

# Application of Ozonation and Bioremediation for Integrated Treatment and Valorization of Drilling Waste: Technology Development and Monitoring of Microbial Dynamics

M. Koutinas<sup>1</sup>, I. Vyrides<sup>1</sup>, K. Andreou<sup>1</sup>, G. Kazamias<sup>2</sup>, M. Chatzicharalampous<sup>2</sup>, C. Varavvas<sup>2</sup>

<sup>1</sup> Cyprus University of Technology, Limassol, Cyprus

<sup>2</sup> IESC Innovating Environmental Solutions Center Ltd., Limassol, Cyprus

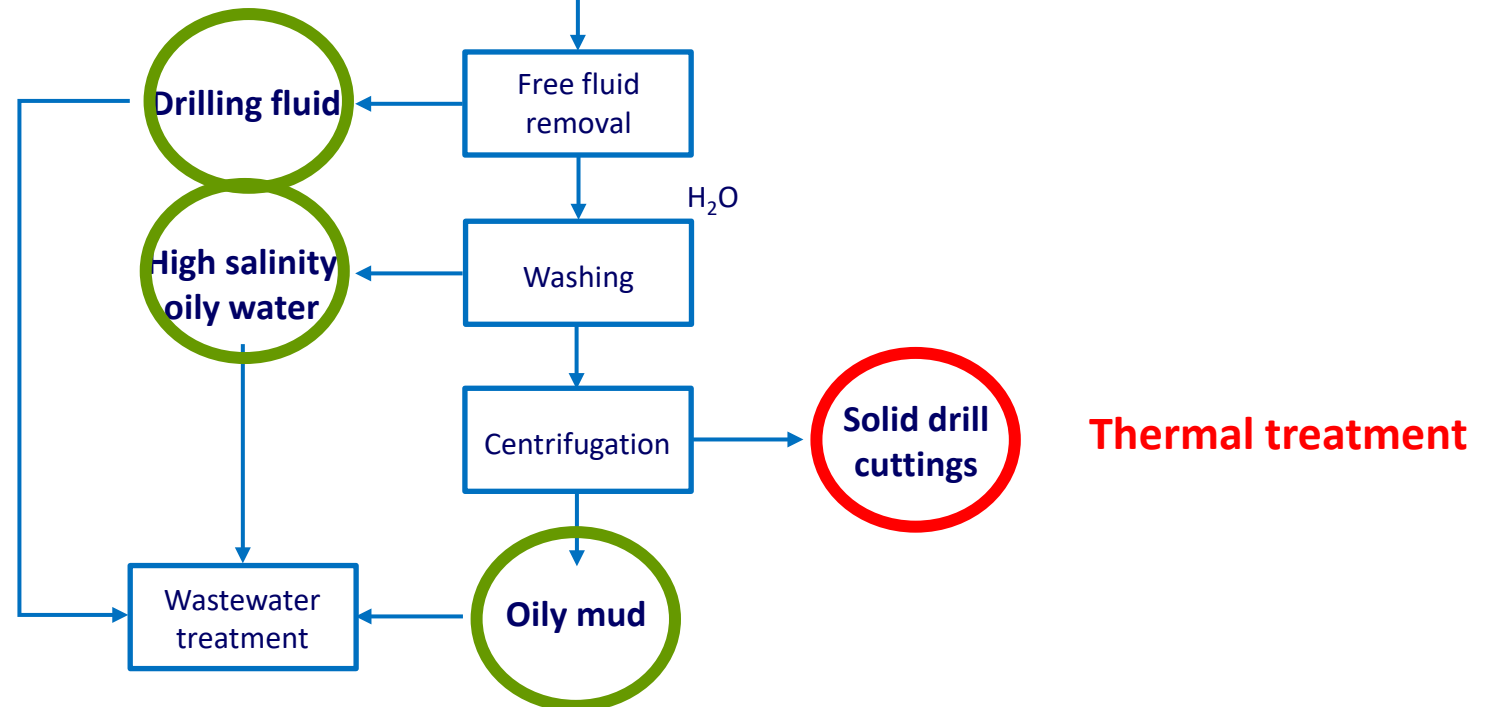
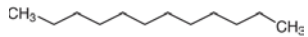
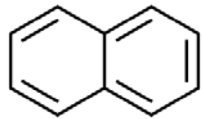


# Drilling Waste: Need for Environmental Friendly Methods

- Drilling waste:  $25 \times 10^6 \text{ m}^3 \text{ y}^{-1}$
- O&G wastewater discharges:  $14.5 \times 10^9 \text{ m}^3 \text{ y}^{-1}$
- Drilling fluid:  $11000\text{-}19000 \text{ m}^3$  per drill hole
- Toxic & persistent pollutants (TPH, PAH)

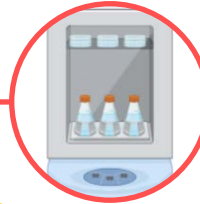
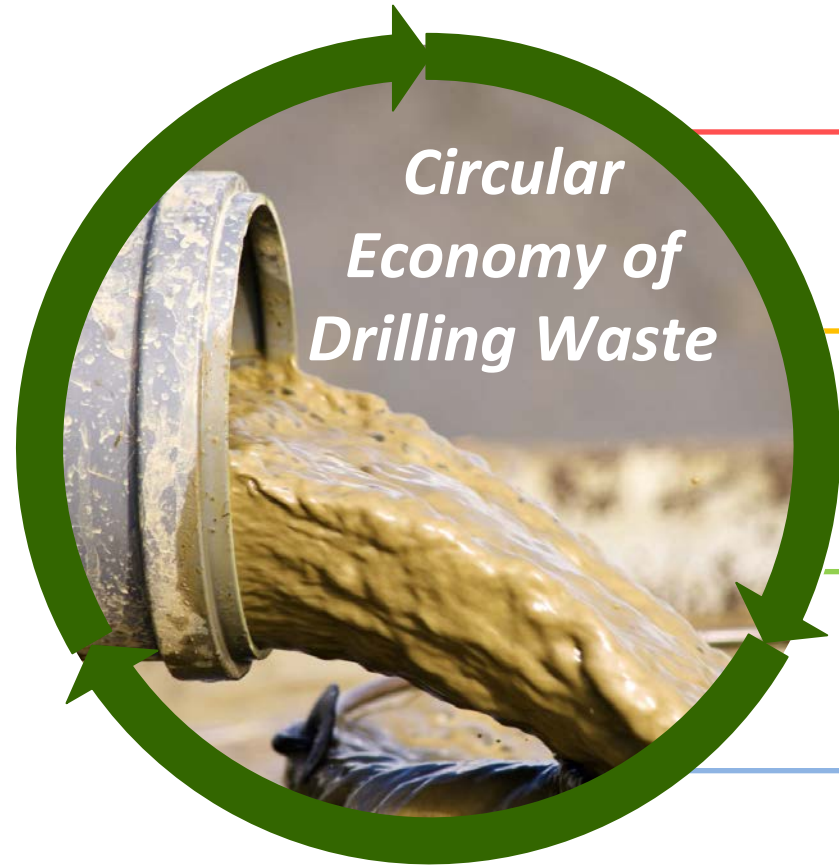


Drilling waste



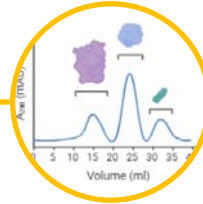


# Biodegradation & Valorisation of Drilling Waste



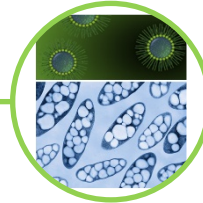
## Drilling waste detoxification

- 1) Microbial isolation
- 2) Culture conditions
- 3) Drilling wastewater and oily mud biotreatment



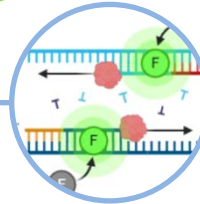
## Bioprocess analysis

- 1) COD, TPH and PAH biodegradation
- 2) Biosurfactant and PHA quantification and properties
- 3) Gene expression by qPCR



## Valorization of drilling waste

- 1) Biosurfactant production
- 2) PHA production



## Gene transcription monitoring

- 1) Stimulation of TPH and PAH biodegradation pathways
- 2) Stimulation of biosurfactant and bioplastic bioproduction pathways
- 3) Insights into the metabolic basis of the bioprocess



# Drilling WasteWater Biodegradation

*Pseudomonas citronellolis* SJTE-3 (KU860463.1)

*Pseudomonas citronellolis* A13 (MT437044.1)

*Pseudomonas citronellolis* PY1 (MH685460.1)

*Pseudomonas citronellolis* L8 (KX832710.1)

*Pseudomonas citronellolis* SLP6 (MN173542.1)

*Pseudomonas citronellolis* LCB03 (FJ194516.1)

*Pseudomonas citronellolis* JBLB (KP792286.1)

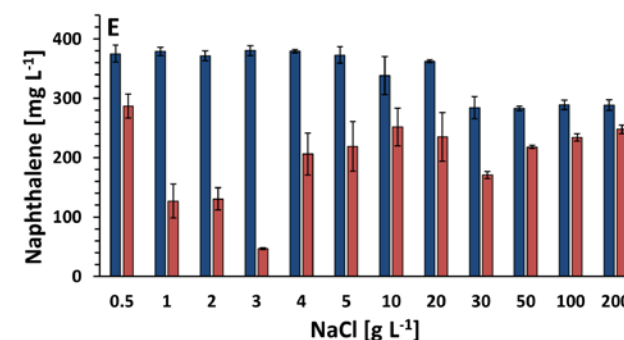
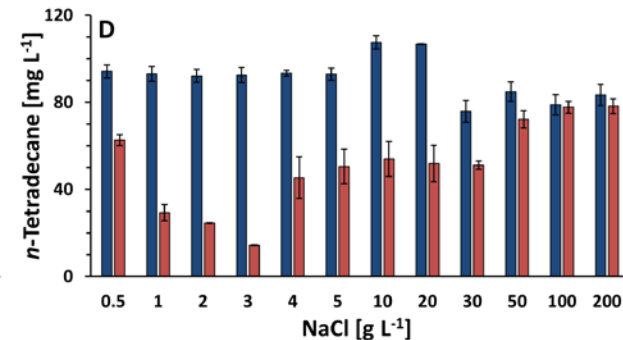
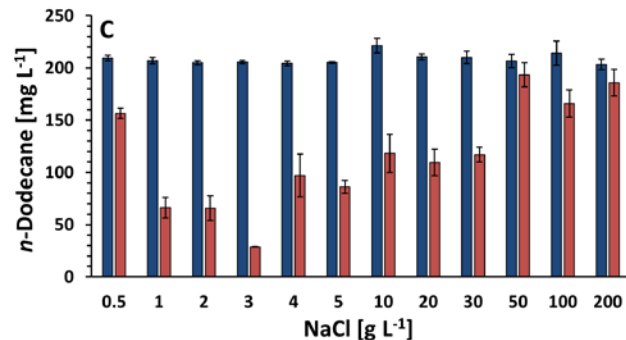
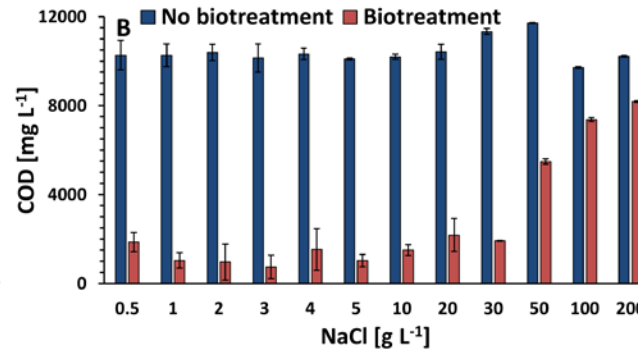
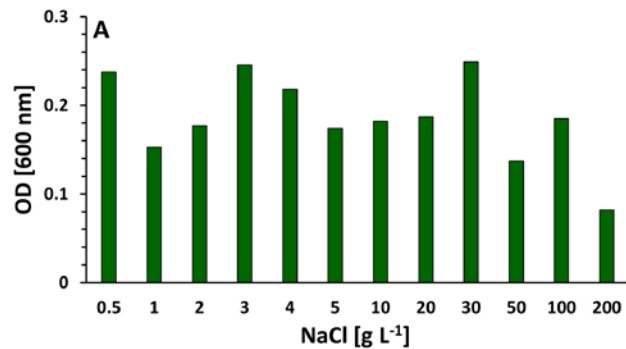
*Pseudomonas aeruginosa* S5 (MG807442.1)

*Pseudomonas putida* IAM 1236 (NR\_043424.1)

*Escherichia coli* (J01859.1)

0.100 0.080 0.060 0.040 0.020 0.000

- Hydrocarbon contaminated **hypersaline** wastewater
- 0.5-200 g L<sup>-1</sup> NaCl, 1% (v/v) DF, 60 h incubation
- 79-93% COD removal for 0.5-30 g L<sup>-1</sup> NaCl
- 3 g L<sup>-1</sup> NaCl: 177 mg L<sup>-1</sup> *n*-dodecane, 79 mg L<sup>-1</sup> *n*-tetradecane & 333 mg L<sup>-1</sup> naphthalene biodegradation



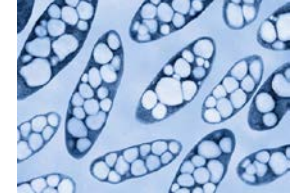




Experimental conditions	Methyl decanoate (% of DCW)	Methyl myristate (% of DCW)
<b>30 °C, pH 7, 0.5 g L<sup>-1</sup> NaCl</b>	<b>17.9</b>	<b>6.1</b>
30 °C, pH 7, 1 g L <sup>-1</sup> NaCl	13.9	3.9
30 °C, pH 7, 2 g L <sup>-1</sup> NaCl	11.9	2.8
30 °C, pH 7, 3 g L <sup>-1</sup> NaCl	11.8	4.1
30 °C, pH 7, 4 g L <sup>-1</sup> NaCl	5.6	5.2
30 °C, pH 7, 5 g L <sup>-1</sup> NaCl	5.3	4.9
30 °C, pH 7, 10 g L <sup>-1</sup> NaCl	4.2	3.9
30 °C, pH 7, 20 g L <sup>-1</sup> NaCl	5.0	4.6
28 °C, pH 7, 3 g L <sup>-1</sup> NaCl	12.8	7.4
37 °C, pH 7, 3 g L <sup>-1</sup> NaCl	8.0	4.3
28 °C, pH 6, 3 g L <sup>-1</sup> NaCl	7.1	2.8

## Medium-chain-length PHA

- 1% DF at different conditions
- **24% of DCW**
- Low salinity levels
- SJTE-3 converts DF into similar quantities of the promising biodegradable thermoelastomer to other studies **without additional strategy for hydrocarbons solubilisation** (e.g. surfactants, solvent)



## Biosurfactant

- **53%** water surface tension reduction
- **43.3%** emulsification index (E24)

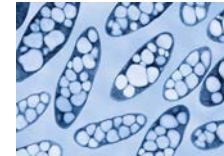




# Expression from Biosynthetic & Biodegradation Routes

- Transcription of *Pseudomonas* spp metabolic pathways monitored at different time points during biodegradation of 1% (v/v) DF

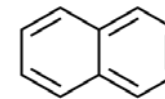
- *phaG* gene, putatively involved in the biosynthesis of medium-chain-length PHA



- *arfB*, *amsY*, *psoA* and *rhlB* genes associated to arthrofactin, amphisin, putisolvin and rhamnolipid



- *ndoB* gene encodes for naphthalene dioxygenase driving naphthalene biodegradation



- *alkB* gene constitutes universal marker for oil biodegradation









# Hybrid Ozone-Bioprocess for Drill Cuttings Valorisation

Drilling waste



Ozonation

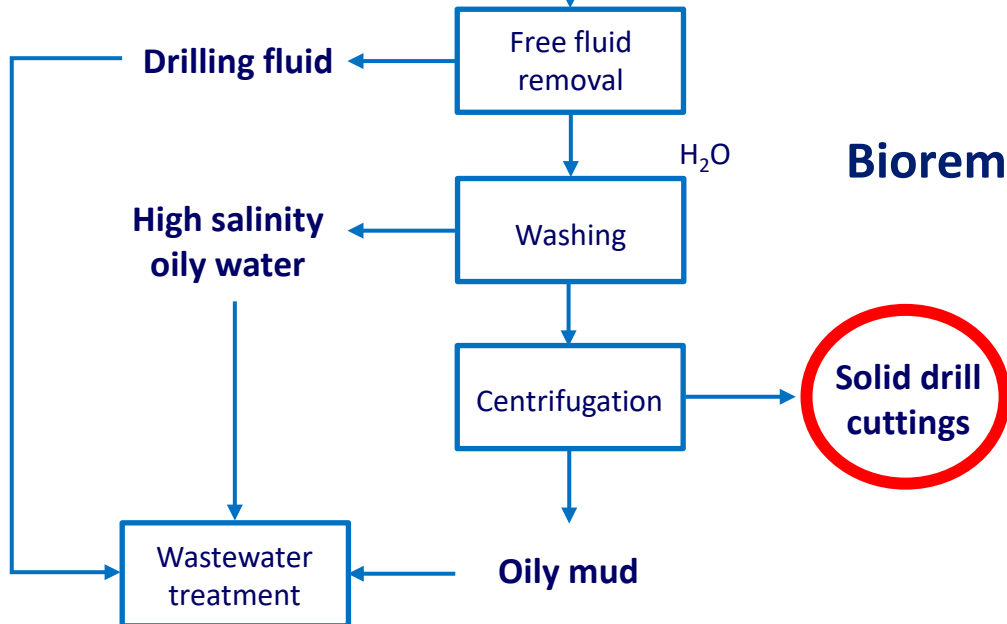


Bioremediation



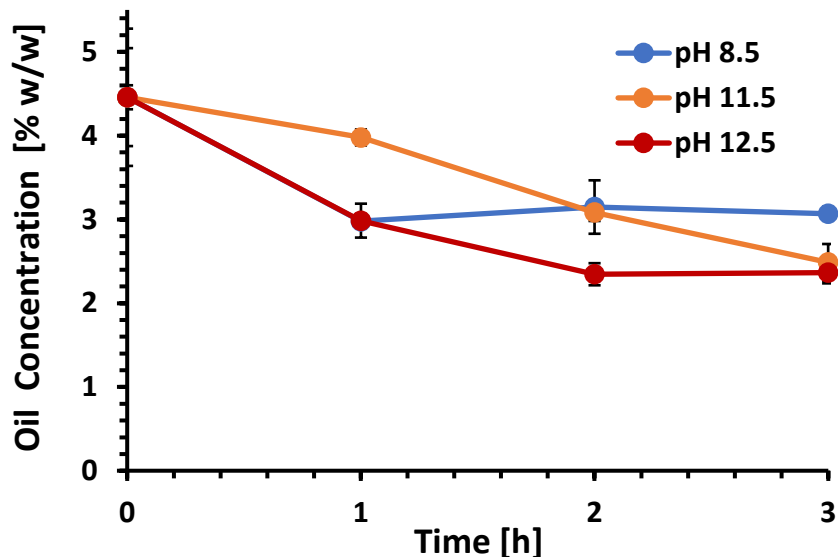
Tree prunings  
Activated sludge

Compost





# Ozonation & Bioremediation as Single Drill Cuttings Treatments



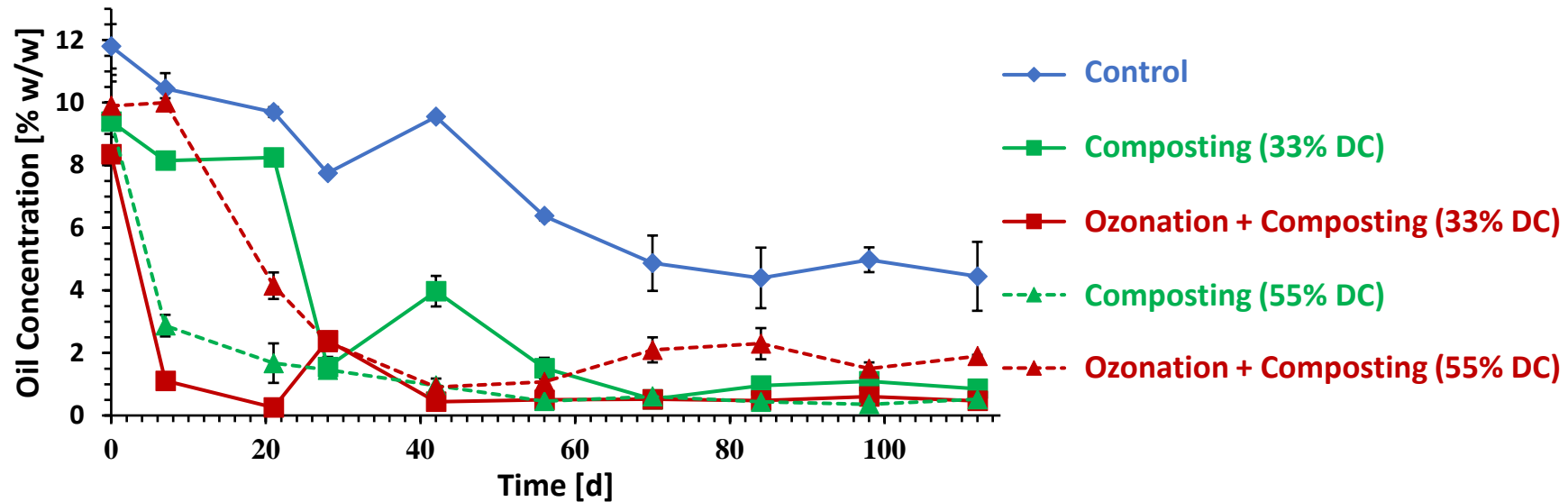
- Untreated DC: pH 8.5 and 40% (w/w) moisture
- 150 Kg DC
- Faster kinetics in **pH 12.5 (47.3% removal)**
- 44.2% removal in pH 11.5
- Additional moisture inhibited the process

	Oil Concentration [% w/w]	
	7 d	110 d
Control (Composting only)	2.27	0.35
Ozonation + Composting	1.65	0.36
Ozonation + Composting + Biostimulation	1.74	0.27
Ozonation + Composting + Biostimulation + Bioaugmentation	1.79	0.21
Ozonation + Composting + Biostimulation + Bioaugmentation + Biochar	1.97	0.23

**150 Kg DC**  
 +  
**250 Kg Prunings**  
 +  
**50 Kg Activated Sludge**



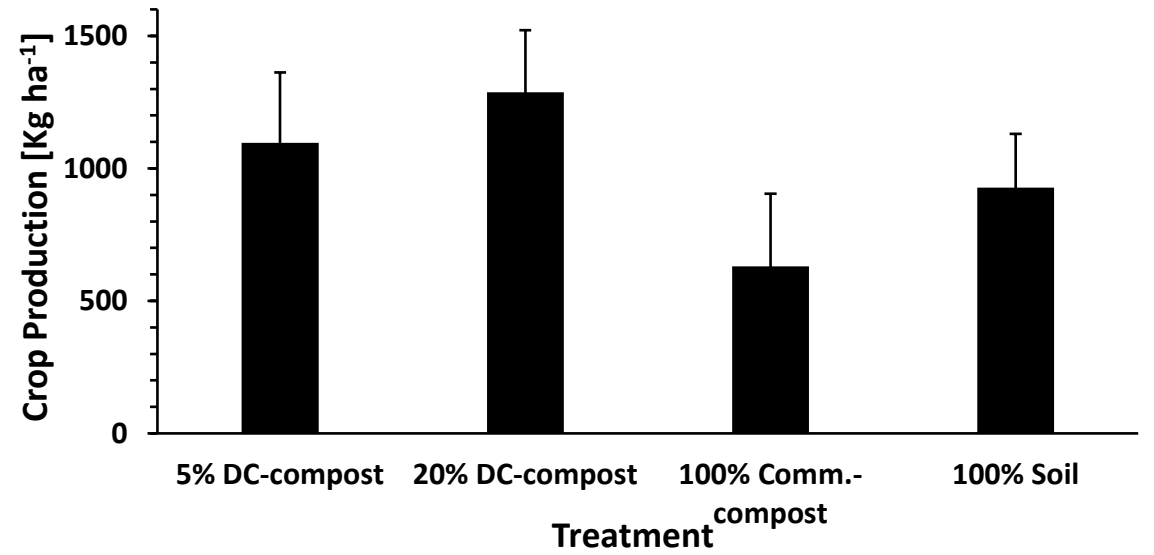
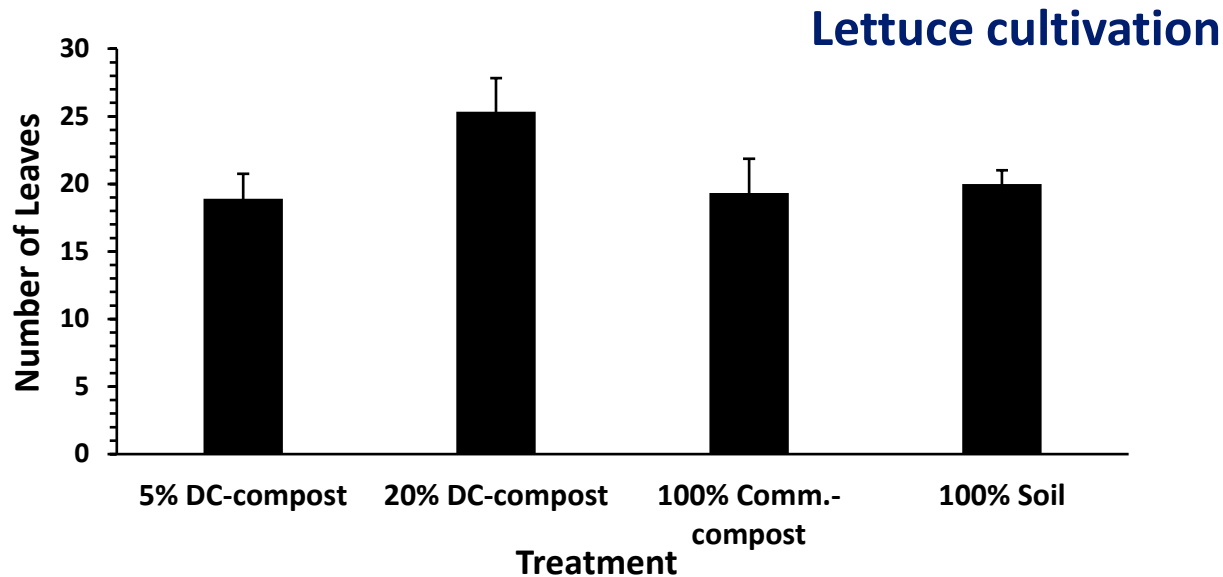
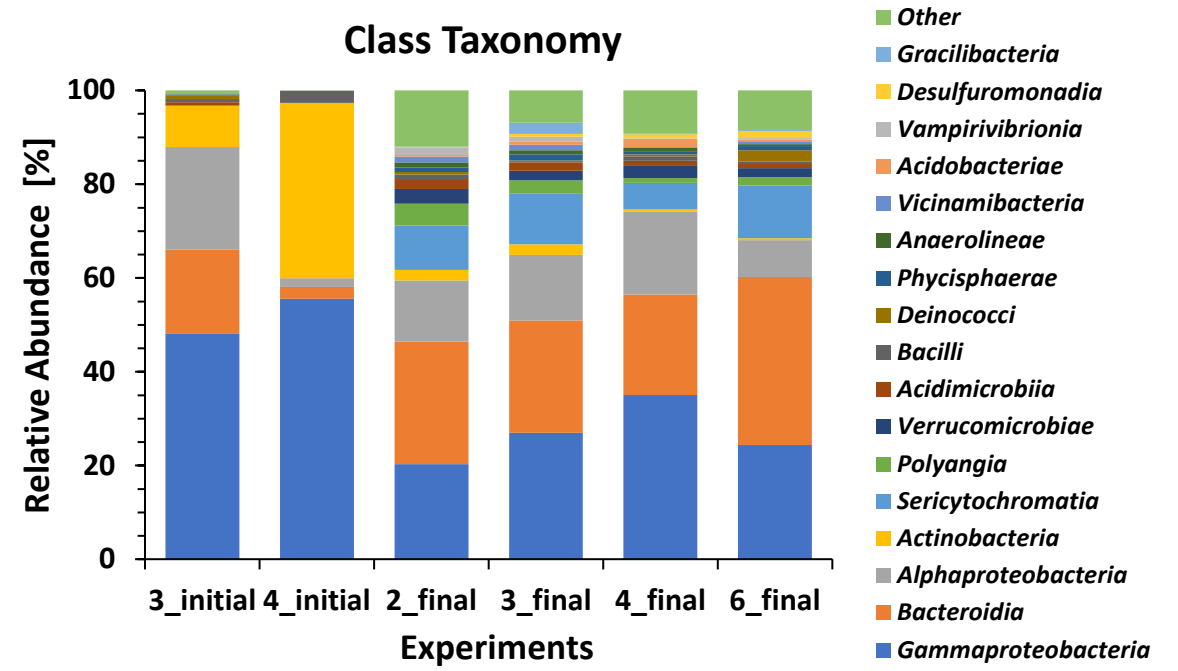
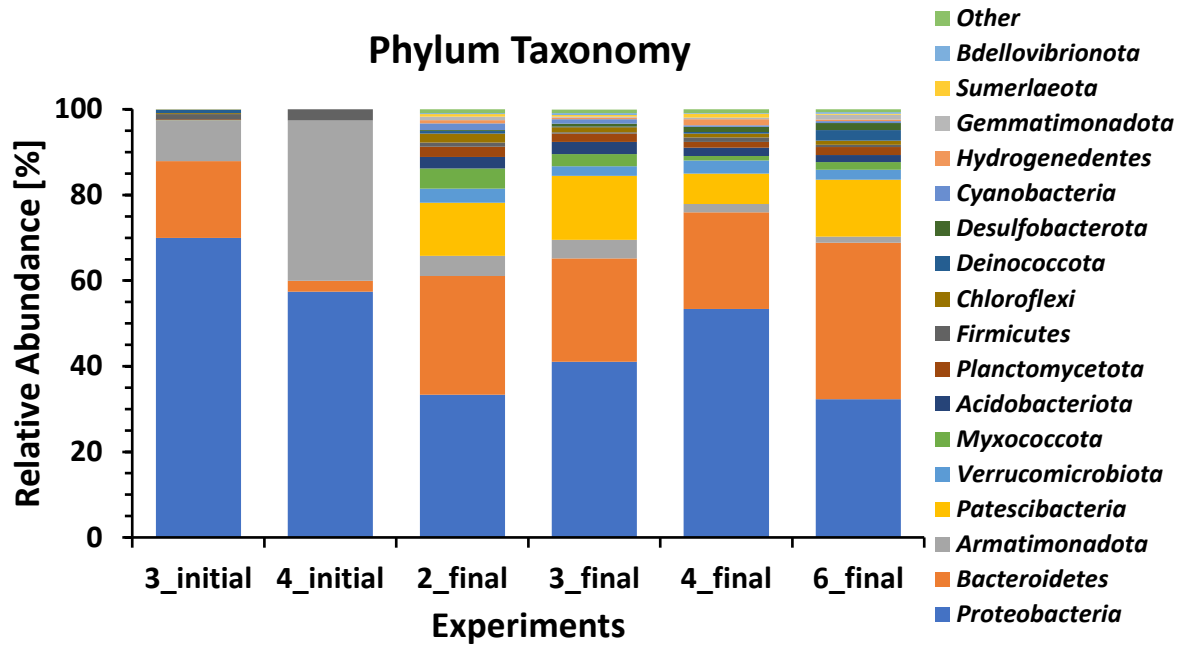
# Hybrid Ozone-Bioremediation for Drill Cuttings Valorisation



- **Ozonation vs no ozonation**
- 33% DC + 55% Prunings +12 AS
- **55% DC + 44% Prunings +12 AS**
- Ozonation + 33% DC fastest kinetics
- **0.3-0.6% oil following 21 d**
- 33% DC without ozonation: 0.6% oil at **70 d**
- 55% DC: reduced performance with ozonation
- Ozonation + 55% DC failed to reach 0.5% of oil
- 55% DC bioremediation performed 0.5% oil at **70 d**
- Increase of AS reduced performance of both systems



# Microbial Dynamics and Use of Compost as End Product





# Profit and Loss for Each Treatment Approach

	Thermal - TCC	Hybrid Ozone-Bioprocess	Bioprocess Only
	(€)	(€)	(€)
SALES	2,280,960	2,160,000	1,296,000
COST OF SALES			
Raw materials	703,296	1,312,000	491,520
Labour	265,200	89,700	119,600
Manufacturing overhead	1,258,790	740,000	1,122,702
	2,227,286	2,141,700	1,733,822
Net annual (loss)/profit	53,674	18,300	(437,822)

- 47,520 t<sub>DC</sub> yr<sup>-1</sup>, 10% oil and moisture, 24 h d<sup>-1</sup> for 330 d
- Thermal desorption (Thermomechanical Cuttings Cleaner – TCC)
- 21 d of Ozone + Biotreatment (33% DC+55% Prunings+12% AS)
- 70 d Biotreatment Only (55% DC+33% Prunings+12% AS)
- TCC and hybrid treatments **exhibit profit**
- Biotreatment only: prolonged process duration
- Hybrid process: prunings transportation was a key cost parameter



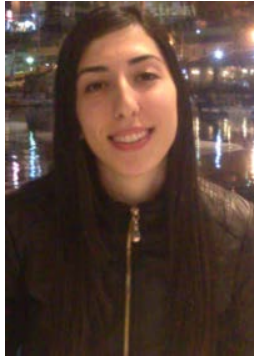
# Conclusions

- **Holistic approach** for sustainable drilling waste treatment
- *P. citronellolis* SJTE-3 enabled enhanced removal of **TPH** and **PAH** from DF
- **In situ** production of **bioplastics** and **biosurfactants**
- Activation of **putisolvin** biosynthetic pathway
- 47.3% oil removal via ozonation
- Similar microbial community composition in all treatments
- **Hybrid ozonation-bioremediation is cost-competitive**



# Thank you!

## PhD Students



Kyriakou M.



Nikodemou A.



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## Organisers of THESSALONIKI2021

