescine	NH_3
FAs dehydes etones	VFAs Aldehydes Ketones	VFAs Aldehydes Ketones	VFAs Aldehydes	VFAs Acetone
cohols		Alcohols	Ethanol	
romatic HCs		Ar-HCs		Toluene

Odor measurement

UNE-EN 13725
Reference gas: n-butanol

$1\ OU_E = 123\ \mu g\ n\text{-}BuOH/m^3$

se study: Full scale bioreactors treating 1200 m3/h
aste gases from anaerobic WWTP in a brewery

(van Groenestijn et al., 2005)

		Inlet	Outlet	Removal		
H_2S	ppm	800	1.7	99.8%		

Regulations

- Based on air **quality standards** and limit values
- On direct **exposure** assessment: Maximum Impact Standards (MIS)
- Based on **no-annoyance**: Maximum Annoyance Standard (MAS)
- Regulations based on **best practice**

Exposure criteria in terms of ground level odor concentration (UK)

Relative "offensiveness" of odor *(Belgiorno et al., 2013)*

Indicative criterion (98 th percentile)

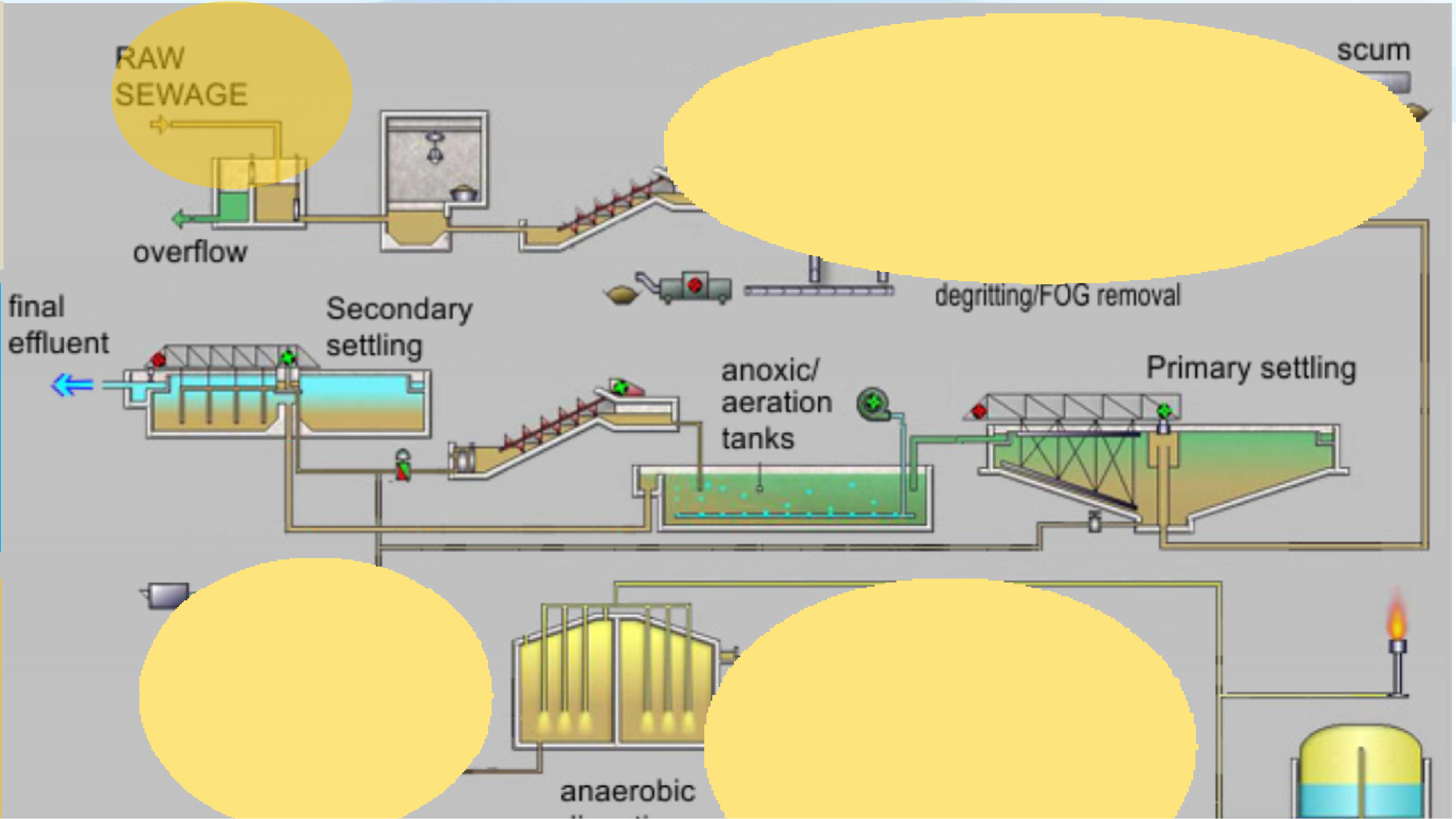
HIGH	**1,5**	ou_E/m^3	*activities involving putriscible waste, processes involving animal of fish remains,*

n-CO_2 Greenhouse Gases
IGs)

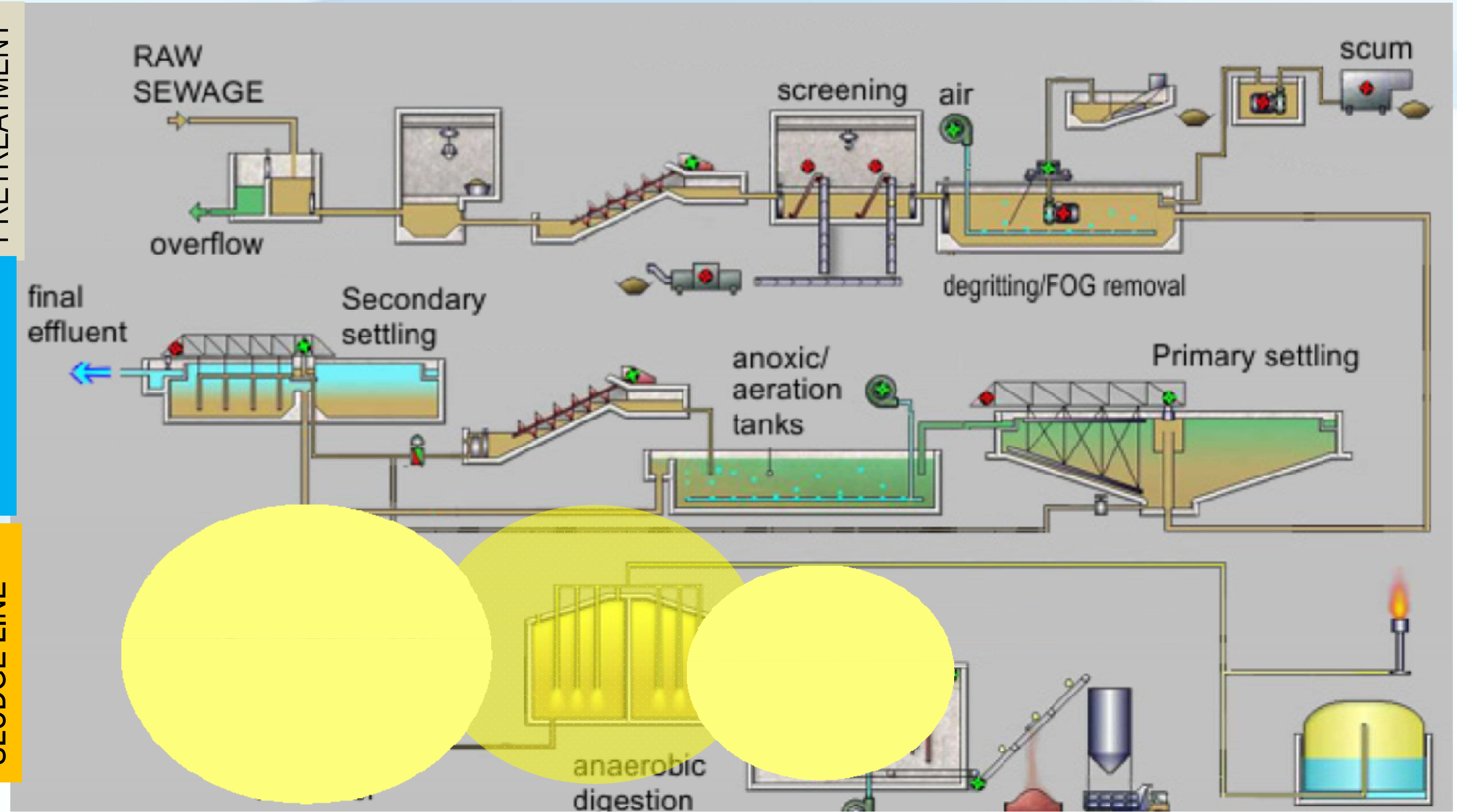
- GHGs: Methane
  - CH_4 has 25 times more impact on global warming than CO_2
  - Wastewater treatment: 2.5% US emissions (2012)
  - Dumps, WWTPs and other wastes: up to 31% of CH_4 emissions (Spain, 2007)
- GHGs: Nitrous oxide
  - N_2O has 310 times more impact on global warming than CO_2
  - Wastewater treatment: 1.6% US emissions (2012)
  - Around 0.4% of the oxidized NH_3 during

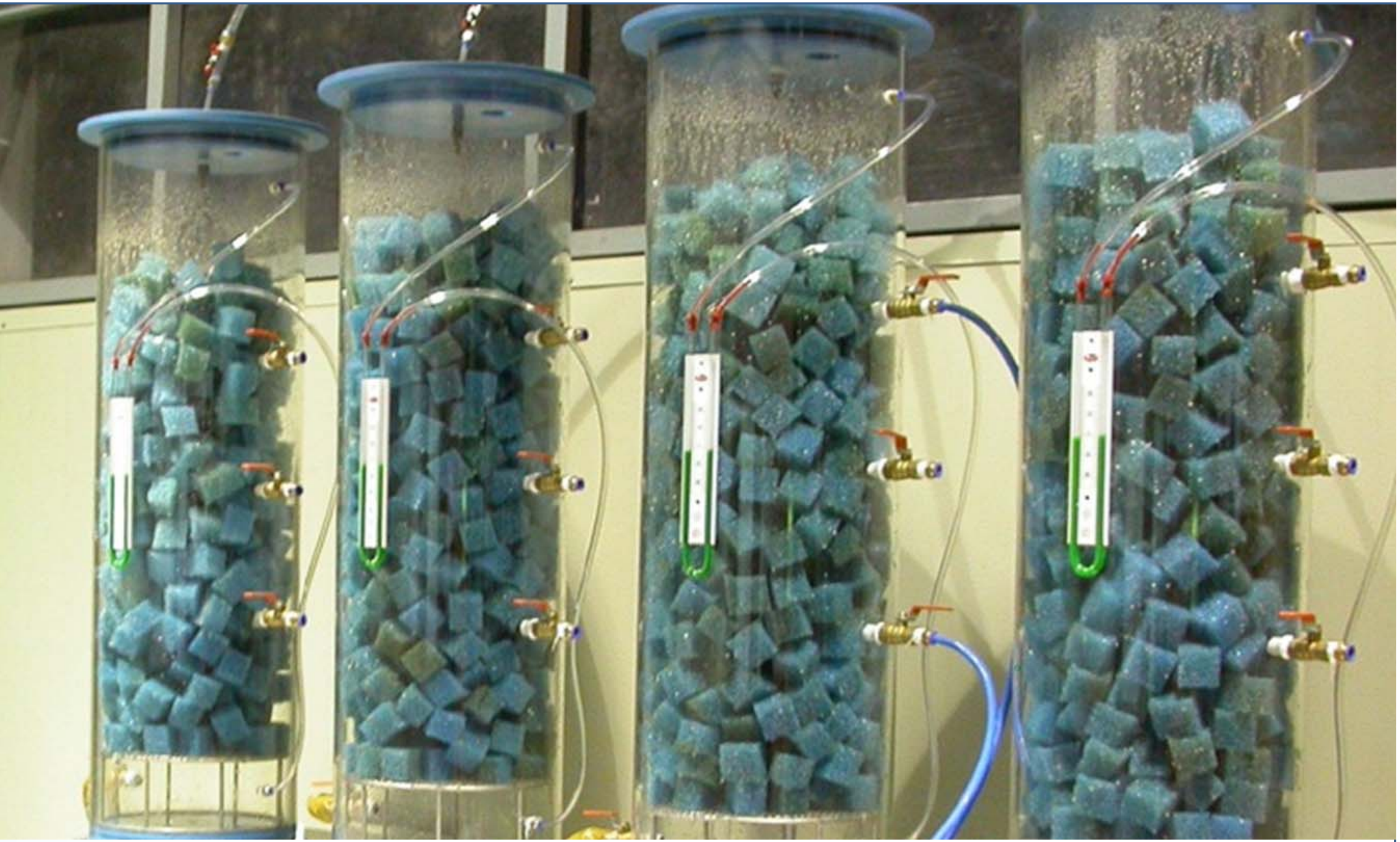
ccurrence in STPs

VOCs and Odours



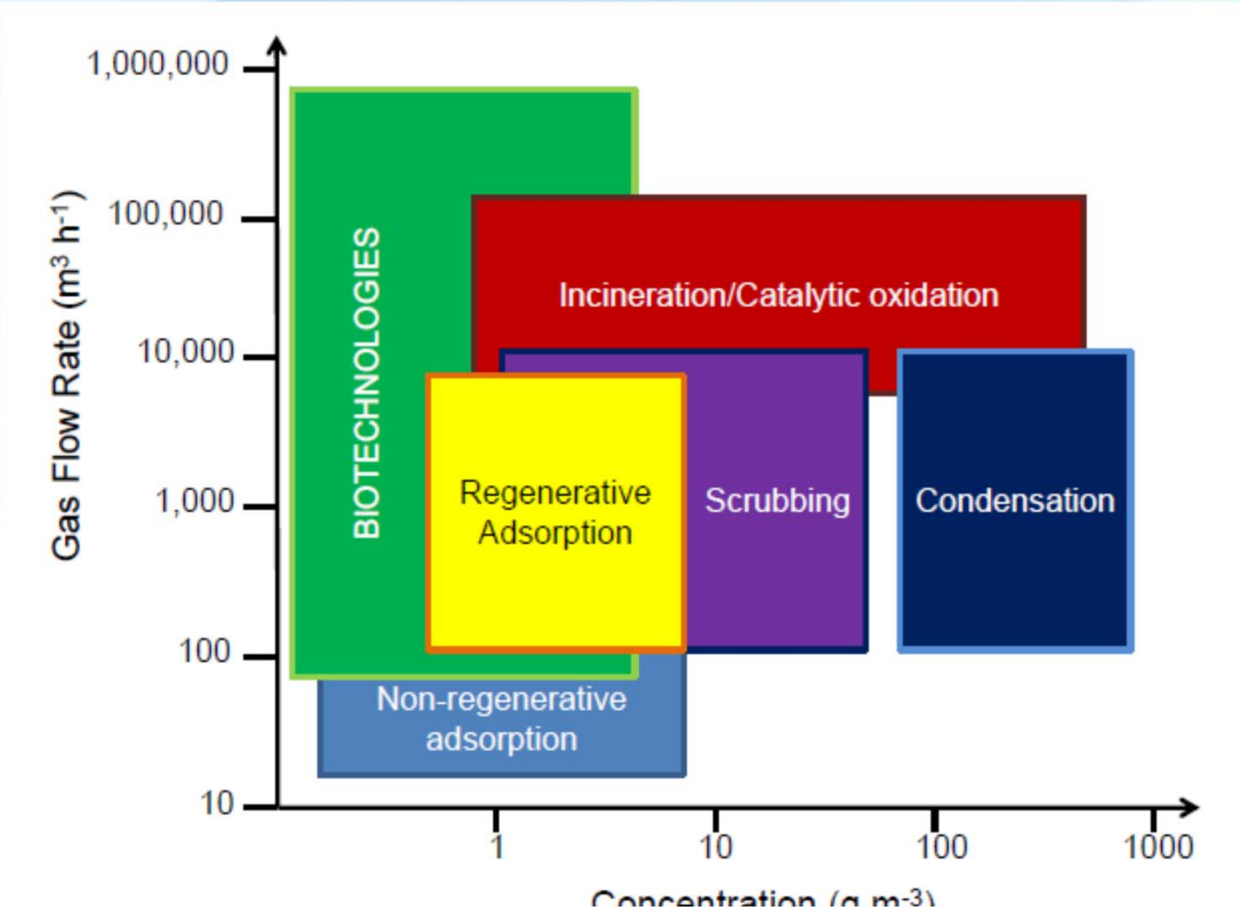
GHGs (CH_4 and N_2O)





Biological treatment technologies

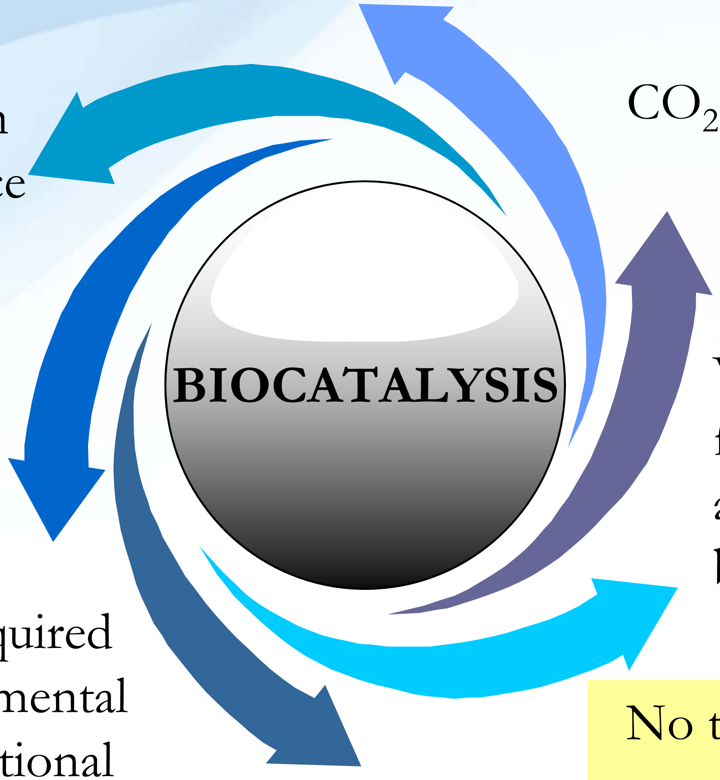
aseous effluents treatment technologies



logical treatment

$$ {}_2 + \text{Nutrients (N,P,S,trace elements)} \xrightarrow{\text{Microorganisms}} CO_2 + H_2O + \text{Microorganisms} + \text{Energy} $$

VOCs as carbon and energy source



CO_2 footprint is much lower than incineration

No fuel is required

Ambient T and P conditions

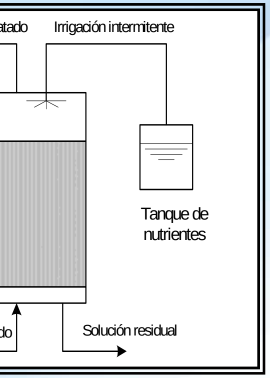
VOCs are transferred from gas phase to aqueous phase prior to biodegradation

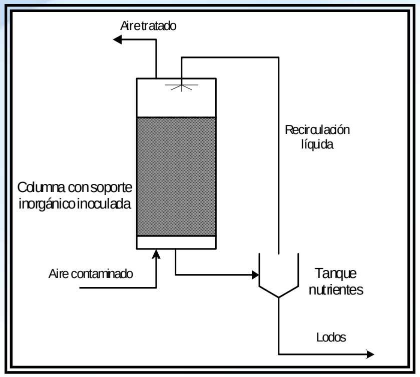
Less energy is required (thus less environmental impact and operational

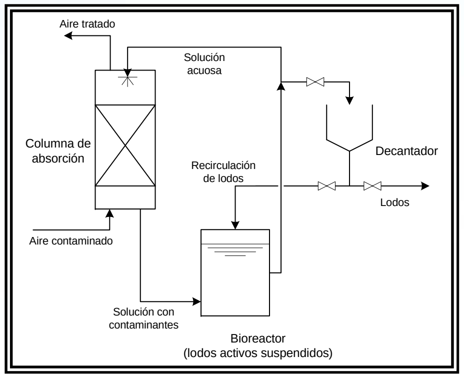
No toxic byproducts are used/generated

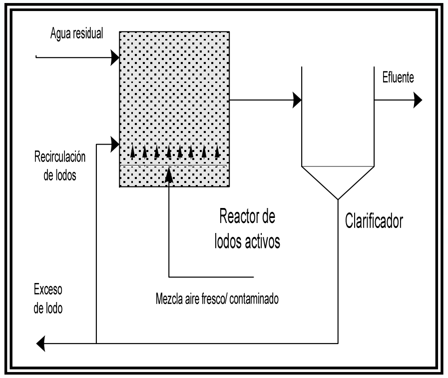
otechnologies

iofilter (BF)	Biotrickling filter (BTF)	BioScrubber (BS)	Activated Sludge Diffusion (ASD)









ationary eous phase	Mobile aqueous phase	Mobile aqueous phase	Stationary aqueous phase

Biomass in biofilm	Suspended biomass

ofilters (BF)

Most common used biotechnology

Removal of odours, organic and inorganic pollutants as air flows through beds of soils, compost, peat or other natural organic media.

Characteristics

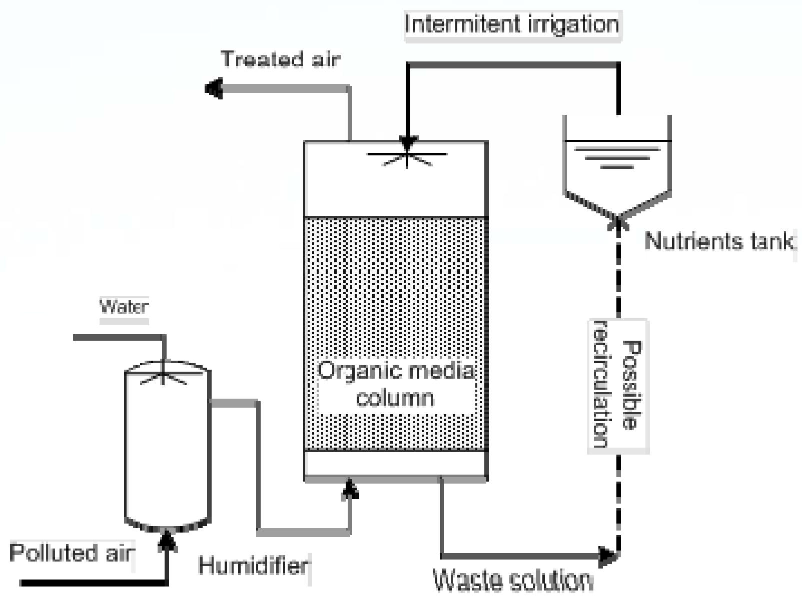
- Immobilised biomass
- No Mobile liquid phase
- One single reactor

Advantages:

- High interfacial gas/liquid area
- Easy to start and to operate
- Low operation costs

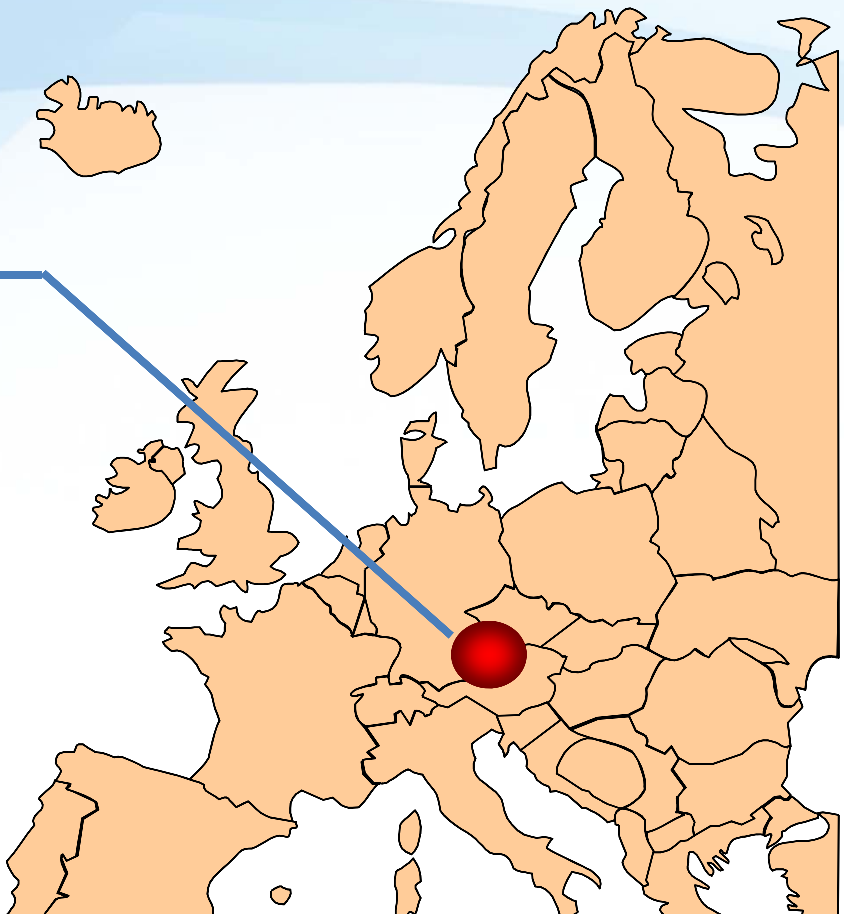
Disadvantages:

- Poor control of reaction conditions
- Poor adaptation to fluctuations to inlet gas streams



7500 biofilters in Europe and
alf aprox. are located in **WWTP**
and composting plants

Groenestijn and Kraakman, 2005



BIOFILTER

Generation Biofilter

2nd Generation Biofilter

acteristics of some common packing materials used in BFs

	Natural		Inert		
	Compost	Pine bark	Perlite	GAC	Lava rock
	7,6	4,5			
kg m^{-3}	674	367	94,5	166	866,7
-	0,5		0,4	0,5	0,5
%	54	67			
mm	3 - 5		4 - 6	1.2 - 3.2	4 - 10
%		53,7	2,5	92,1	
%		39,8	55,4	7,3	50,6
%		5,5			
%	0,011	< 0.3			
%		< 0.3			
%	0,004				
%	0,023	0,063	2,3	0,4	0,9
%	0,012	0,006			2,7
%	0,015	0,037	0,5	0,2	6,2
%	0,031		2,3		4,5
%		0,001	0,4		6,2
%					
%			5,2		8,4
%			31		19,1

Kennes & Veiga, 2013

Carrier	*Volume ratio*
Compost	1
Compost–yard trash	1/3
Compost–wood chips	—
Compost–perlite	1/1
Compost–diatomeas earth	—
Compost–polystyrene	1/1
Compost–chaff	1/1
Peat	1
Peat–polyurethane foam	7/3
Peat–polyurethane foam–vermiculite	2/2/1
Peat–polyurethane foam–perlite	2/3/5
Peat–perlite	2/3
Peat balls	1
Peat–compost	1/1
Peat–glass beads	2/1
Wood bark	1
Wood waste–perlite	1/1
Soil	1
Soil–sand–peat–compost	20/2/3/3
Seaweeds	1
Dry wastewater sludge	1

es

Iranpour et al., 2005

		Removal of VOCs			Removal of S and N		
	EBRT	Pollutant	Concentration	RE	Pollutant	Concentration	RE
	s		mg/m3	%		mg/m3	%
Sewage treatment plants:	14 - 69	**Benzene**	0,002-0,003	0	**H2S**	10-50	>99
		Xylenes	0,18-0,66	0-23	**Carbon disulfide**	0,02-0,03	32-36
		Toluene	0,077-0,23	0-17	**MM**	0,3-0,33	91-94
		Dichlorobenze	0,024-0,049	0-6	**DMS**	0,02-0,03	0-21
		Chloroform	0,25-0,40	0	**Carbonyl sulfide**	0,05-0,13	30-35
		PCE	0,35-0,97	0	**Odor (D/T)**	35000-46360	> 99
		PCE	0,35-0,97	0			
	18 - 54	**MTBE**	1,8	20	**H2S**	0,01 - 42	>99
		Acetone	1,6	80			
		Toluene	2,3	60			
		Xylenes	1,3	40			
		DCM	3,5	30			
		Chloroform	0,3	15			
	45 - 180	**Benzene**	3	83-93	**H2S**	13,9	>99
		Toluene	4	88-97	**Odor**	1,20E+06	> 99
		Xylene	0,4-1,1	88-93			
	45	**α-pinene**	675 ppb	100	**H2S**	7-120	100
		β-pinene	345 ppb	100	**DMS**	0,02	100
		limonene	70 ppb	97	**DMDS**	0,16	100
					CS2	0,01	100
					Odor (D/T)	214	94
	36	**Benzene**	0,03	59	**H2S**	0-2	>99

se studies: VOCs, VICs and odours
)

Iranpour et al., 2005

		Removal of VOCs			Removal of S and N		
	EBRT	Pollutant	Concentration	RE	Pollutant	Concentration	RE
	s		mg/m3	%		mg/m3	%
Compost:	55-95				**DMS**	0,08	55
					DMDS	1,1	83
					MM	0,034	>90
					NH3	34-106	98-99
					Odor (D/T)	500-970	> 80
	90	THC (methane)	31	15	**DMS**	0,38	25-36
					DMDS	0,56	19-28
					MM	0,1	20-49
					NH3		59-79
					Odor (D/T)	394	64
Livestock	5				**H2S**	0,01-0,27	75-100
					NH3	1,4-8,2	60-100

se studies: Methane

Study	Packing material	EBRT (min)	Inlet load (g CH_4 m^{-3} h^{-1})	$EC_{average}$ (g CH_4 m^{-3} h^{-1})	RE (%)
lelse et al., 2005	Compost (40%) Perlite (60%)	7	4	1.2	30
			25	5	20
		21	4	2.6	65
			15	8	53
irard et al., 2011	Inorganic material (gravel)	4.2	5	2.3	46
			15	6.7	45
			28	12.3	43
Hernández & Omil, 2012	Pine bark (50%) Compost (15%) Perlite (35%)	4.4	17	11	62
valos et al., 2012	Inorganic material + Tween 20	4.2	68	45	65

BIOFILTER

Advantages	Disadvantages
• High transfer area gas/solid • Easy start-up and operation • Low operation costs	• Poor control of operating parameters • High footprint (low EBRTs) • Inhibition due to metabolite accumulation: ≈ 25 g SO_4^{2-} / kg compost

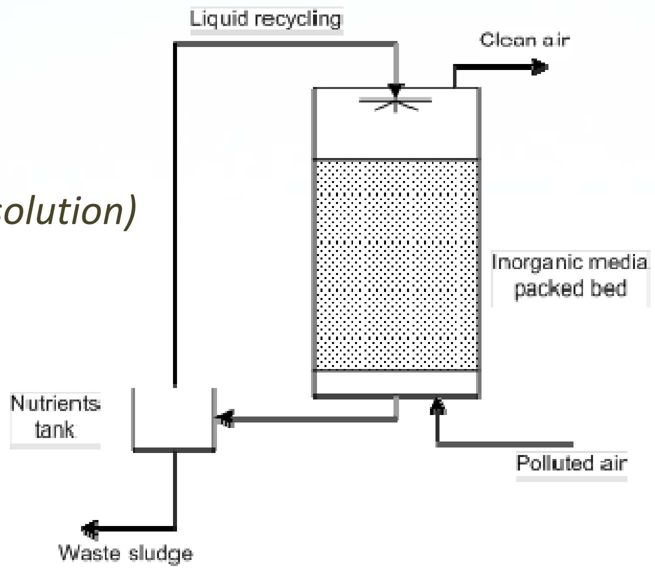
HIGH EFFICIENCIES
AT EBRT 20s - 2 min
H_2S y COVs 90-100 %

Henry Law < 10 ($H=Cg/Cl$)

Investment 5-68 € /(m^3h^{-1})

oTrickling Filters (BTF)

- Most common used biotechnology
  - **Polluted gas flows through a packed media (co-current or counter-current) with a mobile liquid phase, with ensures nutrient supply.**
  - **Characteristics**
    - o Immobilised biomass
    - o Mobile liquid phase *(Nutrients are introduced by continuous recirculation of an aqueous solution)*
    - o One single reactor
  - **Advantages:**
    - o relatively small footprint
    - o bed porosity usually > 70%
    - o Less compaction problems
    - o free liquid phase: easy control



acteristics of some common packing materials used in BTFs

	Size	Specific surface area	Void fraction	Density	Bulk cost
	mm	$m^2\ g^{-1}$	-	$kg\ m^{-3}$	€ m^{-3}
	2 - 5	800 - 1200	0.30 - 0.60	400 - 500	300 - 500
eramic rings	10 - 15	300 - 400	0.55	600 - 700	
k	20	0,60 - 0,65	0.50	750 - 850	40 - 80
s - polypropylene	50	100 - 300	0.90 - 0.95	50 - 80	400 - 500
expanded)	4 - 6	2 - 10	0.40 - 0.60	50 - 150	60 - 100
hane foam	25	500 - 600	0.90 - 0.97	20 - 50	30 - 40

Kennes & Veiga, 2013

es

Iranpour et al., 2005

	EBRT	Removal of VOCs: Pollutant	Concentration	RE	Removal of S and N: Pollutant	Concentration	RE
	s		mg/m3	%		mg/m3	%
Sewage treatment plants:	24	**Benzene**	0,002-0,003	0	**H2S**	10-50	>99
		Xylenes	0,18-0,66	0-23	**Carbon disulfide**	0,02-0,03	0
		Toluene	0,077-0,23	0-17	**MM**	0,3-0,33	64-72
		Dichlorobenze	0,024-0,049	0-6	**DMS**	0,02-0,03	0
		Chloroform	0,25-0,40	0	**Carbonyl sulfide**	0,05-0,13	0
		DCM	0,14-0,32	0	**Odor (D/T)**	35000-46360	97-99
		PCE	0,35-0,97	0			
	2	**Benzene**	0,5	32	**H2S**	7-35	>99
		Xylenes	0,5-2,1	41-44	**Carbon disulfide**	0,22	35
		Ethyl benzene	0,6	41	**MM**	0,39	67
		Chloroform	1,6	30	**COS**	0,2	44
		DCM	0,5	36	**Odor (D/T)**	1980	65
		TCE	0,08	46			
		PCE	1,5	28			
	11-20	**Benzene**	0-0,11	19-29	**H2S**	1,8-16	87-99
		Xylenes	0,08-0,42	6-57			
		Toluene	0,10-0,74	50-74			
		1,1,1-TCE	0,08-0,64	0-38			
		CCl4	0,003-0,012	2-15			
		Chloroform	0,05-0,17	0-25			
		DCM	0,07-0,57	0-61			
		PCE	0,36-4,8	0-8			
		TCE	0,01-0,04	0-24			
	36	**Benzene**	0,03	59	**H2S**	0-2	>99
		Xylenes	3,5	92			
		Toluene	0,7	85			

BIOTRICKLING FILTER

Advantages	Disadvantages
Easy control of the operation parameters (pH, moisture, nutrients)	• Low transfer area
Microorganisms retention	• Low efficiency for hydrophobic compounds
Low EBRT	• Excessive biomass growth

HIGH EFFICIENCIES AT LOW EBRT: 1-10 s
H_2S 90-100 % COVs < 40 %

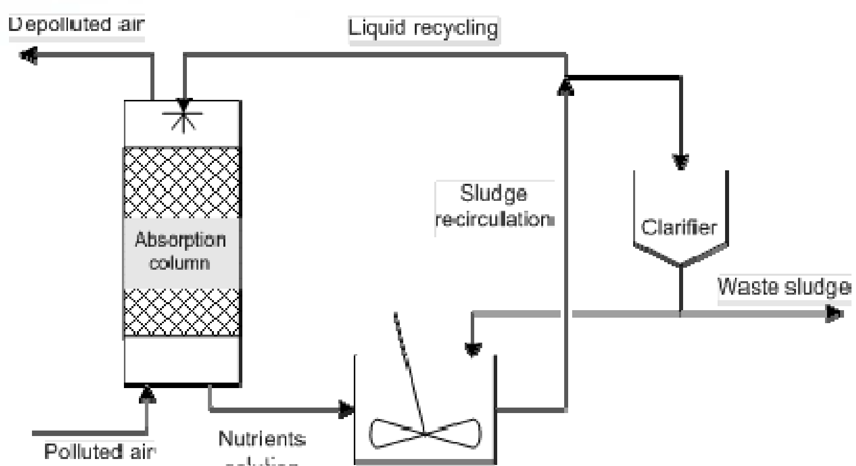
Henry Law < 1 (H=Cg/Cl)

Investment 5-20 € /(m^3h^{-1})

Operation 2-8 € /(m^3h^{-1})

oScrubbers (BS)

- Two separated units
  - **Absorption Tower (Scrubber):**
    pollutants transferred to the recirculating aqueous phase
  - **Suspended growth bioreactor:**
    pollutants are biodegraded by suspended biomass



BIOSCRUBBER

pplications of full-scale BioScrubbers in industry

l activities	VOCs	Waste gas flow rate ($m^3\ h^{-1}$)
	Butyl acetate, butanol and xylene	54 000
of drink cans	Alcohols, glycols, toluene and ethyl acetate	10 000 - 57 000
rd packaging	Ethanol, ethyl acetate and 1-methoxypropane-2-ol	150 000
ts and cosmetics	Alcohols, acrylate monomers and toluene	30 000
m foundry	Phenol	120 000
	Alcohols, ester and glycol	60 000
ustry	Nitrogenous and oxygenated molecules	10 000 - 50 000
ter treatment	Sulfur compounds (H2S and mercaptanes)	600 - 2 000
aste treatment	Sulfur, nitrogenous and oxygenated molecules	10 000
mposting	Sulfur, nitrogenous and oxygenated molecules	up to 600 000

Kennes & Veiga, 2013

BIOSCRUBBER

Advantages

- Easy control of the operation parameters (pH, nutrients)
- Avoids by-products accumulation
- Low ΔP

Disadvantages

- Low growth rate microorganisms are washed-out
- High costs compared to other bioreactors

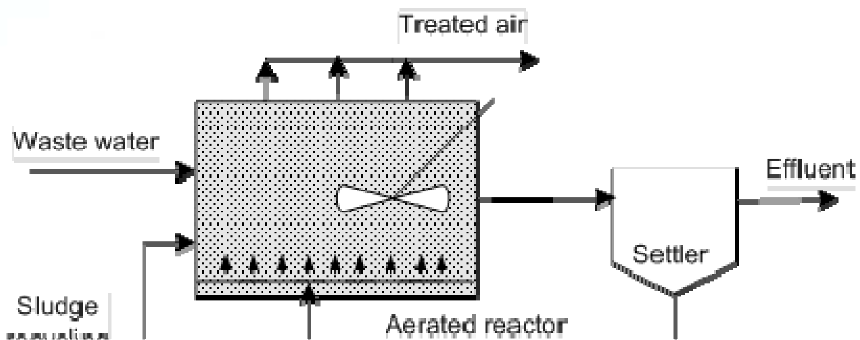
HIGH EFFICIENCIES FOR SOLUBLE ODOROUS COMPOUNDS
90-100%
Henry Law < 0.01
($H = C_g / C_l$)

Investment 23-92 € /(m^3h^{-1})

Operation 2-8 € /(m^3h^{-1})

ctivated Sludge Diffusion (ASD)

- Main characteristics
  - Malodorous air is treated in the activated sludge tank
  - Corrosion can be avoided: adequate corrosion resistant materials
  - Total polluted air < aeration requirements (20-100%)
  - Specially advantageous for STPs using diffused aerated systems



ACTIVATED SLUDGE DIFFUSION

Advantages

- Parameters control (pH, nutrients, humidity, biomass)
- Existing unit of the STP
- High transfer areas

Disadvantages

- Sludge bulking
- Possible corrosion
- Lack of knowledge on VOCs removal efficiencies

Removal efficiencies in STPs:
99.7% > H_2S
odour > 99.9 %

Investment ~0 € / (m^3h^{-1})

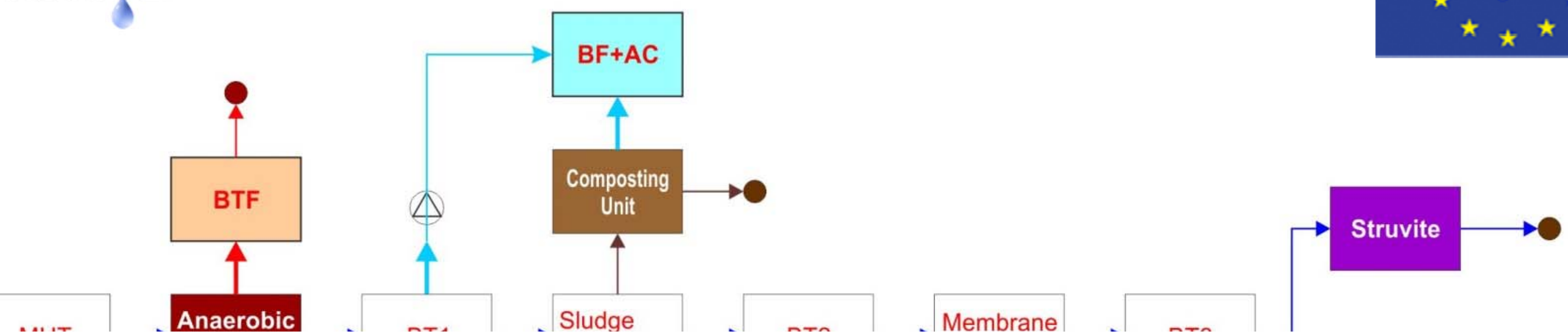
ther configurations

- Membrane bioreactors
- Two-phase partitioning bioreactors
- Rotating biological contactors
- Other innovative bioreactors
  - **Monolith bioreactor**
  - **Horizontal flow biofilm reactor**
  - **Rotary switching biofilter**
  - **Etc.**
- Two-stage systems
  - **Hybrid configurations (GAC+BF; GAC+BTF; etc.)**

veWaste project strategy (LIFE+ programme)

To develop an innovative integrated scheme for the complete treatment of livestock effluents in Cyprus

- **optimize the post-treatment of the generated anaerobic digestate**
- **Recovery of nutrients (struvite)**
- **Biotechnologies for gas treatment (odours, VOCs, H2S)**

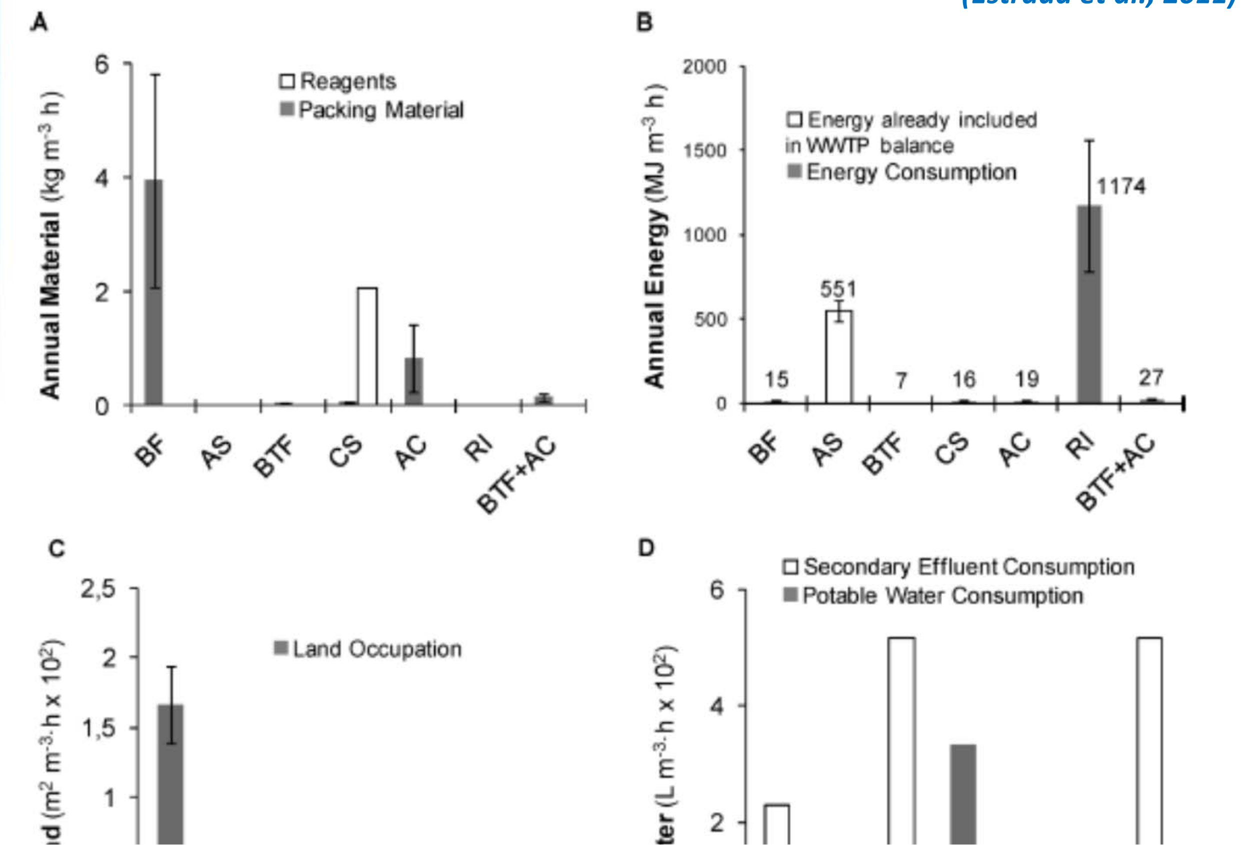


vironmental and economic indicators

nvironmental performance

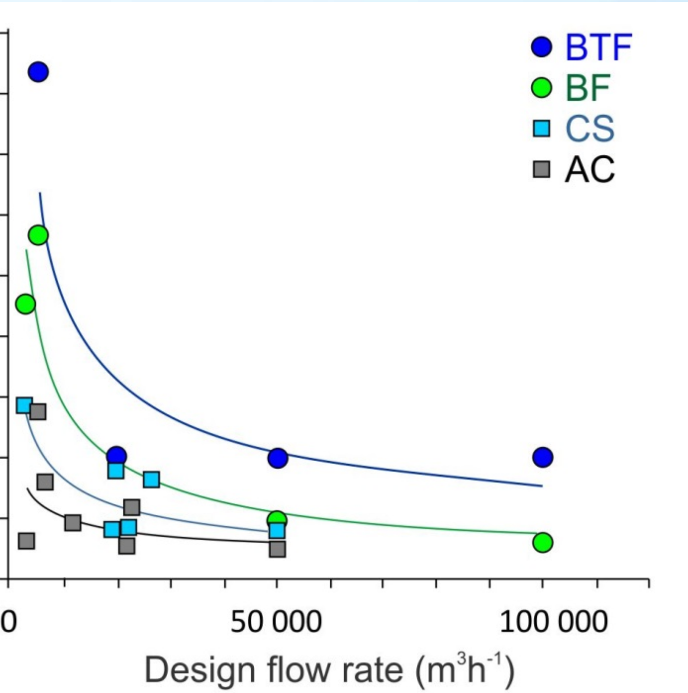
- Removal of odors in STPs (H_2S)
- Physico-chemical vs. biological

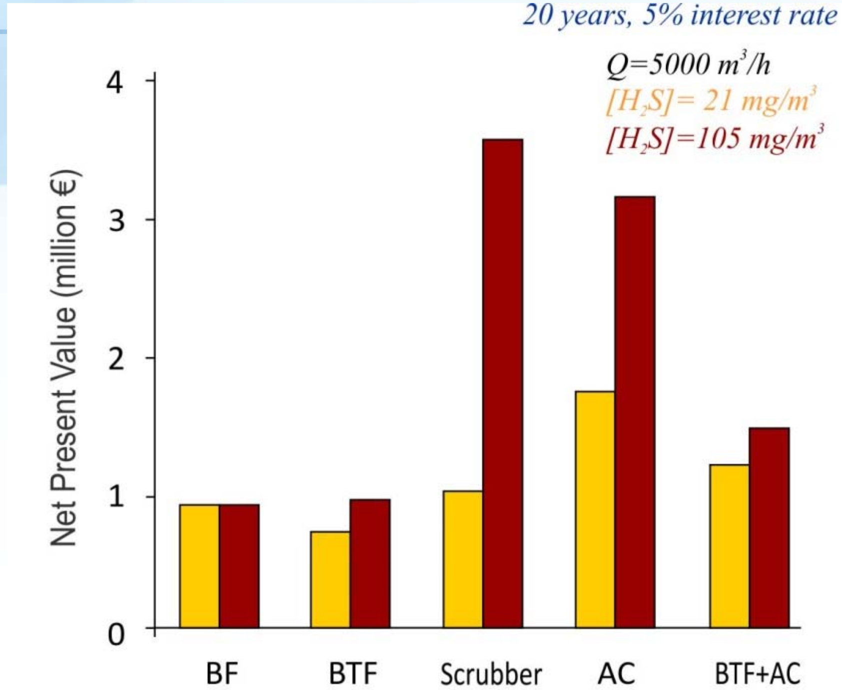
(Estrada et al., 2011)

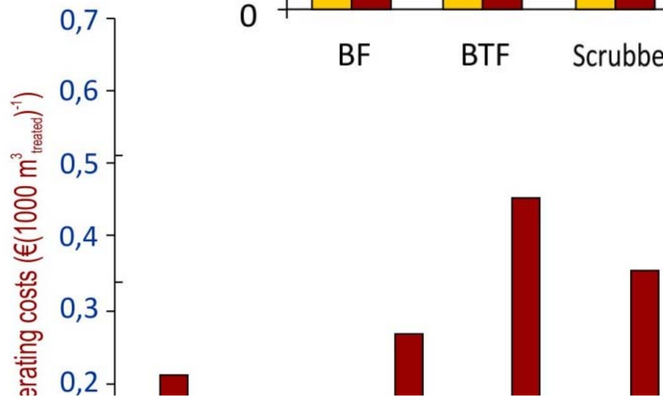


(Estrada et al., 2011)

onomic indicators







Net Present Value the most convenient analysis

nclusions and future challenges

onclusions and challenges

- Biological technologies for air pollution control (and other gaseous emissions) constitute nowadays a demonstrated alternative, in terms of economics and sustainability, especially interesting for low pollutant concentrations.
- Economic analysis indicate that these technologies imply the lowest operating costs being less sensitive to design parameters or commodity prices.
- It is necessary to study and overcome their main limitations (problems at long-term operation such as clogging, characterisation of biomass, development of inocula, identification of mass-transfer limitations, hydrophobic pollutants, etc.) and promote their applicability.
- New technological or microbiological approaches should be

cknowledgments

- This work was supported by the European Union through the project LiveWaste (LIFE12 ENV/CY/000544).
- The authors belong to the Galician Competitive Research Group GRC2010/37.