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Presence and fate of volatile methylsiloxanes in anaerobic digesters from WWTPs

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Kerkyra (Corfu, Greece), 16 June 2022

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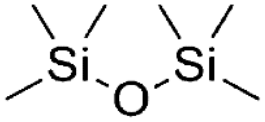
ALiCE ASSOCIATE LABORATORY IN CHEMICAL ENGINEERING

CORFU2022 15-18 JUNE

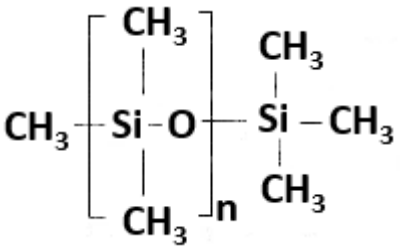
Siloxanes in WWTPs

Siloxanes

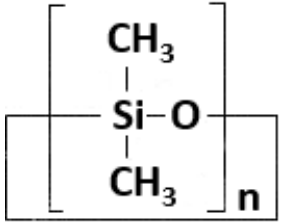


SILOXANES

Silicone + Oxygen + Alkanes



Linear Methyl Siloxanes - **Ln**



Cyclic Methyl Siloxanes - **Dn**

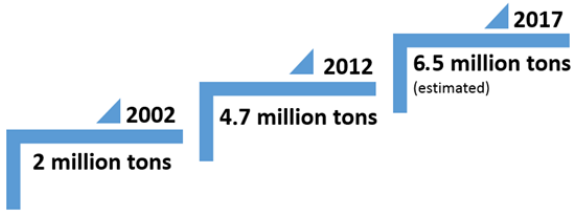
Anthropogenic organic compounds

Backbone of Si and O atoms with alkyl side chains

Linear (L) or Cyclic (C) structures

Low water solubility, low viscosity, low surface tension, low resistance to polymerization

Massively produced worldwide



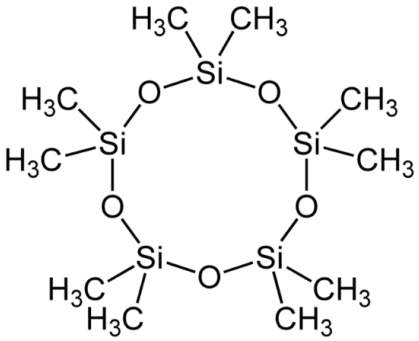
Siloxanes

- Cosmetics
- Personal Care Products
- Foods and drugs
- Detergents
- Electronics
- Medical devices
- Paints
- …

Siloxanes in the environment

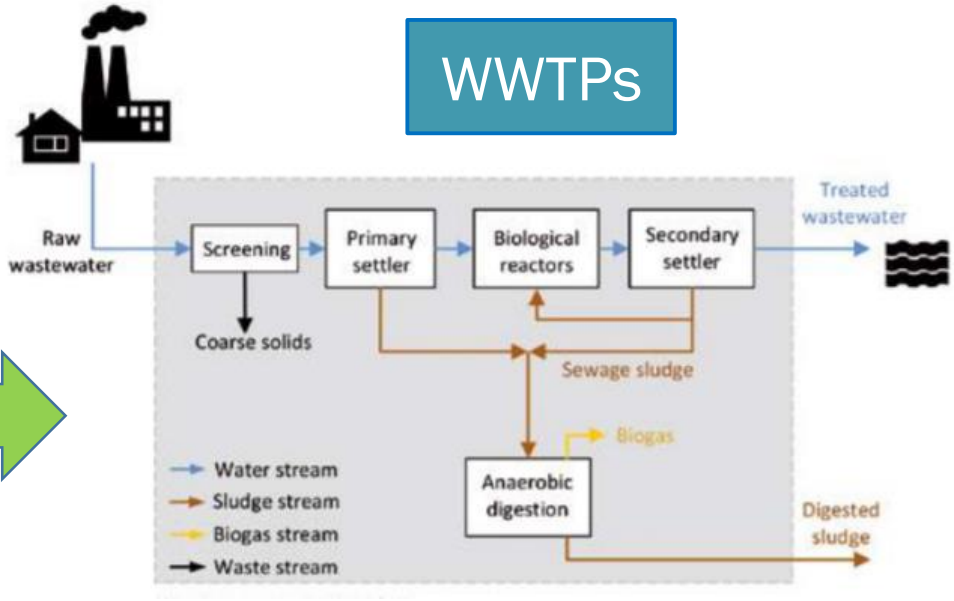
90%

Air



10%

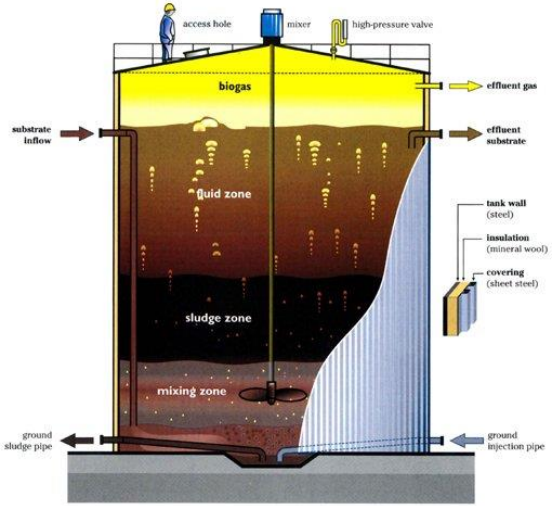
WWTPs

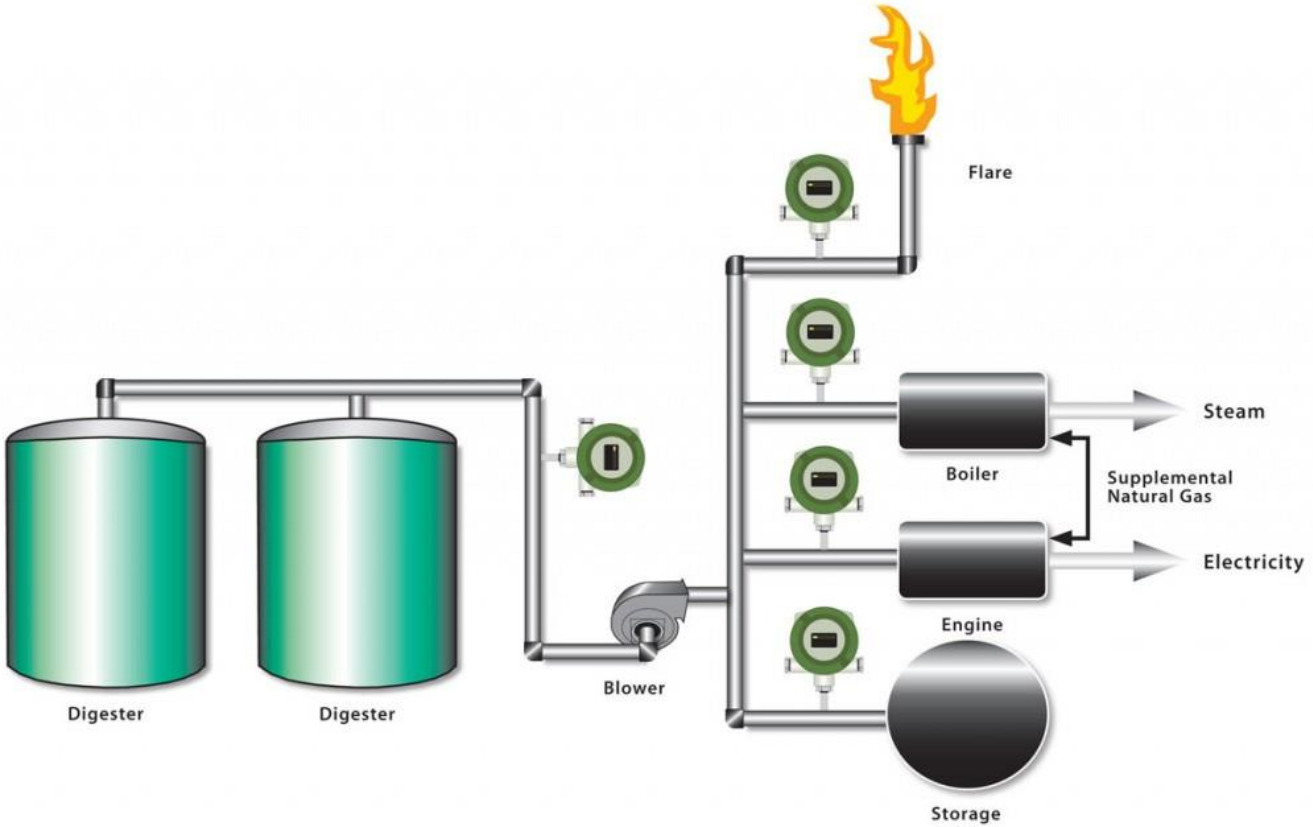


de Arespacochaga et al., *Renewable and Sustainable Energy Reviews* 52 (2015), 366-381

Bachmann, N. Sustainable biogas production in municipal wastewater treatment plants. IEA Bioenergy, 2015.

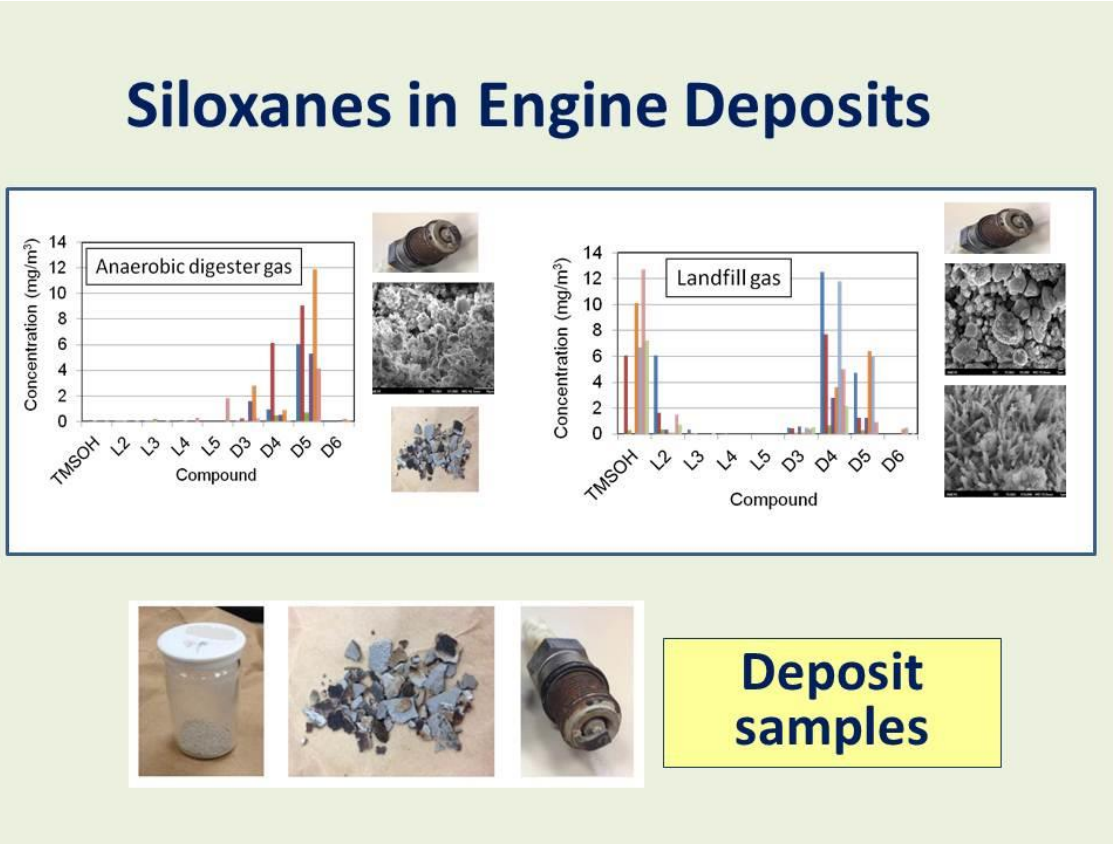
Biogas in WWTPs





- Production of heat and electricity usually via cogeneration

The main problem of VMSs in WWTPs



- Siloxanes deposit as SiO_2 particles during biogas combustion

Project LANSILOT

LAunching New SILOxane Treatments: assessing effluent, sludge and air quality and improving biogas production in WWTPs

Project FCT – POCI-01-0145-FEDER-032084 (€ 224 968,43)

LEPABE-FEUP (Portugal)

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- Vera Homem
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- Guillaume Erny
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FCT - University of Lisbon (Portugal)

- Valentina Vassilenko (Consultant)

Department of Health, Wadsworth Center (New York, USA)

- Kurunthachalam Kannan (Consultant)

Methodology

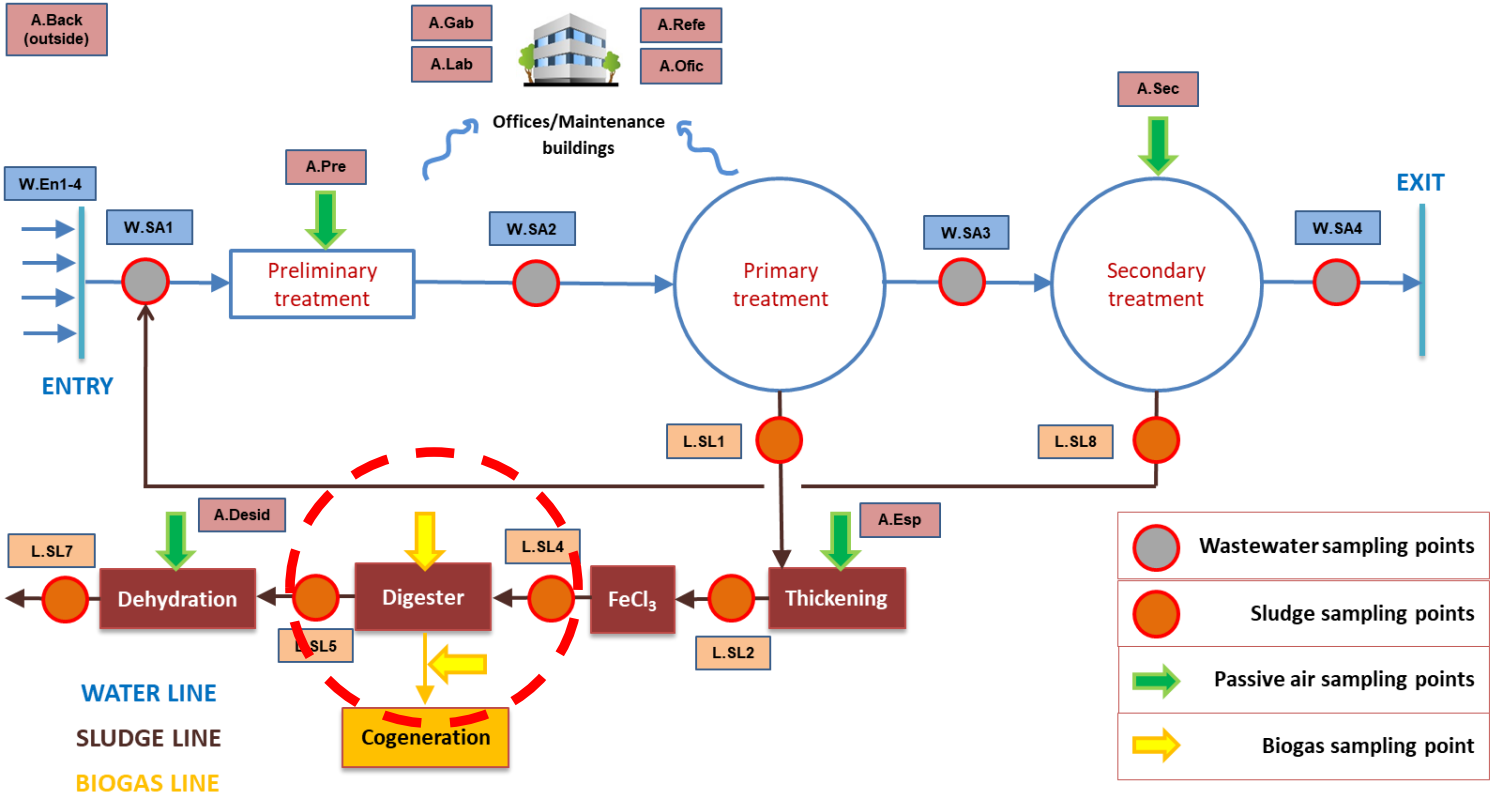
Target volatile methylsiloxanes (VMSs)

Name (a.k.a.) LINEAR	Formula	MW ($g\ mol^{-1}$)	Vapor pressure (mmHg @ 25°C)	Boiling point (°C)	Water solubility ($mg\ L^{-1}$ @ 25°C)
Hexamethyldisiloxane (L_2)	$C_6H_{18}Si_2O$	162	31	101	0.93
Octamethyltrisiloxane (L_3)	$C_8H_{24}Si_3O_2$	236	3.9	152	0.035
Decamethyltetrasiloxane (L_4)	$C_{10}H_{30}Si_4O_3$	310	0.55	194	$3.75x10^{-1}$
Dodecamethylpentasiloxane (L_5)	$C_{12}H_{36}Si_5O_4$	384	0.07	284	$1.07x10^{-4}$

Name (a.k.a.) CYCLIC	Formula	MW ($g\ mol^{-1}$)	Vapor pressure (mmHg @ 25°C)	Boiling point (°C)	Water solubility ($mg\ L^{-1}$ @ 25°C)
Hexamethylcyclotrisiloxane (D_3)	$C_{12}H_{18}O_3Si_3$	222	10	135	1.56
Octamethylcyclotetrasiloxane (D_4)	$C_8H_{24}O_4Si_4$	297	1.3	176	0.056
Decamethylcyclopentasiloxane (D_5)	$C_{10}H_{30}O_5Si_5$	371	0.4	211	0.017
Dodecamethylcyclohexasiloxane (D_6)	$C_{12}H_{36}O_6Si_6$	445	0.02	245	0.005

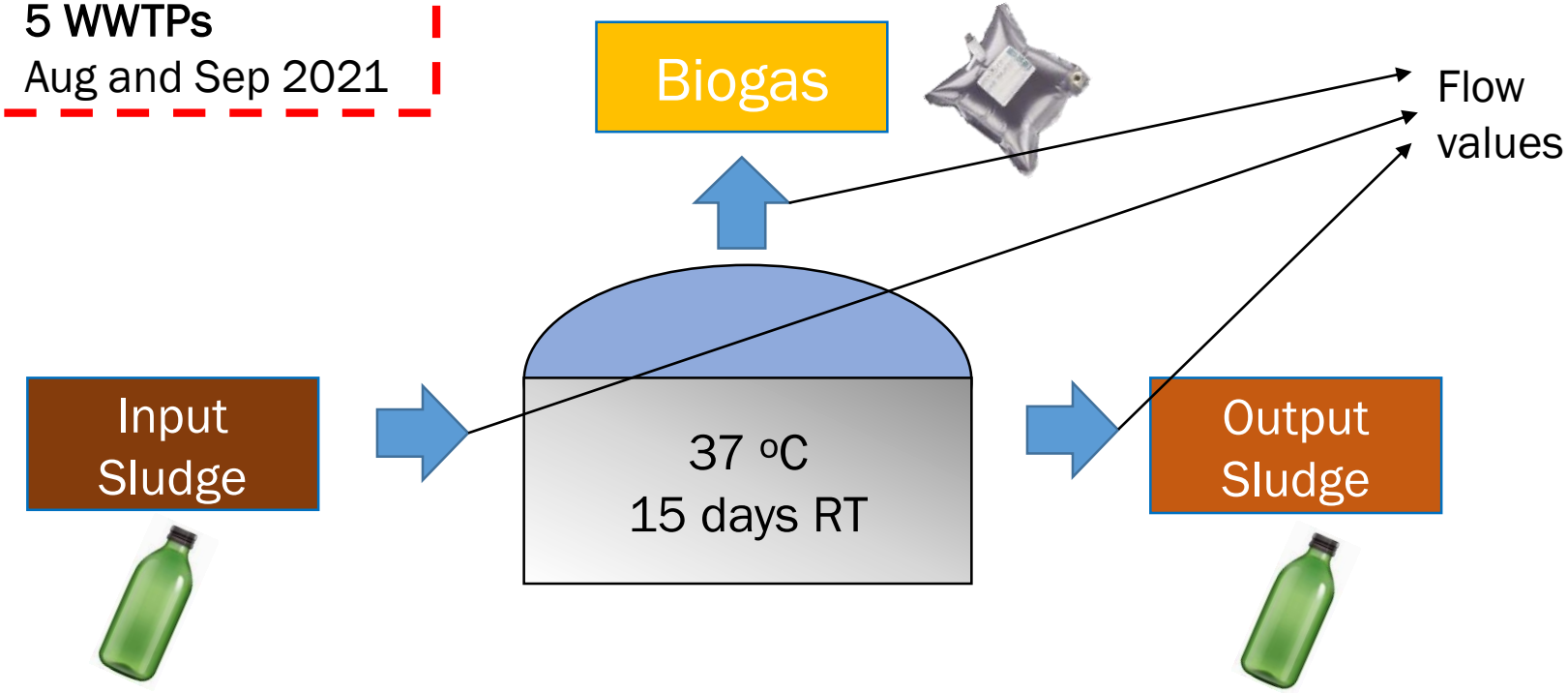
Internal standard - Tetrakis(trimethylsilyl)silane (TKS)

Sampling scheme



Sampling scheme

- 5 WWTPs
- Aug and Sep 2021



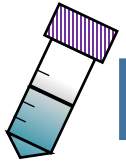
Analytical protocols

10 mL Hex
10 mL Ace

20 mL Sludge

500 ppb IS

Vortex
Orbital Shaking
Centrifuge



N_2 reduction

GC-MS

L3
L4
L5
D3
D4
D5
D6

Based on: *Oshita et al. (2015); Energy Conversion and Management* 96 (2015), 384-391

LODs (lower) = 0.001 - 1 ng/g (dw)

1 L Biogas

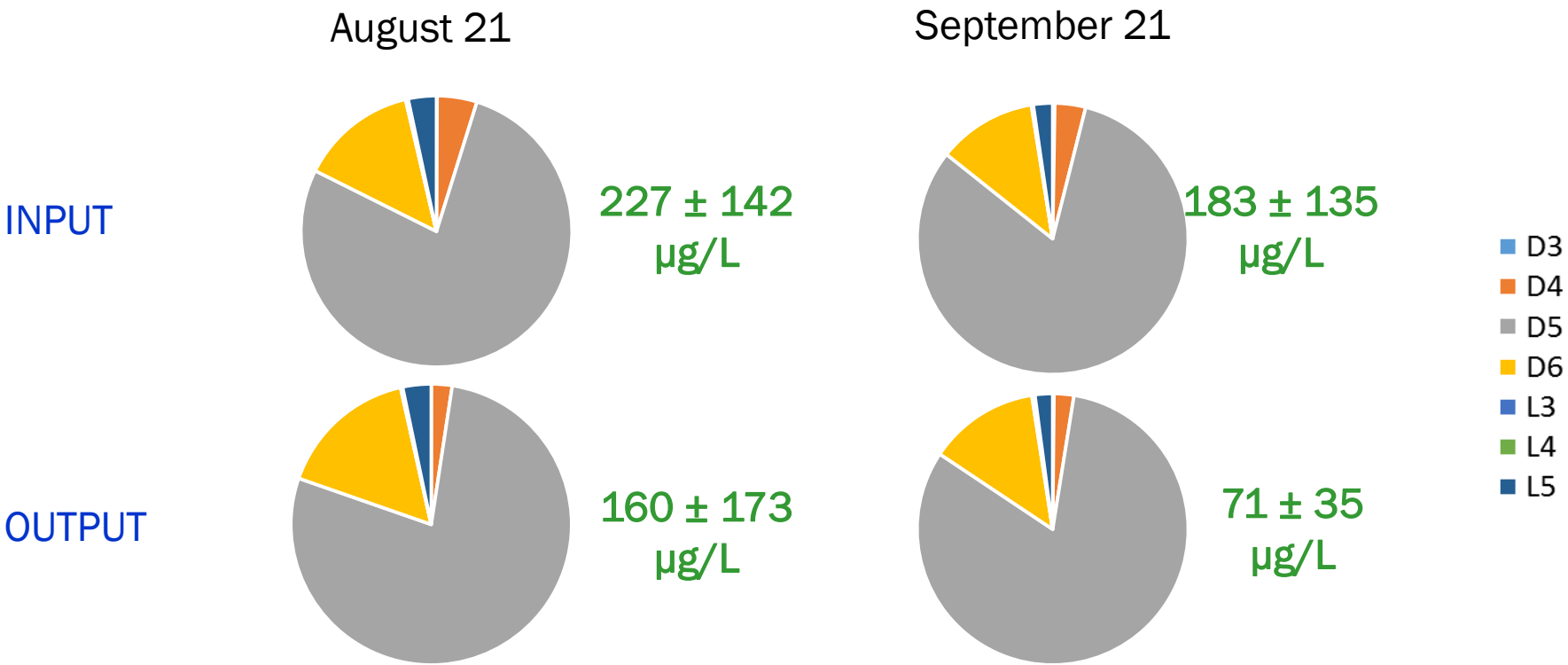
GC/IMS Silox

L2
L3
L4
L5
D3
D4
D5

LODs = 0.03 (lower) – 7.20 (upper) mg/m^3

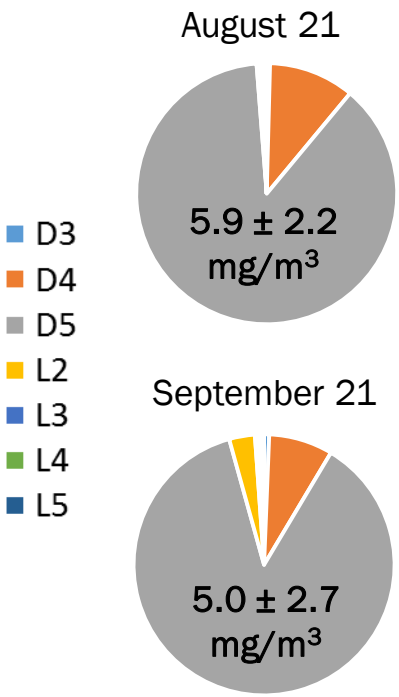
Results

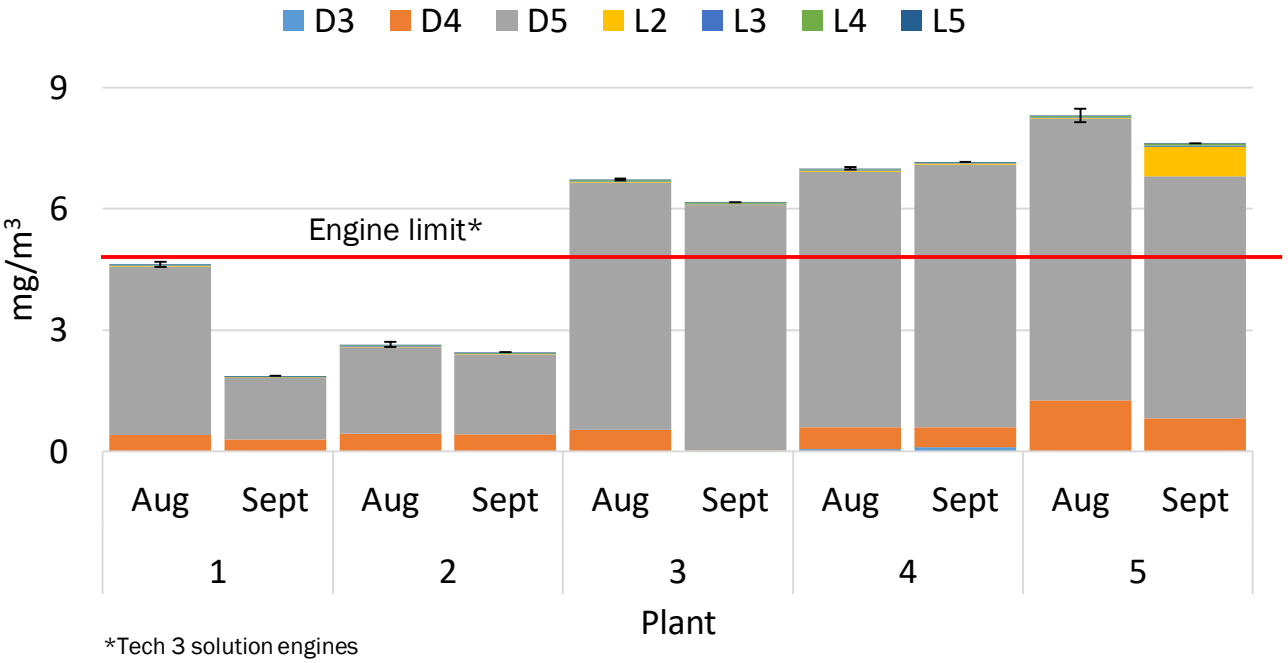
Sludge overview



D5 is the predominant VMS

Biogas overview

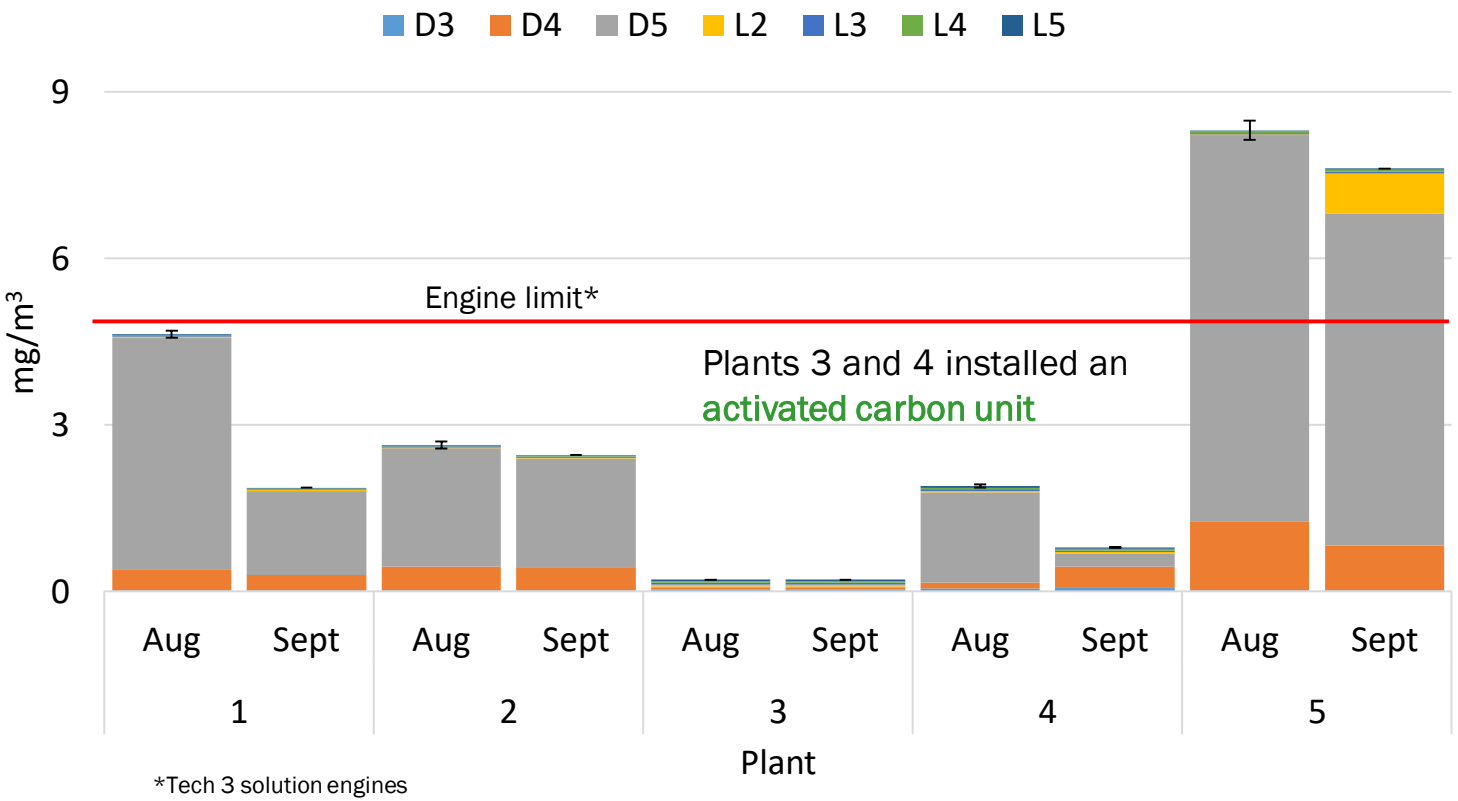




*Tech 3 solution engines

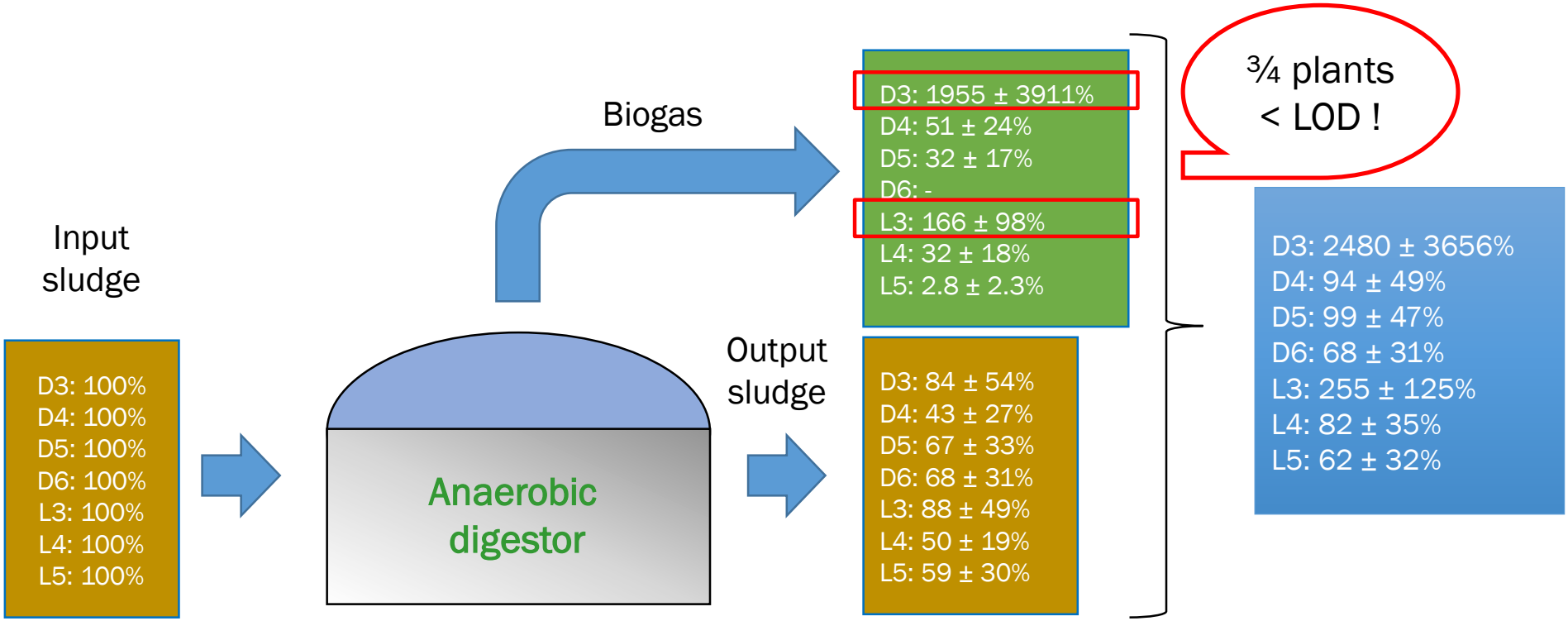
D5 is the predominant VMS

Biogas after treatment



*Tech 3 solution engines

Mass balance of VMSs (*e.g.*, August 2021)



Conclusions

- No significant differences in VMSs content were found between the two months assessed. However, **differences among plants are noticed**
- Regardless of matrix and plant, **cyclic VMSs (especially D5) were predominant**
- **Consistent mass balance** results were obtained overall. WWTP-based analysis should be conducted to study possible VMSs transformations
- **Treatment of input sludge could be an alternative** to reduce VMSs concentrations in output sludge and biogas

Outputs

So far:

- 4 SCI articles
- 1 book and 2 book chapters
- 17 works in international Conferences (7 oral)
- 1 PhD Thesis (ongoing)
- 5 Master Theses


Environmental Chemistry Letters (2021) 19:2723–2732
https://doi.org/10.1007/s10311-021-01191-1

ORIGINAL PAPER

Levels of volatile methylsiloxanes in urban wastewater sludges at various steps of treatment

Joana Silva[1] · Fábio Bernardo[1] · Mónica Jesus[2] · Tiago Faria[2] · Arminda Alves[1] · Nuno Ratola[1] · Vera Homem[1]

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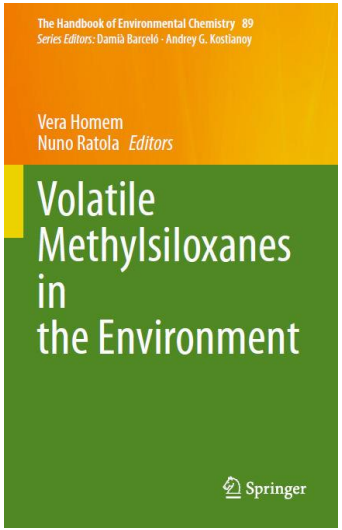

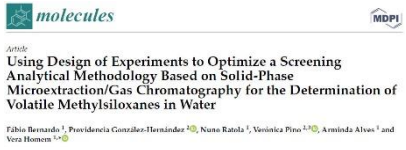
molecules
MDPI

Article

Using Design of Experiments to Optimize a Screening Analytical Methodology Based on Solid-Phase Microextraction/Gas Chromatography for the Determination of Volatile Methylsiloxanes in Water

Fábio Bernardo [1], Providencia González-Hernández [2], Nuno Ratola [1], Verónica Pino [2,3], Arminda Alves [1] and Vera Homem [1,*]


Biomass and Bioenergy 143 (2020) 105878

Contents lists available at ScienceDirect

Biomass and Bioenergy

journal homepage: http://www.elsevier.com/locate/biombioe

Impurities in biogas: Analytical strategies, occurrence, effects and removal technologies

Idalina Bragança [1], Francisco Sánchez-Soberón [1], Gabriel F. Pantuzza, Arminda Alves, Nuno Ratola

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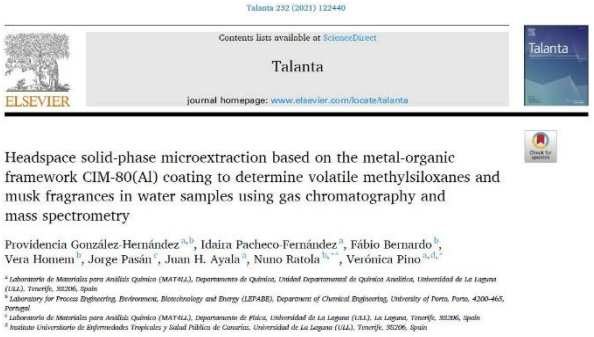
Talanta 232 (2021) 122440

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Headspace solid-phase microextraction based on the metal-organic framework CIM-80(Al) coating to determine volatile methylsiloxanes and musk fragrances in water samples using gas chromatography and mass spectrometry

Providencia González-Hernández [a,b], Idaira Pacheco-Fernández [a], Fábio Bernardo [b], Vera Homem [b], Jorge Pasán [c], Juan H. Ayala [a], Nuno Ratola [b,*], Verónica Pino [a,d,*]

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- All the people that helped in sampling campaigns
- The CORFU 2022 Conference Organization

People




















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ΕΥΧΑΡΙΣΤΩ ΠΟΛΥ

MANY THANKS

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