

PRODUCED WATER MIDDLE EAST 2019

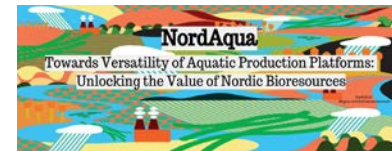
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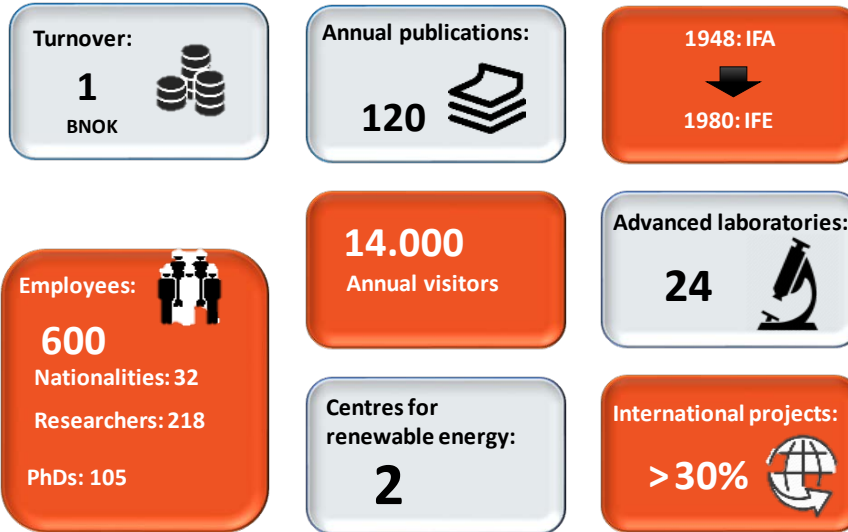
Exploring the removal of scale and corrosion inhibitors in produced water and seawater: photodegradation and bioremoval

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Institute for Energy Technology (IFE)



Services and work areas



Renewable energy



Nuclear technology



Materials technology



Digitalization



Radiopharmacy and health



Oil and gas



Industry and environment



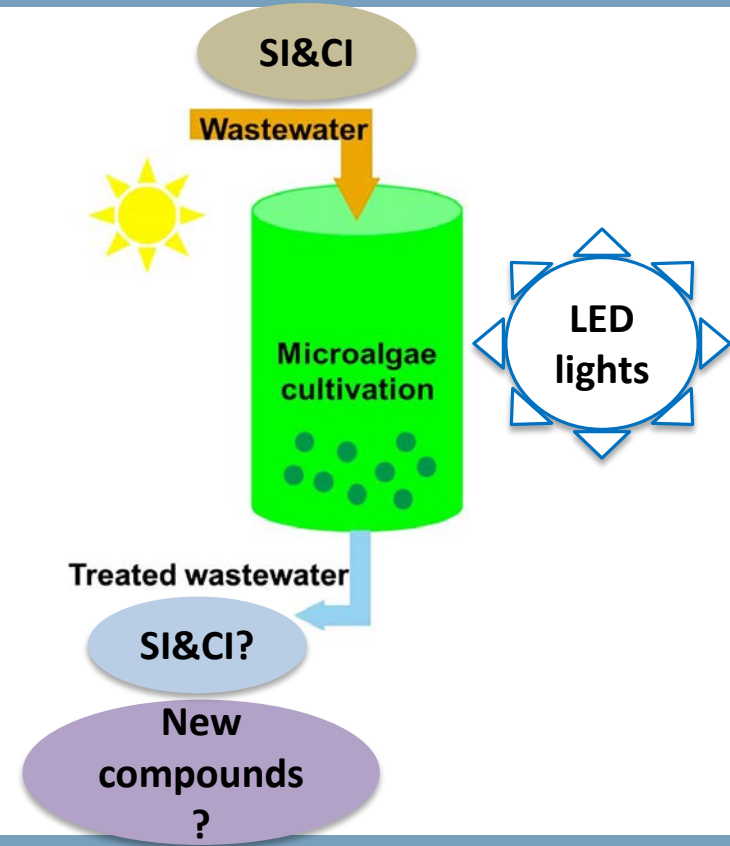
Safety and security



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Objectives

- ❖ Explore the removal of some scale inhibitor (SI) and corrosion inhibitors (CI) by direct photolysis and microalgae in seawater (SW) and produced water (PW) under batch experiments.
- ❖ Assess the transformation processes and identify the transformation products generated under the processes.



Why microalgae?

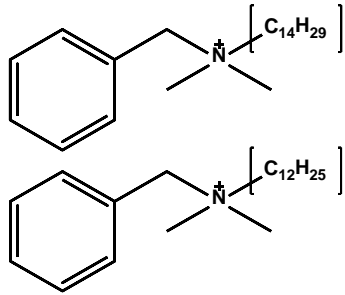
- ❑ Capacity to remove nutrients, heavy metals and emerging pollutants.
- ❑ Benefit to close the mass-to-energy loop, since their content of carbohydrates and oils allows them to be considered as a potential feedstock for the production of biofuels.
- ❑ They remove CO₂ and they can be a powerful tool in the abatement of this gas, whilst helping building a Circular Bioeconomy model.



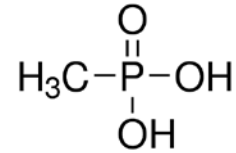
Target chemicals

Quaternary amines and phosphonates are commonly part of chemical composition of SI and CI

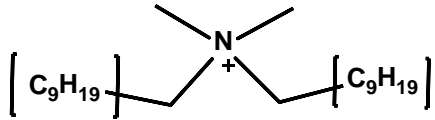
Benzalkonium chloride (BAC)



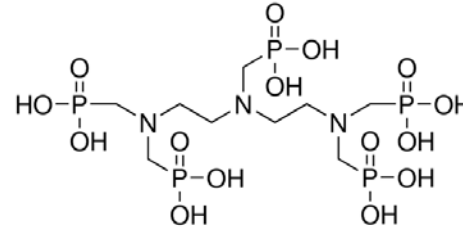
Methylphosphonic acid (MPA)



Didecyldimethylammonium chloride (DDA)



Diethylenetriaminepentakis (DTPMPA)



1. Selection and growth of microalgae

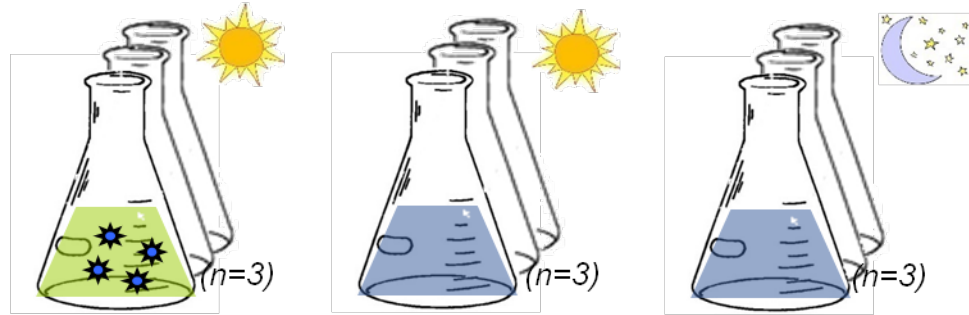
The collection of microalgae (NORCCA) and the technology



Microalgae
Attheta septentrionalis
Dunaliella salina
Dunaliella tertiolecta
Emiliana huxleyi
Isochrysis galbana
Nannochloropsis oculata
Phaeodactylum tricornutum
Skeletonema marinoi
Rhodomonas salina
Tetraselmis suecica

Selection based on: i) Literature review, ii) Biomass productivity and iii) Survival to saline water

2. Microalgae/Photolysis experiments in sea water



	Light Biomass (LB)	Light Abiotic (LA)	Dark abiotic (DA)
Biotransformation	✓	✗	✗
Phototransformation	✓	✓	✗
Other processes (i.e. hydrolysis, sorption)	✓	✓	✓



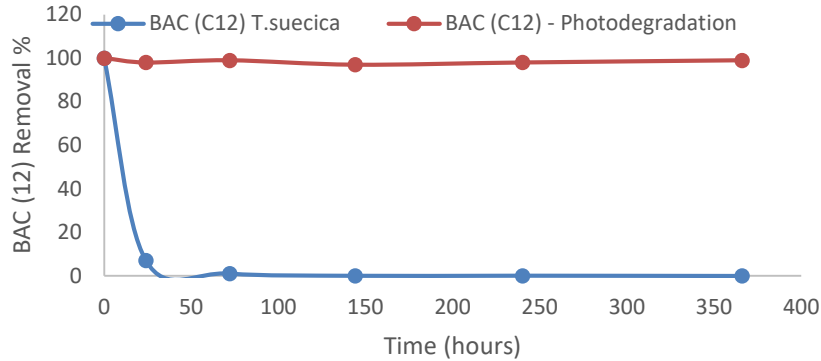
3. Growth of microalgae in presence of pollutants

	DDA	BAC	MTA	DTPMPA
R. salina	↓	↓	↑	↑
N. oculata	↓	↓	↓	↓
E. huxleyi	↓	↑	=	=
D. tertiolecta	↓	↓	↑	↑
I. galbana	↓	↓	↑	↑
T. suecica	=	↑	↑	↑
D. salina	↓	↓	↓	↓
P. tricornutum	↓	↓	↓	=

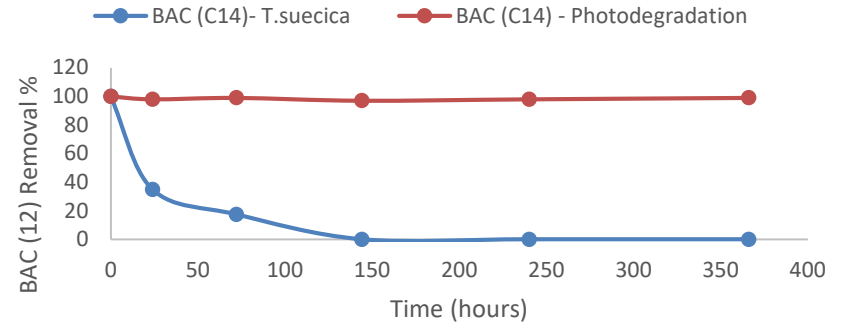


4. Removal of BAC (C12-C14)

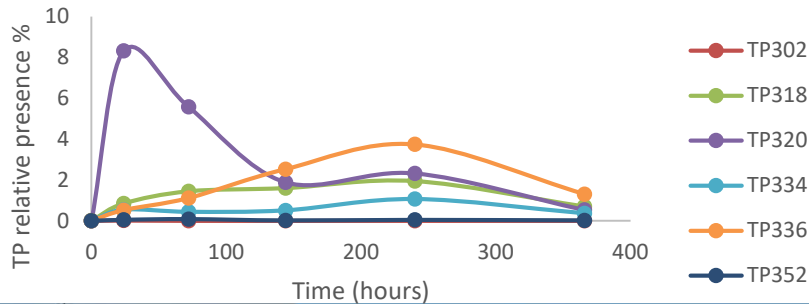
BAC (C12) Removal by *T.suecica* vs Photodegradation



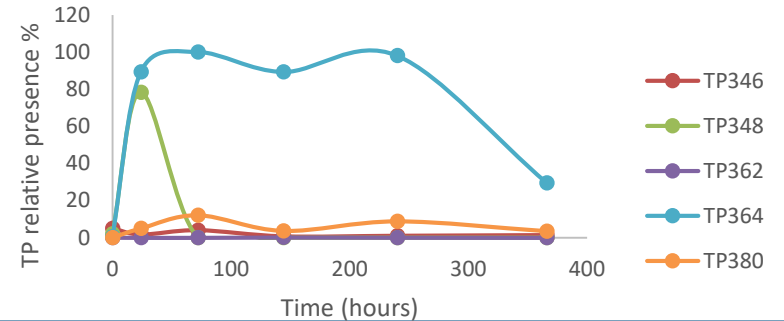
BAC (C14) Removal by *T.suecica* vs Photodegradation



BAC(C12) TPs by *T.suecica*

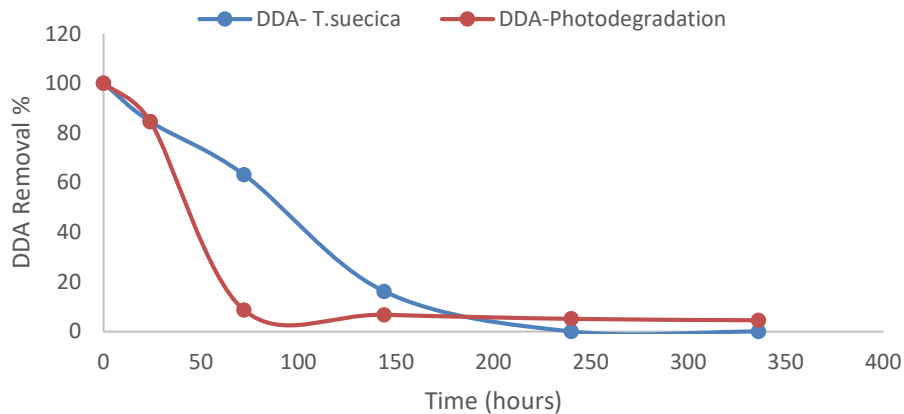


BAC(C14) TPs by *T.suecica*

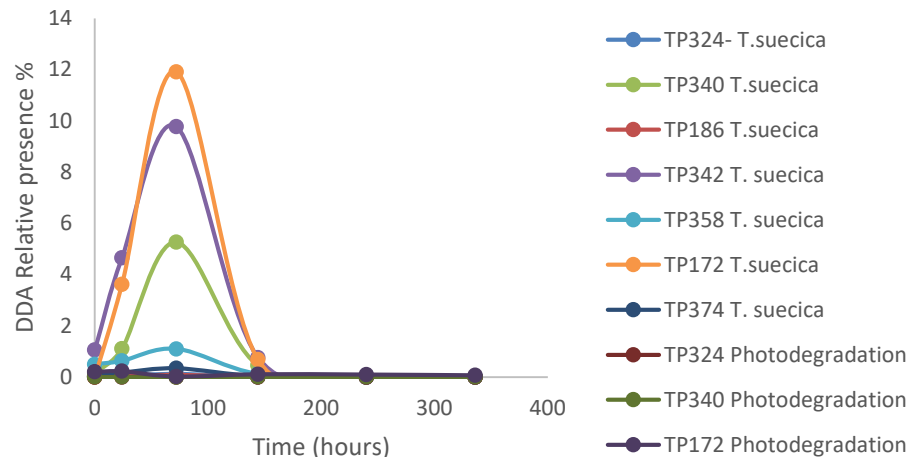


5. Removal of DDA

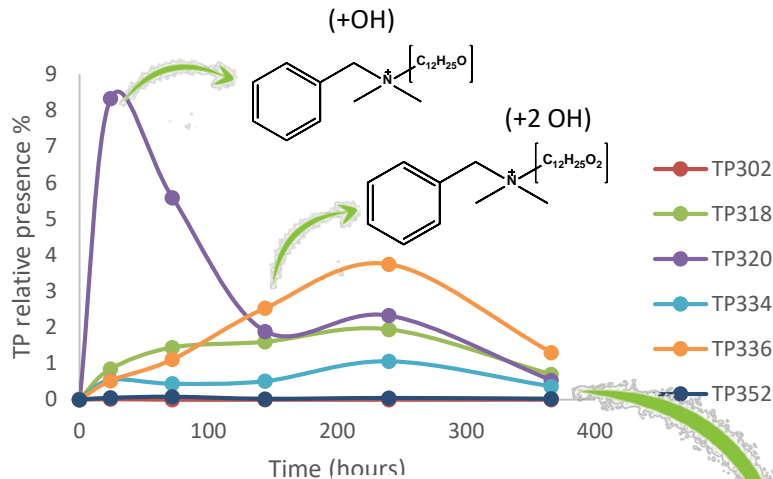
DDA removal T.suecica vs Photodegradation



DDA TPs T.suecica vs Photodegradation



6. Identification of transformation products - BAC



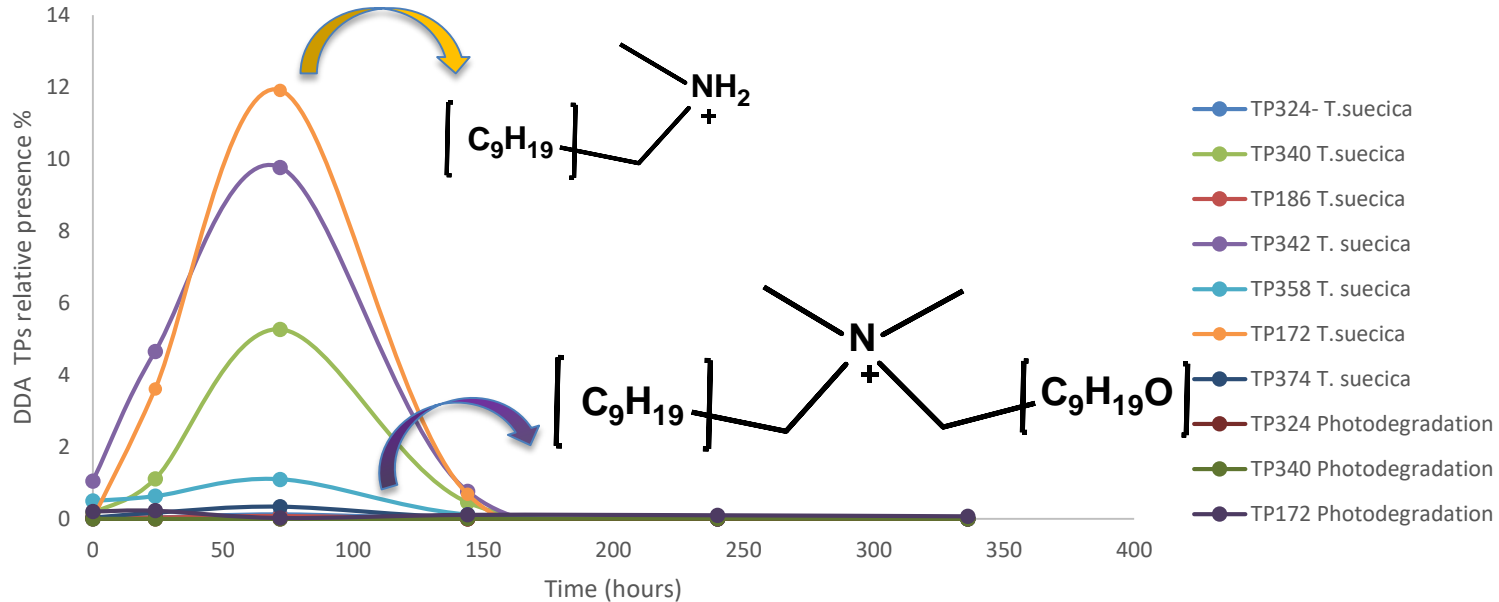
UPLC-HRMS (Orbitrap) coupled to cutting-edge data processing tool (Compound Discoverer)

Rt (min)	Compound	Ion	Molecular formula	Theoretical exact mass	Experiment exact mass	Error mass (ppm)	RDBE	Suggested chemical structure
0.73	BAC (C11)	[M] ⁺	C ₁₁ H ₁₄ N ⁺	304.25904	304.25974	-0.47	3.5	
		[M ⁺ -(C ₂ H ₄)]	C ₉ H ₁₀ N ⁺	212.23728	212.23720	-0.37	0.5	
		[M ⁺ -(C ₂ H ₄) ₂ -(C ₂ H ₄ O)]	C ₇ H ₆ N ⁺	136.11208	136.11197	-0.80	3.5	
		[M ⁺ -(C ₁₀ H ₁₆ N)]	C ₁ H ⁺	91.05423	91.05466	4.72	4.5	
		[M ⁺ -(C ₁₀ H ₁₆ N)]	C ₁ H ⁺	91.05423	91.05466	4.72	4.5	
0.15	TP302	[M] ⁺	C ₁₁ H ₁₄ N ⁺	302.284227	302.28424	0.04	4.5	
		[M ⁺ -(C ₂ H ₄)]	C ₉ H ₁₀ N ⁺	210.221626	210.22157	-0.26	1.5	
		[M ⁺ -(C ₁₀ H ₁₆ N)]	C ₁ H ⁺	91.05423	91.05410	-1.42	4.5	
		[M ⁺ -(C ₁₀ H ₁₆ N)]	C ₁ H ⁺	91.05423	91.05410	-1.42	4.5	
6.47	TP318	[M] ⁺	C ₁₁ H ₁₄ NO ⁺	318.279141	318.27930	0.49	4.5	
		[M ⁺ -(C ₂ H ₄)]	C ₉ H ₁₀ NO ⁺	226.216541	226.21661	0.30	1.5	
		[M ⁺ -(C ₂ H ₄) ₂ -(C ₂ H ₄ O)]	C ₇ H ₆ N ⁺	136.11208	136.11198	-0.73	3.5	
		[M ⁺ -(C ₁₀ H ₁₆ NO)]	C ₁ H ⁺	91.05423	91.05404	-2.00	4.5	
		[M ⁺ -(C ₁₀ H ₁₆ NO)]	C ₁ H ⁺	91.05423	91.05399	-2.83	4.5	
6.31	TP320	[M] ⁺	C ₁₁ H ₁₄ NO ⁺	320.294791	320.29474	-0.16	3.5	
		[M ⁺ -(C ₂ H ₄)]	C ₉ H ₁₀ NO ⁺	228.232191	228.23218	-0.04	0.5	
		[M ⁺ -(C ₂ H ₄) ₂ -(C ₂ H ₄ O)]	C ₇ H ₆ N ⁺	212.237277	212.23730	0.11	0.5	
		[M ⁺ -(C ₂ H ₄) ₂ -(C ₂ H ₄ O)]	C ₇ H ₆ N ⁺	136.11208	136.11212	0.29	3.5	
		[M ⁺ -(C ₁₀ H ₁₆ NO)]	C ₁ H ⁺	91.05423	91.05399	-2.83	4.5	
5.16	TP334	[M] ⁺	C ₁₁ H ₁₄ NO ⁺	334.274056	334.27393	-0.37	4.5	



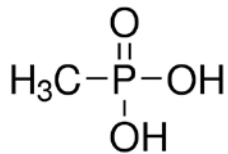
7. Identification of TPs DDA

DDA TPs T.suecica vs Photodegradation

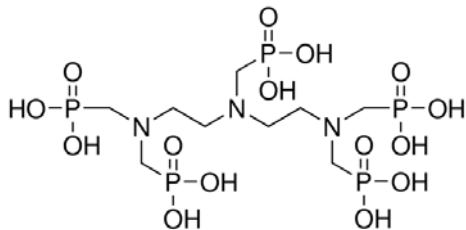


8. MPA & DTPMPA analysis on going

Methylphosphonic acid (MPA)



Diethylenetriaminepentakis (DTPMPA)



- Preliminary results looks promising for the elimination of pollutants under *T. suecica*
- P containing compounds boost the growth of microalgae

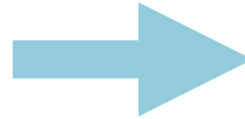
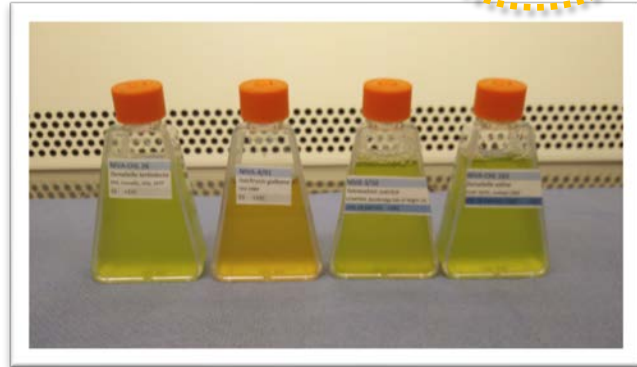
	DDA	BAC	MTA	DTPMPA
<i>T. suecica</i>	=	↑	↑	↑



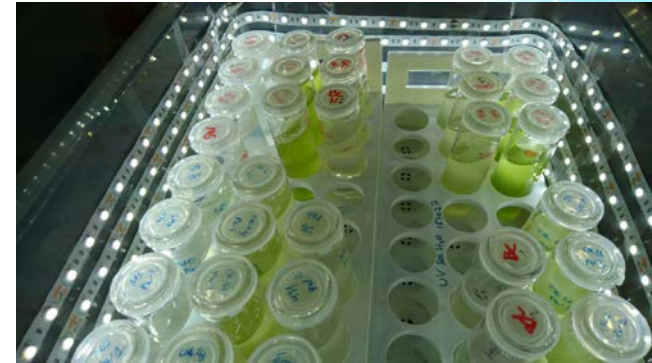
9. Batch experiments with produced water

Selected microalgae

D. tertiolecta, *I. galbana*, *T. suecica* and *D. salina*



PW from Gullfaks
(Norway)

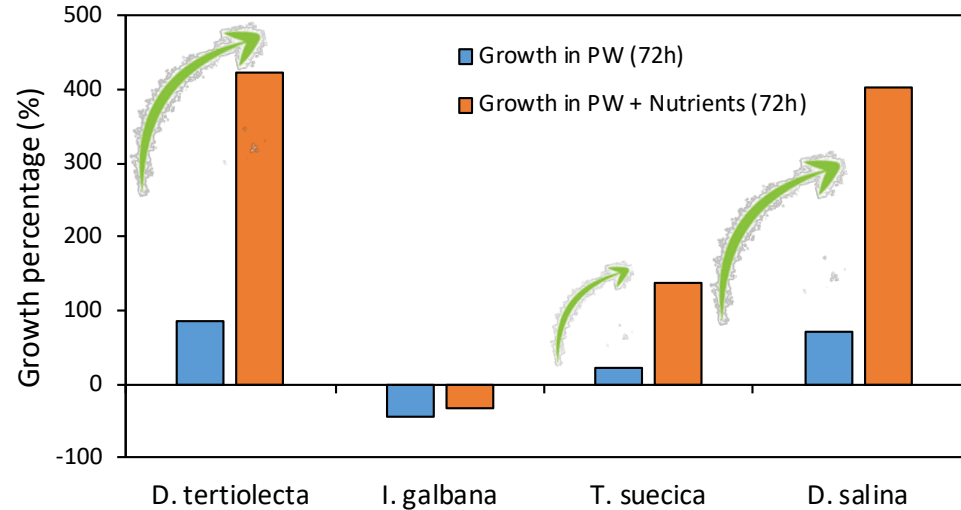
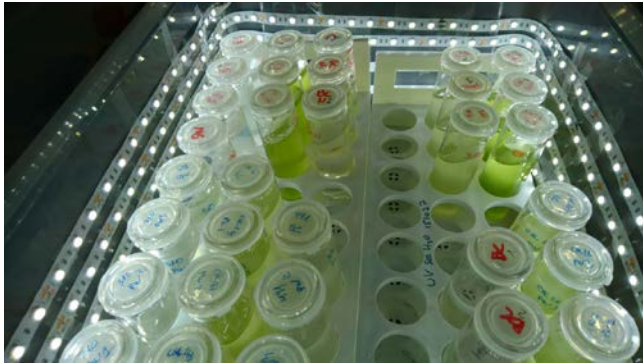


Spiked with:

- MTPA
- DTPMPA
- BAC (only for *T. suecica*)



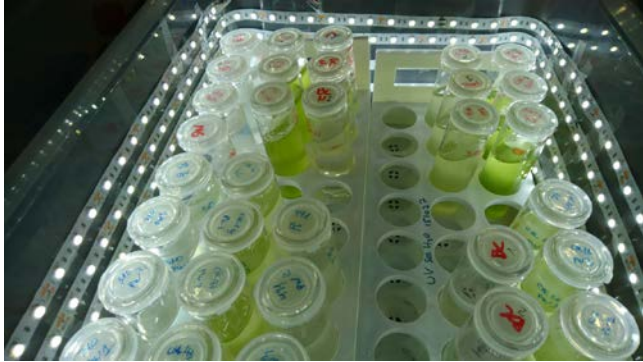
10. Batch experiments with produced water



The addition of nutrients to PW allow a better growth of microalgae except for *I. galbana*

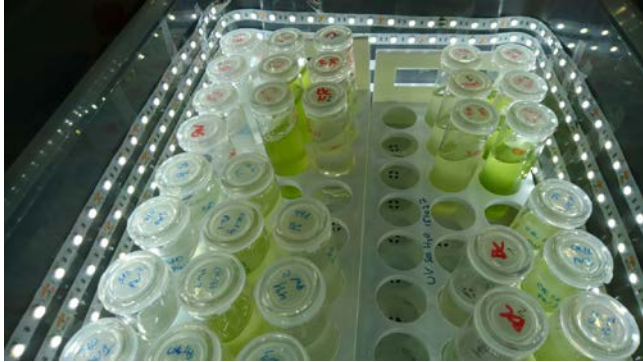


11. Batch experiments with produced water



- Preliminary results indicates similar profiles in PW experiments
- Same data processing tools will be employed to elucidate TPs
- It is expected to find similar TPs than in SW but other suspected molecules will be also explored for further identification





- ✓ Microalgae *T. suecica* can eliminate almost all the target compounds
- ✓ Photolysis seems to be the right choice for DDA elimination, although stronger conditions have to be tested
- ✓ Sorption seems to be the primary mechanism and afterwards biodegradation takes place.
- ✓ Several TPs are generated along the treatment
- ✓ Identifying and tracking the TPs becomes of paramount relevance for the development of more efficient PW treatment schemes



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Institute for Energy Technology (IFE), Norway



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Thanks!